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Treatment of Children with Problem Behaviors: The Efficacy of Conjoint Behavioral Consultation versus Videotape Therapy and the Impact on Parent-Teacher Collaboration

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Abstract

The purpose of the present study was to compare the effectiveness of three indirect models of service delivery in treating children with externalizing and internalizing behavior problems: the highly individualized behavioral consultation model (CBC); minimal consultation with videotape therapy (GVT); and self-administered videotape therapy only (VT). This study also sought to ascertain whether parent and teacher consultation increases parental involvement in their children's education. Specifically, the relationship between perceived self-efficacy and mothers' involvement in their children's education was examined. Thirty-five preschool and elementary school children, their mothers, and teachers were assigned to one of the three treatment conditions. An A-B repeated measures group research design was used to analyze the effectiveness of consultation. Outcome variables included mothers' and teachers' direct observation of target behavior, their ratings of social skills, internalizing, externalizing, and general problem behaviors, and an observational measure of child deviance behaviors and parenting skills. Results indicated that children's target behaviors improved from baseline to treatment in all three treatment conditions. Overall, children's social skills increased and behavior problems decreased over the course of treatment. Pretreatment and posttreatment self-efficacy was assessed via rating scales. Although results suggest that parent and teacher self-efficacy did not change as a result of treatment, self-efficacy ratings were associated with more hours of mother involvement in educational activities per week. These results are discussed in light of their practical and theoretical implications.

Résumé

La présente étude vise à comparer l'efficacité de trois modèles indirects de prestation de services pour le traitement d'enfants ayant des problèmes comportementaux d'intériorisation ou d'extériorisation: le modèle de consultation comportementale, hautement individualisé (CBC); le modèle de consultation minimale, accompagnée d'un traitement par vidéo-enregistrement (GVT); et le modèle de traitement auto-administré uniquement par vidéo-enregistrement (VT). L'étude vise également à découvrir si la consultation des parents ou des enseignants est un moyen efficace pour accroître la participation des parents dans l'éducation de leurs enfants. On a examiné de façon plus précise le lien entre la participation des mères dans l'éducation de leurs enfants et la perception d'auto efficacité par ces dernières. Trente-cinq enfants d'âge scolaire et d'âge préscolaire, leurs mères et leurs enseignants furent regroupés dans l'une des trois situations de traitement. La méthodologie de recherche utilisée pour analyser l'efficacité de la consultation était le groupe de mesures répétées en A-B. Les variables observés au niveau des résultats étaient l'observation directe par les mères et par les enseignants du comportement cible, leur évaluation des compétences sociales, des comportements problématiques d'intériorisation et d'extériorisation ainsi qu'une mesure observable des comportements aberrants chez les enfants et des compétences parentales. Les résultats démontrent une nette amélioration des comportements cibles chez les enfants entre la ligne de base et le traitement pour toutes les trois conditions de traitement. En somme, les compétences sociales des enfants ont augmenté et les comportements problématiques ont baissé au cours du traitement. Une échelle d'évaluation a été utilisée pour mesurer l'auto efficacité aux stades du pré-traitement et du post-traitement . Quoique les résultats ne démontrent aucun changement au niveau de l'auto efficacité des parents et des enseignants à la suite du traitement, les taux d'auto efficacité sont étroitement liés au nombre d'heures consacrées par la mère par semaine aux activités éducatives. Ces résultats sont discutés en termes de leurs conséquences aux niveaux pratique et théorique.

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CHAPTER 1

Introduction

Statement of the Problem

Researchers and theorists studying developmental psychopathology have investigated two broad categories along the continuum of behavior problems: problems related to undercontrol, known as externalizing difficulties and problems related to overcontrol, referred to as internalizing difficulties (Rubin & Mills, 1991). Externalizing difficulties involve acting-out behaviors directed towards others, such as verbal or physical aggression, hyperactivity, noncompliance, and impulsivity (Achenbach & Edelbrock, 1991). In contrast, internalizing difficulties involve underactive behavior in relation to environmental stimuli such as anxiety, fear, depression, and social withdrawal (Achenbach & Edelbrock, 1991). These two patterns of socially atypical behavior are stable over time, with negative implications for children's future social and academic functioning (Mattison & Spitznagel, 1999; Serbin, Peters, McAffer, & Schwartzman, 1991). The combination of externalizing and internalizing patterns of behavior, typically characterizing children who evidence both persistent aggressive and withdrawn behavior present a specifically poor prognosis for future psychosocial functioning (Hymel, Bowker, & Woody, 1993; Ledingham, 1981; Milich & Landau, 1984; Serbin et al., 1991; Somersalo, Solantaus, & Almqvist, 1999).

Children who exhibit a pattern of externalizing problem behaviors are at risk for continued social dysfunction, problematic behavior, and poor school adjustment (Coie, Terry, Lennox, & Lochman, 1995; Kazdin, 1987). In addition, Robins (1966), in a classic longitudinal study, demonstrated that antisocial behavior in childhood is predictive of later psychiatric symptoms, criminal behavior, and physical and social adjustment problems. Less attention has been given to the long-term correlates of internalizing problem behavior in childhood, and as a result, the prognosis is uncertain (Elliott & Busse, 1993). However, Rubin and his colleagues (1995) posit that persistent internalizing behavior problems in childhood have negative consequences related to poor social skills and weak problem solving abilities. Moreover, Rubin and his colleagues argue that these consequences produce "costs" for children in the form of low self-esteem (Rubin, Hymel, & Mills, 1989), social competence deficiencies, such as fewer social problem-solving initiations (Stewart & Rubin, 1995), loneliness and depression (Rubin & Asendorpf, 1993), and low school competence (Moskowitz & Schwartzman, 1989). Individuals who display characteristics of both externalizing and internalizing problem behavior, typically evidenced by both aggression and social withdrawal, are of particular concern. Children who are aggressive and withdrawn are at particular risk for poor occupational success, low social status, and unsuccessful social relationships (Moskowitz, & Schwartzman, 1989). Consequently, these occupational and interpersonal problems may lead to severe psychopathology in adulthood (Hymel et al., 1993).

The prevalence of children evidencing a behavior problem considerably exceeds the personnel and resources available (Webster-Stratton, 1990). In fact, Canadian children with behavior problems are presently under served and are receiving less consideration than in the early 1980's (Dworet & Rathgeber, 1990). Moreover, of immediate concern, the province of Quebec, facing the likelihood of future cuts in educational and psychological services, has one of the highest prevalence rates of behavior problems in Canada (Dworet & Rathgeber, 1996). Specifically, 12% of children at the kindergarten level, and between 2% and 2.6% of elementary and high school students have been identified as having behavior problems (Dworet & Rathgeber, 1996). In fact, children with behavior difficulties represent the second largest category of students with special needs (19.3%) in the province (Ministère de l'Éducation du Québec [MEQ], 1999). Consequently, children with behavioral problems, characterized by either externalizing difficulties, internalizing difficulties, or a combination of both, require the attention and assistance of researchers, parents, teachers, and practitioners (Hymel et al., 1993).

Involving significant individuals in the child's life (i.e., parents and teachers) facilitates the analysis of a child's behavioral difficulties across multiple contexts thereby providing a more comprehensive understanding of the factors which are maintaining the child's undesired behaviors (Sheridan, 1997). According to ecological-systems theory, a child is an inseparable part of a system or network of interconnected systems and therefore behavior occurs as a function of a child's interaction with the different systems of which he or she is a part (Sheridan, 1997). Systems overlap, and hence what happens to a child in one system will effect the child's behavior in a second system. Home and school settings typically comprise the major settings and systems in a child's life and therefore the interconnection between these two systems has a significant impact on the child's development (Sheridan, 1997). Specifically, influences within and between families and school are reciprocal; a relationship exists in which a child's school experiences will influence home behavior, and family experiences effect the child's behavior at school (Sheridan, 1997). Clearly, it is important to combine efforts across home and school in order to maximize treatment efficacy (Fine & Carson, 1992;

Sheridan, 1997; Sheridan, Kratchwill, & Elliott, 1990; Tremblay, LeMarquand, & Vitaro, 1999; Webster-Stratton, 1993).

Simultaneous consultation with parents and teachers may be used as an approach for working within and between systems to initiate behavioral changes (Bergan & Kratochwill, 1990; Kratochwill & Bergan, 1990; Sheridan, 1997). Conjoint behavioral consultation (CBC: Sheridan & Kratochwill, 1992; Sheridan, Kratochwill, & Bergan, 1996) in particular, is a systematic service delivery model designed to facilitate home and school interactions and responsibility for the academic, social, and behavioral needs of a child. Specifically, CBC provides a framework in which a consultant collaborates with teachers and parents in an effort to help a child with a specific behavior problem. CBC involves an indirect form of service delivery whereby a consultant guides parents and teachers to elicit change in a child using behavior management skills. This process involves four stages: Problem Identification, Problem Analysis, Treatment Implementation, and Treatment Evaluation (Sheridan & Kratochwill, 1992). Structured interviews are associated with three of the four stages, with the exception being Treatment Implementation.

Briefly, during the Conjoint Problem Identification Interview (CPII), the consultant and consultees identify the most salient problem(s) and agree upon a data collection procedure for the purpose of gathering baseline information. During the Conjoint Problem Analysis interview (CPAI), the baseline data are reviewed in order to assess the magnitude of the problem. Next, a comprehensive functional and conditional analysis of the target behavior across settings is carried out before the intervention plan is designed and appropriate guidelines for implementation are set. The treatment phase follows in which the intervention plan is implemented according to the agreed upon strategies and data continues to be collected systematically. Finally, following the end of the intervention plan, the Conjoint Treatment Evaluation Interview (CTEI) is undertaken. During this final interview, the treatment data are compared to the baseline data in order to assess the effectiveness of the treatment plan. The parent, teacher, and consultant then discuss continuation, modification, or termination of treatment. The interview is concluded once strategies for maintaining and promoting the generalization of treatment effects are considered (e.g., Bergan & Kratochwill, 1990; Sheridan & Colton, 1994; Sheridan & Kratochwill, 1992).

Although the behavioral approach to consultation has received considerable research attention, there are few studies to date that have examined the efficacy of CBC. Nevertheless, based on available research, there is evidence that CBC provides a promising framework to address the academic, social, and behavioral needs of an individual (Galloway & Sheridan, 1994; Sheridan, 1997; Sheridan & Kratochwill, 1992; Sheridan et al., 1996). More specifically, CBC has been used effectively to treat children with internalizing and externalizing behavior difficulties (e.g., Johnson, 1994; Sheridan & Colton, 1994; Kratochwill, Elliott, Loitz, Sladeczek, & Carlson, 1999; Sheridan, Kratochwill, & Elliott, 1990; Sladeczek, 1996; Sladeczek, Kratochwill, & Elliott, 1996). However, more research is needed to further document the usefulness of CBC for providing services to children with specific behavior disorders (i.e., children evidencing aggressiveness and social withdrawal). Moreover, there is a need to investigate the efficacy of CBC in treating externalizing and internalizing type difficulties as compared with other indirect service delivery models that provide varying levels of consultation.

Specifically, conjoint behavioral consultation (CBC) can be compared with group videotape therapy with minimal consultation (GVT) and a self-administered videotape program (VT).

Videotape therapy is a multicultural parent-training program developed by Carolyn Webster-Stratton (1987) for children with behavior problems. Videotape therapy may be offered to parents as an individually, self-administered videotape modeling treatment (VT) or completed in groups of 8 to 12 parents led by a therapist (GVT). Videotape therapy is a useful treatment modality to compare with CBC for three reasons. First, videotape therapy is gaining empirical support indicating that parents who participate in the training are able to significantly reduce children's behavior problems and increase prosocial behaviors (Webster-Stratton, 1993; Webster-Stratton, Hollinsworth, Kolpacoff, 1989; Webster-Stratton, Kolpacoff, & Hollinsworth, 1988). Second, videotape therapy, like CBC, is an appealing alternative to the more costly, traditional forms of treatment for children with behavior difficulties. Third, videotape therapy can be disseminated to a large number of parents, and can be self-administered without a therapist (Webster-Stratton, Holinsworth, & Kolpacoff, 1989).

Videotape therapy teaches participants (i.e., parents and teachers) how to interact with children during play, how to motivate and teach children to learn, the art of effective praise and rewards, and how to appropriately set limits and handle misbehavior. Hence, parents and teachers, through the process of watching the videotape intervention series, may learn alternative child rearing strategies, improve problem-solving skills, and develop more effective communication skills. Basic child rearing concepts are portrayed with brief vignettes of parents interacting with their children in family life situations.

Parents and teachers can identify their own mistakes and learn alternative strategies by watching examples of parents "doing it right" and "doing it wrong".

Webster-Stratton's work has targeted children with externalizing difficulties. It is therefore necessary to examine the efficacy of videotape therapy versus CBC for parents of children with externalizing and internalizing difficulties (Webster-Stratton & Hammond, 1997). Moreover, it is important to facilitate the use of videotape therapy for teachers, as there few studies that has successfully used videotape therapy with teachers in the classroom (Kratochwill et al., 1999).

Sheridan and Kratochwill (1990) were the first to outline a rationale for incorporating both parents and teachers into the behavioral consultation framework. The researchers based their rationale on the parent involvement literature showing that active parent participation in the school is believed to have positive outcomes for children, parents, and teachers (Fine & Carlson, 1992; Hoover-Dempsey, Bassler, & Brissie, 1987; Kroth, 1989). Conjoint behavioral consultation was suggested by Sheridan and Kratochwill (1990) as one form of home-school service delivery system that can address problems between parents, teachers, and students strategically and effectively thereby fostering productive partnerships, and stengthening the contribution of both the school and the family on children's development. Behavioral consultation has been proposed as an intervention approach that systemmatically increases parent-teacher collaboration (Kramer, 1990; Zins, Kratochwill, & Elliott, 1993). In fact, a fundamental premise of the conjoint behavioral consultation framework is to increase home and school partnerships (Sheridan,1997). However, there is little research evaluating the actual strength of the parent/teacher partnership before consultation services have been initiated and after consultation has terminated.

Purposes and Original Contributions

The data examined in the present study are part of a larger study, the Parent-Teacher Intervention Project Canada (P-TIP), being conducted at McGill University under the direction of Dr. Ingrid Sladeczek. The goal of the following study is to determine the efficacy of conjoint behavioral consultation and videotape therapy in treating children with behavior problems. A second goal of this study is to extend the current consultation literature by systematically examining the effectiveness of consultation for children evidencing internalizing behavioral problems. The third goal is to initiate an analysis of parent-teacher collaboration within the consultation framework by ascertaining whether consultation increases parental involvement in their children's education.

CHAPTER 2

Literature Review

The literature review is divided into three main sections. The first section begins with an overview of the stability of externalizing behavior problems, internalizing behavior problems, and the combination of externalizing and internalizing problem behaviors. Next, the long-term consequences of these problems and their specific developmental pathways are presented.

In the second section, conjoint behavioral consultation and videotape therapy are proposed as treatment options for children with behavior problems. The research pertaining to the efficacy of the treatment models is reviewed. In the third section, a discussion and consideration of the importance of enhancing home and school cooperation during behavioral intervention is presented and the parent involvement literature reviewed. Finally, the factors that influence parent involvement in their children's education are discussed.

Externalizing Problems

Externalizing ("acting out") problems refer to a group of behaviors characterized by noncompliance, aggression, destructiveness, attention problems, impulsivity, hyperactivity and delinquency (Achenbach & Edelbrock, 1991). This broadband grouping has been consistently identified in multivariate classification studies of childhood behavior problems (Achenbach & Edelbrock, 1991; Mattison & Spitznagel, 1999; Quay, 1986) and represents the most common reason for referring a child for psychological and psychiatric treatment (Grizenko, Papineau, & Sayegh, 1993). Specifically, it has been estimated that one third to one half of child and adolescent cases referred to outpatient clinics relate to aggression, conduct problems, and antisocial behavior (Achenbach & Howell, 1993; Gilbert, 1957; Robins, 1981; Kazdin, 1988). The prevalence of externalizing difficulties vary depending on the given behavior (e.g., aggression or conduct problems) and the sample of children investigated (e.g., preschool versus adolescence). Nevertheless, the incidence typically cited falls between 4% and 10% of young children (Breton, 1993; Rutter, Cox, Tupling, Berger, & Yule, 1975; Rutter, Tizard, & Whitmore, 1970), with current estimates falling between 7% to 25% of young children (Webster-Stratton & Hammond, 1997; Webster-Stratton, 1998).

The predominant interest in and identification of externalizing difficulties in childhood is based on several important factors. First, externalizing problems are easy to detect, as the behavioral manifestations are salient and tend to evoke a negative response, such as anger from teachers and caregivers (Mills & Rubin, 1990; Rubin & Mills, 1991). Second, the disruption associated with externalizing behavior is viewed as a significant barrier to the delivery of satisfactory education (Rubin & Mills, 1991). Third, externalizing difficulties have been shown to persist through adolescence.

The stability of externalizing difficulties from early childhood to later childhood (e.g., Campbell, 1991), and from later childhood to adolescence (Barkeley, Fischer, Edelbrock, & Smallish, 1990; Offord & Bennett.1994) have been documented using community and clinic-referred samples. In addition, there have been numerous studies concerning externalizing difficulties which suggest that aggressive behavior is salient and stable throughout childhood (Moskowitz, Schwartzman, & Ledingham, 1985; Olweus, 1979) and that there is an association between childhood aggression and later antisocial activity (Huesmann, Eron, Lefkowitz, & Walder, 1984; Loeber & Dishion, 1983; Parker & Asher, 1987; Robins, 1966, 1986; Webster-Stratton, 2000). Furthermore, aggression, impulsivity and other externalizing behaviors have been associated with many other difficulties such as weaknesses in understanding others' perspectives, feelings and intentions (Dodge, 1986; Rubin & Mills, 1991), and peer rejection (Coie & Kupersmidt, 1983; Dodge 1983). Such problems have chronic, serious consequences not only for the symptomatic child but also for parents, siblings, peers, teachers, neighbors, and society at large (Olson, Bates, Sandy, & Lanthier, 2000).

Internalizing Problems

In contrast to the rich empirical bases for understanding externalizing behavior problems, there exists a paucity of literature on internalizing difficulties in childhood. Internalizing ("over control") problems refer to a broad range of behaviors which typically include anxiety, depression, somatic symptoms and fear (Achenbach & Edelbrock, 1991), with the prime behavioral manifestation being social withdrawal (Rubin & Mills, 1991). Similar to externalizing difficulties, internalizing problems have been continually identified in factor analytic studies of childhood behavior problems (Achenbach & Edelbrock, 1978; Mattison, & Spitznagel, 1999; Quay, 1986). Nevertheless, the population of children evidencing internalizing difficulties is presently under-identified and under-serviced (Rubin & Mills, 1991). Unlike aggressive behavior, the behavioral manifestations of internalizing problems, such as social withdrawal and peer neglect, are likely to go unnoticed by teachers and caregivers (Rubin & Mills, 1991). In fact, children who are socially withdrawn from their peers are frequently reinforced by their teachers for their quiet behavior in the classroom (Rubin & Mills, 1991). For this reason, the incidence of internalizing behavior problems is uncertain.

The research examining the long-term consequences of early social withdrawal and peer neglect has typically been fraught by methodological shortcomings (Janes & Hesselbrock, 1978; Janes, Hesselbrock, Myers, & Penniman, 1979; John, Mednick, & Schulsinger, 1982; Michael, Morris, & Soroker, 1957; Morris, Soroker, & Burress, 1954; Robins, 1966). First, clinic-referred samples rather than samples obtained from children in schools were often obtained, thereby limiting the generalizability of the findings (Janes & Hasselbrock, 1978; Janes et al., 1979; John et al., 1982; Michael et al., 1957; Morris et al., 1954; Robins, 1966). Second, the majority of studies have been retrospective rather than prospective thereby limiting their predictive value (e.g., Germezy, 1974; Kohlberg, LaCrosse, & Ricks, 1972; Loeber & Dishion, 1983; Robins, 1966). Third, researchers have traditionally used predictive variables of the externalizing-type such as delinquency and aggression, thereby overlooking the possibility of internalizing-type outcomes such as depression and loneliness (Kohlberg et al., 1972; Parker & Asher, 1987). Last, researchers used different conceptual meanings to define social withdrawal. Social withdrawal can occur for different reasons, ranging from exclusion by the peer group to anxious withdrawal from the peer group (Rubin & Mills, 1988). However, researchers have not made the distinction between the different subtypes of the phenomenon. Hence, there is a lack of a clear, specific definition of this construct across research studies (e.g., Strain & Kerr, 1981; Coie & Kupersmidt, 1983: Honig, 1987). Terms, such as "social isolation," "sociometric rejection," and "behavioral inhibition" have been used interchangeably with the term "social withdrawal" causing confusing and inconclusive research findings (Rubin et al., 1989).

Recent longitudinal studies, such as the Waterloo Longitudinal Project (WLP) and the Concordia Study of Children at Psychological Risk, have improved on the weaknesses plaguing past research examining the prognosis for children who are socially withdrawn. Researchers have demonstrated that social withdrawal is stable over time and associated with feelings of insecurity and poor self-perception. Moreover, negative self-image, social anxiety and withdrawn behavior together have been shown to be predictive of later internalizing problems, such as depression and loneliness (Rubin & Mills, 1991). Longitudinal research has also examined the prognosis for children evidencing behavior problems related to both aggression and withdrawal.

Externalizing and Internalizing Problems

There is evidence of the coexistence of externalizing and internalizing behaviors (Kraatz-Keiley, Bates, Dodge, & Pettit, 2000). Children who evidence extreme behaviors from both the externalizing and internalizing dimensions are typically referred to in the literature as aggressive-withdrawn and are of particular concern to researchers and clinicians (Hymel et al., 1993; Somersalo et al., 1999). As compared with other children with behavioral difficulties, children who are aggressive-withdrawn were found to be least liked by their peers, especially as the children get older (Ledingham, 1981). In addition, these children were viewed by their parents and teachers as more distractible, and by teachers as more dependent on peers, more resistant to changing tasks and slower to complete their work (Ledingham, 1981). In a 3-year follow-up, the aggressive-withdrawn children were found to be more likely to exhibit academic difficulties such as, failing a grade, or special class placement, as compared with children who were socially withdrawn or comparison control children (Legingham & Schwartzman, 1984). Recently, Serbin, Peters, and Schwartzman (1996) have shown that girls who were highly aggressive and withdrawn during childhood evidence poor school achievement, high social service usage, substance abuse and elevated use of medical services. Consequently, children who exhibit both aggressive and withdrawn behavior represent a group of children at risk for later pathology of the externalizing and internalizing nature (Hymel et al., 1993).

The Developmental Pathway of Externalizing Problems and Internalizing Problems

The quality of peer relationships is a significant indicator of social and emotional adjustment (Boivin, Hymel, & Bukowski, 1995; Chen, Rubin, & Li, 1997; Chen, Rubin, & Sun, 1992; Coie, Dodge & Kupersmidt, 1990). Indeed, there has been an established link between early social difficulties (i.e., externalizing and internalizing problem behavior) of low-status children and later adjustment problems in adolescence and adulthood, such as school dropout, delinquency, and psychopathology (Chen et al., 1997; Coie et al., 1990; Rubin, Bukowski, & Parker, 1998).

Typically, researchers have investigated the relationship between early peer rejection and aggression, and subsequent externalizing difficulties (Asher & Coie, 1990; Coie, Lochman, Terry, & Hyman, 1992; Hymel, Rubin, Rowden, & LeMare, 1990; Kohlberg et al., 1972; Panak & Garber, 1992; Parker & Asher, 1987). Children who are aggressive-rejected in childhood are actively disliked by their peers (Coie & Kupersmidt, 1983; Dodge, 1983). These children are at risk for pervasive externalizing-type difficulties through adolescence and adulthood (Hymel et al., 1990).

Another type of low-status children are neglected-withdrawn children, those frequently overlooked and not noticed by their peer group. The distinction between rejected and neglected children has emerged in the literature as a result of conceptual concerns that these two groups of children are developmentally distinct (Rubin, LeMare, & Lollis, 1990; Rubin, Hymel, LeMare, & Rowden, 1989). While rejected children have been labeled aggressive and hostile, neglected children have been described as withdrawn and shy (Bierman, 1986; Krehbiel, & Milich, 1986), with the risk of becoming rejected by their peers during the middle and later years of childhood (Coie, Dodge, & Coppotelli, 1982; French, 1990; Younger, Gentile, & Burgess, 1993). As social withdrawal has been shown to become increasingly non-normative with age, children who are isolated from their peers tend to become increasingly rejected by their peers, thereby accentuating internalizing problems (Boivin, Hymel, & Bukowski, 1995; Rubin, Hymel, Mills, & Rose-Krasnor, 1991; Younger, Gentile, & Burgess, 1993). Hence, the differences in profiles of the two groups are consistent with the notion that children who are neglected and rejected in childhood are "at risk" for different behavior problems and outcomes (Rubin, LeMare, & Lollis, 1990). The neglected child is expected to have difficulties of an internalizing nature, such as depression, while the rejected child is more likely to develop externalizing problems such as delinquency (Rubin, LeMare, & Lollis, 1990). Neglected children are beginning to receive the attention of researchers and practitioners, as they evidence a pattern of behavior that could significantly influence their social competence later in life (Boivin, Hymel, & Bukowski, 1995; Cassidy & Asher, 1992; Rubin et al., 1989).

It is possible for children to be high on both aggression and withdrawal, placing them at risk for psychopathology in adulthood (Ledingham, 1981; Schwartzman, Ledingham, & Serbin, 1985). There is a paucity of literature with regard to the stability and outcome of aggressive-withdrawn behavior. There is evidence that the subgroup of unpopular children who are both aggressive and withdrawn experience relatively greater peer rejection than either the aggressive-rejected (but not withdrawn) or the withdrawn-neglected (but not aggressive) children (Hymel, et al., 1993). This subgroup of children clearly exhibit the greatest number of problems within both nonsocial and social domains and represent a group of children at risk for later pathology of the externalizing and internalizing nature (Hymel et al., 1993).

Recent longitudinal research, notably the Concordia Study of Children at Psychological Risk (Schwartzman et al., 1985), provides evidence and support for the conclusion that aggressive-rejected children (i.e., externalizing-type difficulties), withdrawn-neglected children (i.e., internalizing-type difficulties) and aggressive-withdrawn children (i.e., externalizing and internalizing-type difficulties) are at risk for later maladjustment. The Concordia study began in 1976 with the screening of over 4000 Quebec school children for aggression and withdrawal using a French translation of the Pupil Evaluation Inventory (PEI; Pekarik, Prinz, Liebert, Weintraub, & Neil, 1976). Subsequently, over 1700 children in grades 1, 4, and 7 were selected and placed in one of four groups: an aggressive group, a withdrawn group, an aggressive-withdrawn group, and a "contrast" group consisted of children who received non-deviant scores on both aggression and withdrawal on the PEI. The sample included approximately the same number of girls and boys, and hence was one of the first longitudinal studies to follow a large number of aggressive and withdrawn girls into adulthood. Several interesting studies emerged from this project that provide insight into the specific developmental pathways for children evidencing externalizing and internalizing difficulties.

Based on the Concordia Study, Moskowitz and Schwartzman (1989) assessed intelligence, behavioral problems, and social competence of each group approximately 6 years after identification. Results indicated that children from the aggressive group and the aggressive-withdrawn group scored significantly below the children from the control group on total intelligence. The aggressive individuals also scored significantly below the individuals from the withdrawn group on total intelligence. The lower scores obtained by the aggressive individuals indicate that aggression in childhood is predictive of lower intellectual competence in adolescence and adulthood, as these individuals were not different from control individuals on intelligence when initially identified. The lower scores obtained by the aggressive-withdrawn children identifies a continued pattern, as these children were low on intelligence and academic achievement when initially identified. In the case of both the aggressive children and the aggressive-withdrawn children, it is likely that poor academic and intellectual achievement will continue, possibly leading to poor occupational achievement and low social status in adulthood. The children from the withdrawn group were not different from the children in the control group on measures of total intelligence (Moskowitz & Schwartzman, 1989).

The individuals from the aggressive-withdrawn group evidenced more behavior problems than the individuals from the control group. Moreover, the youngest subgroup of aggressive children, those identified at age 7, had more behavior problems than the youngest control and youngest withdrawn group, also identified at age 7. This result is also tentative because the size of the youngest group of aggressive children was small (n = 7) and the standard deviation was large (SD = 13.42). On the externalizing subscale, the aggressive-withdrawn group had higher externalizing scores than the control children and the children from the withdrawn group. Children from the youngest aggressive subgroup had a high externalizing score (M = 69.91) relative to the youngest control subgroup (M = 61.34) and withdrawn subgroup (M = 59.33). Again, this interaction effect should be interpreted with caution because of small sub-sample size and large standard deviation. On the internalizing subscale, the youngest aggressive subgroup had an elevated internalizing score compared with the children from the withdrawn subgroup and control group, however, once again this result is limited by small sample size and large standard deviation. Analysis of social competence indicated that aggressive, withdrawn and aggressive-withdrawn individuals were lower on school competence than the control individuals. Hence, in summary, the aggressive and aggressive-withdrawn individuals scored below the control individuals on intelligence. The aggressive-withdrawn individuals reported problems in the areas of behavior and social competence, including poor school competence, and the aggressive and withdrawn individuals reported problems in school (Moskowitz & Schwartzman, 1989).

Moskowitz and Schwartzman (1989) also examined the physical and psychiatric health of 95% of the original sample. Medical records were gathered for a 4-year period beginning approximately 4 years after identification. Results indicated that 97% of the sample had received medical care during the 4-year period, with approximately 10% of the sample receiving treatment for psychiatric problems. Aggressive individuals were found to be more than twice as likely to receive psychiatric treatment than individuals from the control group, and more frequent psychiatric treatments than all other classification groups. The aggressive females received the highest rate of medical treatment compared with the other groups of females and the aggressive males. In addition, the aggressive females were more likely to have had a gynecological problem. Females from the withdrawn group were more than twice as likely to have had an abortion than females from the control group (Moskowitz & Schwartzman, 1989).

The developmental trajectory of girls' childhood patterns of aggressive and withdrawn behavior was further investigated by Serbin, Peters, McAffer, and Schwartzman (1991). Specifically, Serbin and her colleagues investigated the impact of childhood disorders on adolescent pregnancy, early parenthood, and environmental risk for the next generation. The researchers found that girls who were identified as aggressive or aggressive-withdrawn in grade 1 were significantly more likely to have had gynecological problems and to have used birth control between the ages of 11 and 17 than the girls in the contrast group, who were not evidencing a behavioral disorder. Girls identified as aggressive in grade 4 were significantly more likely, between the ages of 14 and 20, to suffer from a sexually transmitted disease than the girls in the contrast group. Similarly, girls identified as aggressive-withdrawn from the same cohort, were significantly more likely to have experienced pregnancy between the ages of 14 and 20 than the girls from the contrast group. Girls identified in grade 7 as aggressive were significantly more likely to have used birth control, to have had gynecological problems, and to have experienced pregnancy, across the 17 to 23 year age span, as compared with the contrast participants.

A similar study conducted by the same researchers (Serbin et al., 1991) examined the home environment and parenting behavior of the women from the Concordia Study who became mothers in their late teenage years or in their early 20's. In addition, the study investigated whether mothers' aggression and social withdrawal in childhood impacted on their children's early developmental progress. The researchers found that mother's childhood aggression is predictive of poor developmental progress in the child, and a mother's childhood withdrawal is predictive of low overall quality of their adult home environment when these girls do become mothers. Quality of the home environment was based on factors such as the mother's emotional and verbal responsiveness and the physical and temporal environment.

Further support of the conclusion that children who have behavior problems are at risk of later maladjustment is supported by findings from the Waterloo Longitudinal Project. The Waterloo Longitudinal Project (WLP) was conducted from 1980 to 1990 and examined the stability and predictive outcomes of early aggression, social withdrawal and social competence. The original sample of the WLP consisted of 111 kindergarten students and 88 students in Grade 2 enrolled in public schools in the regional municipality of Waterloo, Ontario. These children were followed in Grades 3, 4, and 5. Although some children were lost over time through attrition, new children were added to the sample each year (Rubin et al., 1989). The outcomes associated with the WLP have been documented most closely by Rubin and his colleagues (Rubin, 1985; Rubin, 1993; Rubin & Asendorf, 1993; Rubin et al., 1989; Rubin & Mills, 1991).

At the onset of the project, the researchers focused on the contemporaneous and predictive correlates of social withdrawal due to the paucity of clear conceptual and empirical research in the area (Rubin, Chen, McDougall, Bowker, & McKinnon, 1995; Rubin, Chen, & Hymel, 1993). The early neglect of social withdrawal as a risk factor was not only a result of the methodological shortcomings of the research concerning withdrawal in childhood, but also from the dominant and urgent concern of researchers and clinicians with aggression as a marker and predictor of childhood psychopathology (Rubin et al., 1995). Aggression is indisputably one of the major reasons for treatment referral in childhood, as aggression is a strong predictor of delinquency and criminal behavior in adolescence (Farrington, 1991; Rubin et al., 1995). Moreover, aggression in childhood is frequently associated with other social and emotional difficulties such as emotional dysregulation, social information-processing deficits, bullying behavior, and peer rejection (Coie & Kupersmidt, 1983; Dodge, 1986, 1991; Olweus, 1993). In contrast, internalizing problems such as social withdrawal do not elicit a sense of urgency, as they are less salient and less likely to evoke a negative response than externalizing problems, such as aggression and attention deficit disorder with hyperactivity (Rubin & Mills, 1991). However, the research that has emerged from the WLP provides convincing evidence that social withdrawal reflects internalizing difficulties. For example, Rubin, Hymel, and Mills (1989) investigated the outcomes of social withdrawal in childhood by studying normal children in kindergarten through grade five. Social withdrawal was defined in this study "...as the observed production of solitary activities...encompassing shyness and fearfulness as well as solitude" (Rubin et al., p. 241, 1989). Rather than relying on a clinical sample, a school sample was obtained consisting of lower-middle to middle-class children of normal intelligence. Predictors of the internalizing type were used to assess difficulties in grades four and five. Internalizing difficulties were assessed using self-reports of social-competence, overall self-worth, loneliness, and depression. Teacher ratings of shy/anxious behaviors were also obtained in later childhood.

Results revealed a modest degree of stability across the 2-year period for observed overall social withdrawal, $r\ (56) = .37$, $p < .002$ and across the 3-year interval when peer perceptions were used to judge withdrawal, $r\ (48) = .30$, $p < .01$. The correlational results in many ways support the hypotheses that social withdrawal, at a young age, is predictive of internalizing problems in later childhood. A significant relationship was found between social withdrawal in kindergarten and grade 2 and internalizing difficulties such as self-reported feelings of depression and negative self-worth, in grades 4 and 5. The self-report measure of social incompetence in grade 2 was the strongest predictor of internalizing difficulties in grade 5. It was concluded, based on the above findings and other reports pertaining to the Waterloo Longitudinal Project (Rubin, 1985; Rubin & Mills, 1988) that social withdrawal reflects a child's poor self-regard and affect. Withdrawing from peer relationships combined with low self-esteem together predict later difficulties-notably internalized feelings of loneliness and depression (Rubin et al., 1989).

The Waterloo Longitudinal Project, in its final year, tracked the initial participants into their first year of high school, grade nine. Social withdrawal in kindergarten, and grades 2 and 5, were significant predictors of ninth-grade self-reports of loneliness, lack of self-competence, and social anxiety (Rubin & Mills, 1991). The WLP advanced the existing research on social withdrawal by demonstrating certain important features. First, it provides evidence that social withdrawal is stable over time. Second, social withdrawal is associated with feelings such as insecurity and poor self-perception. Last, negative self-image, social anxiety, and withdrawn behavior together are predictive of later internalizing problems, such as depression and loneliness (Rubin & Mills, 1991).

In addition to social withdrawal, the researchers involved in the WLP examined different outcomes of childhood aggression and social competence. For instance, Rubin, Chen, McDougall, Bowker, and McKinnon (1995) compared and contrasted the social and emotional outcomes associated with children evidencing early aggression with those evidencing early social withdrawal. Social competence was also included as a predictor of adolescent adaptation. The sample consisted of 60 children (30 boys and 30 girls) from predominantly middle class Caucasian backgrounds. Data consisted of behavioral observations, peer assessments, and teacher ratings was completed at 7 and 14 years of age assessing social withdrawal, aggression, and social competence. Expected outcomes highlighted specific markers of internalizing and externalizing problems. Results indicated that there was a significant positive correlation between childhood withdrawal in grade 2 and loneliness, feelings of peer-group insecurity, and feelings of family group insecurity in grade 9. In addition, social withdrawal in grade 2 was negatively associated with self-regard in grade 9. Hence, by drawing on multiple sources of information measuring social withdrawal, the researchers found that social withdrawal in grade 2 predicted internalizing type problems in grade 9. In contrast, there was a significant positive correlation between second-grade aggression and self-reported serious delinquency, such as carrying illegal weapons or involvement in criminal activity, in the ninth-grade. As expected, the long term correlates of childhood aggression, as assessed by multiple measures, predicted externalizing problem behavior such as delinquent activity, thus supporting previous longitudinal research examining the developmental course of aggression (e.g., Olweus, 1979; Pulkkinen, 1982). In support of developmental models of psychopathology depicting children who are socially competent as protected from negative outcome, findings indicated that social competence positively predicted self-regard and negatively predicted felt peer-group insecurity. Nevertheless, social competence also predicted substance use in adolescence. This finding was interpreted by the researchers such that the positive self-regard of the children may allow them to experiment early with cigarette smoking and alcohol experimenting, however, the researchers expected these children would appropriately monitor their substance use. Overall, the results of the WLP indicate that aggression in childhood predicts adolescent externalizing difficulties and social withdrawal predicts adolescent internalizing difficulties.

In sum, the findings of recent longitudinal research provide a rationale for the early detection and intervention of childhood behavioral difficulties. Therefore, parents, teachers and other professionals who work with children with behavioral difficulties are faced with the need for effective intervention services within an education system that is undergoing budgetary cutbacks (Sladeczek & Heath, 1997). Thus, the next section of this chapter presents the theoretical and empirical research on two cost-effective models of intervention.

Conjoint Behavioral Consultation versus Videotape Therapy

Over the past decade, the literature has provided convincing evidence indicating a strong, positive relationship between home/school collaboration and a child's success (Sheridan, 1997). Simultaneous behavioral consultation between parents and teachers offers one promising intervention approach for treating children with behavioral difficulties that facilitates collaborative partnerships among the most influential people in a child's life (Sheridan, 1997). Simultaneous consultation is based on an integration of ecological systems theory and behavioral theories. The ecological-systems theory reflects the philosophy that behavior occurs as a function of the interaction between children and the social systems of which they are interconnected. The behavioral theories provide the framework for working within and between systems to bring about positive change in a child (Bergan & Kratochwill, 1990; Kratochwill & Bergan, 1990).

Most often, Bergan's (1977) model of behavioral consultation and the extended model by Bergan and Kratochwill (1990) have been used as a blueprint for the provision of consultation services in the United States. In contrast, behavioral consultation has failed to appear in the Canadian school psychology literature and inevitably, has received less attention in the field (Sladeczek & Heath, 1997). In both countries, however, there is a striking absence of empirical data comparing behavioral consultation to other methods of service delivery (Noell & Witt, 1996). This line of inquiry is particularly relevant since scholars in the field have acknowledged that the behavioral consultation model can be implemented in a variety of ways and should be compared to other intervention approaches (Kratochwill et al., 1998; Noel & Witt, 1996). There is a need to investigate the efficacy of CBC as a service delivery model for children with specific behavior problems as compared with other cost-efficient models of intervention, such as videotape therapy.

Videotape therapy is a social learning-based approach that is gaining recognition for its effectiveness with children with a behavior problem (Webster-Stratton et al., 1989). Specifically, there is increasing evidence supporting the effectiveness of a videotape therapy parent training program developed by Carolyn Webster-Stratton (1987) in decreasing behavior problems (Webster-Stratton, 1993; Webster-Stratton et al., 1989; Webster-Stratton, Kolpacoff, & Hollinsworthn 1988).

Conjoint Behavioral Consultation

Conjoint behavioral consultation (CBC) is a systematic model for delivering interventions that can be used to service children with behavioral difficulties (Sheridan, Kratochwill, & Bergan, 1993). It is a treatment of choice for children with behavioral difficulties for at least three reasons. First, it is a form of service-delivery in which a large number of children can be helped (Erchul & Chewing, 1990; Gutkin & Conoley, 1990; Martens, Erchul, & Witt, 1992). Second, the empirical effectiveness of this process has been documented in past American-based research (Galloway & Sheridan, 1994; Kratochwill et al., 1999; Sheridan & Colton, 1994; Sheridan et al., 1990), and third, conjoint behavioral consultation encourages the collaboration of home and school, an integral ingredient for student achievement (Epstein, 1984, 1985; Fine & Carlson, 1992; Henderson, 1987; Kroth, 1989). Collaboration is an important means of improving the school competence of children with behavior problems (Sheridan & Kratochwill, 1992).

Conjoint behavioral consultation is an indirect form of service-delivery in which parents, teachers and consultants collaborate in order to address the academic, behavioral, and social needs of an individual (Sheridan & Kratochwill, 1992). A key element of behavioral consultation is the reliance on an indirect form of service in which a consultant works collaboratively with another adult or adults to elicit change in the client (e.g., a child) (Erchul & Chewing, 1990; Gutkin & Conoley, 1990; Martens et al., 1992). Involving parents and teachers relieves the caseload of many overburdened school psychologists. Consequently, psychologists are more accessible, enabling a greater number of children to receive treatment at any one time. It is for this reason that consultation is becoming more popular in the schools, as educators are in need of services shown to be efficient and functional. Moreover, preliminary investigations of CBC have indicated that CBC is an effective means of serving children with social withdrawal (Sheridan et al., 1990), academic difficulties (Galloway & Sheridan, 1994; Weiner, Sheridan, & Jenson, 1998) and irrational fears (Sheridan & Colton, 1994). In addition, two recent large scale studies have employed quasi-experimental and experimental research designs and documented the effectiveness of CBC in servicing children with specific disabilities (Sheridan, Colton, Fenstermacher, & Lasecki, 1996; Sheridan, Colton, Eagle, Cowan, & Richard, 1999) and children evidencing internalizing and externalizing problems (Kratochwill et al., 1999; Sladeczek, 1996).

Sheridan, Kratochwill, and Elliott (1990) tested the empirical effectiveness of conjoint behavioral consultation as a means of increasing the social initiations of withdrawn children. This was the first study investigating the effectiveness of CBC with children who are socially withdrawn. Four elementary school children between the ages of 8 and 12 years comprised the sample. These children were of average intellectual and language abilities. They were selected for treatment based on their specific difficulty of initiating interaction with peers. There were two forms of consultation being investigated. Two children received conjoint consultation (parent and teacher), while two children received teacher-only consultation. The treatment was identical across the four cases. Based on direct observation, rating scales, and self-report data, conjoint behavioral consultation was found to be an effective means of increasing social initiation both at home and at school. Teacher-only consultation was shown to be an effective method of increasing the social initiation of withdrawn children at school only. Furthermore, the maintenance of treatment effects was greater when the parents were involved in the consultation process. This research suggests that conjoint behavioral consultation is an effective means for increasing the social behavior of withdrawn children both at home and at school.

Other research documenting the effectiveness of conjoint behavioral consultation is slowly emerging (Galloway & Sheridan, 1994). One study examined CBC as a means of improving academic performance in underachieving children (Galloway & Sheridan, 1994). Six students from grades 1 through 3 and their parents and teachers participated. Two different types of case studies were conducted with the goal of improving accuracy and task-completion in mathematics. The first set of case studies utilized a home note procedure, and the second consisted of the same home note procedure implemented within the conjoint behavioral consultation framework. The students were randomly assigned to either condition. Results showed that all six children showed an improvement in accuracy and task-completion from baseline to intervention. However, consistent performance and statistically significant differences between baseline and treatment conditions were documented only by those children receiving consultation. Furthermore, the maintenance of treatment gains was stronger for those receiving home notes with consultation than the home-note-only group.

Weiner, Sheridan, and Jenson (1998) used CBC as a process through which to introduce a structured homework completion program to improve math homework completion and accuracy. A multiple baseline design involving five students, and their parents and teachers was used to implement the intervention program. Intervention consisted of self-monitoring, rules for homework completion, and reinforcement. At posttreatment, four of the five students evidenced an improvement in homework completion and accuracy rates. Three of the five students maintained these gains one-month later.

Sheridan and Colton (1994) demonstrated the immediate and long-term usefulness of conjoint behavioral consultation as a means for treating the irrational fear of a kindergarten student. This is the only documented study to examine the effectiveness of the conjoint behavioral consultation approach in treating a problem manifested only in the home setting. Mark, the participant in this study, was a six-year old boy who was recommended for consultation by his teacher, based on the distressing stories he was telling her at school. Mark feared that monsters and spiders were living in his bedroom, and hence slept each night on the floor of his parents' room.

Sheridan and Colton (1994) implemented the four stages of conjoint behavioral consultation with the goal of having Mark sleep in his own bed all night (1994). During the problem identification stage, the general characteristics and concerns related to the child's fears of sleeping in his own room were reviewed and procedures outlined for the child's mother and teacher for collecting baseline data. The second phase of CBC involved the conjoint problem analysis interview. During this interview, the baseline data was analyzed and a behavioral program developed to increase the amount of time the child spent sleeping.

The intervention program, implemented by Mark's parents, was a fading technique that consisted of five equidistant steps. Each step marked a small progression from moving the child from the parents' bedroom to his own room. "Mastery", defined as two consecutive successful nights sleep in the designated physical space, was necessary before moving to the next step. A reinforcer of Mark's choice (e.g., a folder, baseball cards) was provided following mastery of each step and a long-term secondary reinforcer (i.e., a life-size poster of Michael Jordan) was provided following Mark's successful completion of an entire night's sleep in his own bed.

The treatment evaluation interview was carried out following 15 consecutive nights of intervention. An AB with follow-up design was used to evaluate treatment effectiveness. In this case, treatment was successful, as the child slept a complete night in his own bed. The success of this study provides further evidence that conjoint behavioral consultation is a useful model and intervention for childhood problems.

In a series of studies, Sheridan and her colleagues (1996; 1999) have investigated the usefulness of CBC in facilitating the inclusion of children and adolescents with various disabilities, such as ADHD, learning disabilities, behavior disorders, and intellectual handicaps, into the regular classroom. Specific academic and social behaviors were targeted for change such as off-task behavior, aggression, and noncompliance. Behavioral interventions were introduced to both teachers and parents that included self-monitoring, token economies, home-notes, and reinforcement. Results from preliminary analyses of 53 cases revealed significant changes in target behaviors across settings (Sheridan, Colton, Eagle, Cowan, & Richard, 1999).

Another study examining the ways to facilitate inclusion in regular education classrooms compared CBC with teacher-only and parent-only consultation (Colton & Sheridan, 1999). Six elementary school children and their teachers and parents participated in the academic intervention aimed to improve basic math and reading skills through individualized tutoring sessions. Student in all three groups evidenced improvements in their math and reading skills following treatment. Gains were maintained at a 2 and 4-week follow up.

A large five-year research project headed by Kratochwill and Elliott investigated the effectiveness of CBC in treating externalizing and internalizing problems. Preliminary findings obtained from the project have been presented at conferences (e.g., Sladeczek et al., 1996; Kratochwill et al., 1999). One hundred and twenty-three preschool children attending Head Start were randomly assigned either to the CBC experimental condition or to a no treatment control group. Each participant was matched for ethnicity, gender, and family background. The CBC framework was used to facilitate an intervention program carried out over two phases. During the first two years of the project (Phase 1), parents and teachers carried out behavioral intervention through a manual-based approach. In the remaining years (Phase 2), behavioral intervention was based on the strategies outlined by Webster-Stratton (1982; 1992b) in her videotape training program.

Sladeczek, Kratochwill, and Elliott (1996) focused on data obtained during the first two years of the study and examined the effectiveness of the CBC approach combined with the self-help manual based treatment for helping children experiencing social withdrawal or conduct problems. The sample consisted of 39 Head Start children (experimental group, $\underline{n} = 31$, control group, $\underline{n} = 8$). The *Social Skills Rating System* (SSRS: Gresham & Elliott, 1990) Teacher Form and Parent Form were used to evaluate the child's social behavior. Results indicated that parents of children in the experimental group rated improvements in social skills and a decrease in problem behavior on the

SSRS from pretest to posttest. However, there was no significant difference between the ratings for children in the experimental group and the control group. Nevertheless, treatment acceptability ratings were high.

Kratochwill and his colleagues (1999) presented data gathered across the five years. They found no statistically significant differences from pretreatment to posttreatment on standardized measures using large sample, multivariate statistics. However, results obtained from small-N analyses, such as effect sizes and reliability of change indices, revealed larger behavioral improvement for children in the manual-based group than for children in the videotape group or control group. Children in the videotape group demonstrated only small improvement when compared with the control group (Kratochwill et al., 1999).

In summary, although the behavioral approach to consultation has received considerable research attention, there have been only a few studies to date that have examined the efficacy of conjoint behavioral consultation. The first study considered the usefulness of CBC as a means of increasing social initiations in withdrawn children (Sheridan et al., 1990). A second study provided evidence that CBC is a successful intervention for improving school performance in underachieving students (Galloway & Sheridan, 1994) and a third study documented the effectiveness of this process in treating irrational fears and childhood phobias (Sheridan & Colton, 1994). Most recently, the usefulness of CBC as a framework in which to facilitate inclusion practices for children and adolescents with specific disabilities was examined (Sheridan et al., 1999). In addition, preliminary findings have emerged from a recent large scale investigation of the effectiveness of the CBC framework in treating children with internalizing and externalizing behavior problems (Kratochwill, 1999). Based on the research available, there is evidence that conjoint behavioral consultation provides an effective framework to treat children with behavior problems. However, more research is needed to further document the usefulness of conjoint behavioral consultation. Although there is an assumption that behavioral consultation is an efficient approach because it requires less of the consultant's time than other interventions (i.e., direct intervention), this assumption should not preclude the study of the effectiveness of CBC as compared with other cost-efficient models of service delivery (Noell & Witt, 1996). One area of research pertaining to behavioral consultation that is well documented, however, is the importance of involving parents in their children's education (Epstein, 1984, 1985; Fine & Carlson, 1992; Henderson, 1987; Kroth, 1989).

Conjoint behavioral consultation is designed to enhance the home-school relationship. The active involvement of parents in their children's education is believed to benefit children, teachers, and parents (Sheridan & Kratochwill, 1992). Saint-Laurent, Royer, Hebert, and Tardif (1994) found that parent involvement reduces the likelihood of school failure. Children who are isolated from their peers reported that they were low on school competence and underestimated their scholastic abilities (Moskowitz & Schwartzman, 1989). Similarly, high aggressiveness, and aggressiveness coupled with social withdrawal, are predictive of low intelligence and poor school achievement (Moskowitz & Schwartzman, 1989). Hence, school-family collaboration is particularly important when treating children who are socially withdrawn, in order to reduce their negative perceptions related to school competence, and when treating children who are aggressive and aggressive-withdrawn, in order to improve school achievement.

The practices, attitudes, needs and expectations of over 630 teachers and 957 parents were investigated in a study (Saint-Laurent et al., 1994). A particularly interesting finding in this study was that parents wanted to cooperate with the school and receive training in order to best achieve a collaborative relationship. In fact, over 70% of parents were interested in becoming involved in their children's schooling. Furthermore, it was found that teachers were in favor of parent involvement and thought that parent training would be useful as a means of helping parents better deal with their children, in cooperation with the school (Saint-Laurent et al., 1994). Preliminary findings suggest that conjoint behavioral consultation is an effective means of providing parent training (Sheridan et al., 1993), and increasing home-school collaboration (Sheridan & Kratochwill, 1992). Indeed, the more teachers and parents work cooperatively, the greater the chances for success in helping the child with a behavior problem achieve behavior change across settings (Sheridan et al., 1990).

Videotape Therapy

Treatment programs designed to reduce problem behavior frequently emphasize parent skills training (Webster-Stratton, 1994, 1998). Parent skills training typically refers to the process by which parents learn to alter the reinforcement contingencies that support the undesirable behavior of children (Webster-Stratton, 1994). The rationale for targeting parenting behavior as a primary focus of intervention arises from the research indicating that parents of children with behavioral difficulties, such as conduct disorder, lack certain fundamental parenting skills (e.g., Patterson, 1982). For example, parents of children with conduct difficulties have been shown to exhibit fewer positive behaviors and to be more violent and critical when disciplining. Moreover, these parents are reportedly more permissive, less likely to monitor their children's behavior, and more likely to attend to negative behavior and ignore positive behavior (e.g., Patterson, 1982; Webster-Stratton, 1994). Results from a survey of over 22 000 Canadian children and their families indicate that parenting style is the strongest predictor of aggressive behavior in children (Stevenson, 1999). Mothers and fathers who used ineffective, inconsistent, and aversive parenting practices were more likely to have a child with behavior problems than parents applying techniques in a positive and consistent manner.

Most traditional parent training programs are costly and time-consuming, and are rarely available to those in need of services (Webster-Stratton, 1990). However, a videotape modeling treatment program provides an approach to parent training that has the potential for being both efficient and cost-effective (Webster-Stratton, 1990). Moreover, there exists a growing body of research which supports the effectiveness of videotape modeling social learning-based approaches for training parents who have children with a behavior problem (Webster-Stratton et al., 1989). Webster-Stratton developed an interactive videotape-based intervention program entitled the BASIC Parent and Child Video Series for children between the ages of 3 to 8 years (1982, 1988, 1992b). The BASIC program is equal in effectiveness to social learning parent training offered one-on-one with a therapist, and requires one-fifth of the therapists time to service the same number of people (Webster-Stratton, 1984). The underlying process is founded on a collaborative relationship between the therapist and parents whereby parents are given shared responsibility for developing solutions along with the therapist (Webster-Stratton & Herbert, 1993).

The content of the videotapes focuses on teaching parents how to play with their children, use praise and tangible rewards to modify behavior, set limits, and manage problem behavior (Webster-Stratton, 1990). The program is also designed to help parents understand what are normal variations in their children's development, emotional reactions and temperaments. The series comprises of 10 videotape programs and 250 short vignettes. Each vignette highlights mothers and fathers of different ages, cultures, socioeconomic backgrounds and temperaments involved in an unrehearsed interaction with their young child or children.

There are three variations in which the BASIC program may be completed: (a) the program may be offered to parents as an individually self-administered videotape modeling treatment (VT); (b) the program may be completed in groups of 8 to 12 parents led by a therapist (GVT); and (c) within the group format, the parents may participate in the discussion groups without viewing the videotapes (GD). In the therapist-led group format, the videotapes serve as stimuli for focused discussion, problem solving, and collaborative learning as parents become involved in the process of sharing and exploring ideas and reactions. The therapist's role is that of consultant, supporting and empowering the parents by teaching, leading, reframing, predicting, and role playing within a collaborative context (Webster-Stratton & Herbert, 1993, 1994).

Research comparing the efficacy of the self-administered videotape modeling treatment, the consultant-led group discussion videotape modeling treatment and the consultant-led group discussion treatment has suggested that all three variations of the BASIC program result in significant improvements in parental reports of their children's behavior and in parent-child interaction (Webster-Stratton, Kolpacoff, & Holinsworth, 1988). The BASIC program has been shown to be effective in improving parental attitudes and parent-child interactions that were maintained 1 year later (Webster-Stratton et al., 1988; Webster-Stratton et al., 1989). The 1-year follow-up results were similar to the immediate posttreatment results, suggesting stability of the initial posttreatment group findings (Webster-Stratton et al., 1989). Furthermore, approximately two thirds of the sample showed "clinically significant" improvements as defined using the following criteria: (a) a score of 63 or lower on the *Child Behavior Checklist*, as identified by Achenbach and Edelbrook (1983) as the cutoff point between normalcy and deviancy; (b) mother reports of target negative behaviors on the *Parent Daily Report* had to be reduced by 50% from baseline; and (c) spanking had to be reported stopped.

Webster-Stratton (1990) conducted a 3-year follow-up study evaluating treatment gains from preschool to early elementary school. Results indicated that parents across all three treatment groups continued to report treatment gains such as fewer total child behavior problems and increased prosocial behavior at the 3-year follow-up, however only the parents who received a combination of videotape modeling with therapist-led group discussion evidenced stable improvements. Further investigation of the individually administered program indicated that treatment was less effective with families who are highly stressed, or mothers' who are depressed or not married. In addition, treatment gains were negatively correlated with the socioeconomic status of the mother, maternal age, and paternal perceptions (Webster-Stratton, 1992a).

ADVANCE, a broader-based treatment model, was developed by Webster-Stratton to supplement the BASIC program (Webster-Stratton, 1992b). ADVANCE was created following an analysis of 218 families who had received the combination group discussion and videotape modeling which revealed that marital distress and the lack of a supportive partner were the most powerful predictors of child deviance. In fact, parent and family characteristics, such as spouse abuse, maternal depression, lack of social support, and high life stress have been associated with fewer treatment gains (Webster-Stratton, 1989, 1994). The ADVANCE series consists of an additional six videotapes, with over 60 vignettes that are viewed in combination with the therapist-led group discussion. The videotapes cover the following content areas: (a) personal self-control; (b) communication skills, (c) problem-solving skills between adults; (d) how to teach children to solve problems; and (d) promoting social support and self -care.

To date, there is little research evaluating the efficacy of the ADVANCE program. A recent study comparing the effectiveness of the ADVANCE program with the BASIC program (combination videotapes and group discussion format) revealed that parents who completed the ADVANCE series enhanced their problem solving and communication skills and reported increased satisfaction with their parenting skills compared to parents who completed the BASIC program only (Webster-Stratton, 1994). However, there were no significant differences between the two treatment modalities with respect to parental report of their children's behavior. Similarly, no significant differences between treatment types were obtained in respect to marital satisfaction, anger, or stress levels (Webster-Stratton, 1994).

In sum, there is an absence of empirical data comparing conjoint behavioral consultation to other methods of service delivery (Noel & Witt, 1996). There is a need to investigate the efficacy of CBC as a service delivery model for children with specific behavior problems as compared with other cost-efficient models of service-delivery. To this end, it would be useful to compare indirect service delivery models which provide varying levels of consultation from structured consultation model (CBC) to the semi-structured model of minimal consultation and videotape therapy (GVT), to an unstructured consultation model of self-administered videotape therapy only (VT).

Another important issue to consider when evaluating the efficacy of the intervention services is the impact of the treatment models on enhancing parenting skills and home and school cooperation (Shriver, Kramer, & Garnett, 1993). Thus, the remainder of this chapter will examine the parent involvement literature, placing specific emphasis on the influence of parental perception of self-efficacy on their decision to become involved in their children's education.

Evaluating Parent Involvement in Education

The underlying support for the notion that parental involvement in a child's education is desirable stems from the assumption that since children spend the majority of their time with parents or family, children would logically benefit from their parents' involvement in their schooling (Shriver, Kramer, & Garnett, 1993). Consultation with parents and teachers provides an indirect service delivery model by which an emphasis is placed on improving parenting skills in order to increase the probability that a parent will work effectively with a child (Shriver, Kramer, & Garnett, 1993).

Sheridan and Kratochwill (1990) were the first to outline a rationale for incorporating both parents and teachers into the behavioral consultation framework. The researchers based their rationale on the parent involvement literature showing that active parent participation in the school is believed to have positive outcomes for children, parents, and teachers (Christenson, 1995; Fine & Carlson, 1992; Hoover-Dempsey et al., 1987; Kroth, 1989). Sheridan and Kratochwill (1990) discuss Conoley's (1987) four levels in which parents may become involved in their children's education. The four levels are: (a) sharing of basic information across home and school; (b) collaborating through home and school programs and establishing feasible systems of communication between parents and teachers; (c) actively becoming involved in school life; and (d) participating in the reciprocal education of parents and teachers by each other. Similarly, Sheridan and Kratochwill (1990) cite the research of Becher (1986) who also suggests several methods of involving parents in their children's education such as: (a) parent meetings and workshops, (b) parent-teacher conferences, (c) written and personal communication, (d) parent visits to the classroom, and (e) encouragement and inclusion of parents in decision-making and evaluation activities. Sheridan and Kratochwill (1990) emphasize that there is little research that compares the effects of the different forms and levels of parent involvement and that the actual involvement of parents is often low. Hence, conjoint behavioral consultation was suggested by Sheridan and Kratochwill (1990) as one form of home-school service delivery that can address problems between parents, teachers, and students strategically and effectively in order to ensue productive partnerships. The rationale proposed by Sheridan and Kratochwill (1990) to involve both parents and teachers in the behavioral consultation framework is clearly deliniated. Specifically, CBC may provide one avenue to stengthen the contribution of both the school and the family on children's development. However, there is little research evaluating the actual strength of the parent-teacher partnership before consultation has begun and after consultation has terminated.

An important methodological issue to consider when evaluating the efficacy of an intervention, and specifically, when evaluating parent involvement in the program, is how involvement is operationally defined. Parents have different expectations about what they should contribute to their child's education based on their own family values, stressors, and community and school expectations. Similarly, teachers will have varying expectations of what they consider to be an optimal level of parent involvement for their classroom or individual student. Hence, in order to effectively evaluate or measure parent involvement in the classroom, it is important that involvement be specifically outlined (Shriver, Kramer, & Garnett, 1993).

Hoover-Dempsey and Sandler (1995) developed a definition of parent involvement which incorporates the range of parental activities discussed in the parent involvement literature. These activities include both home-based activities related to children's learning in school and school-based involvement. The home-based activities include reviewing the child's work, monitoring school progress, helping with homework, discussing school issues, providing enriched activities and talking to the teacher by phone. School-based activities include driving on a field trip, attending conferences, volunteering at school, and serving on an advisory board (e.g., Clark, 1993; Dauber & Epstein, 1993; U.S. Department of Education, 1994).

Factors Influencing Parent Involvement and Collaboration

Hoover-Dempsey and Sandler (1995) developed a model that illustrates the influence of specific variables on the parent involvement process (see figure 1). The model is consisted of five levels of contructs which influence parental involvement in their children's education: (a) influences on parents' basic decision to become involved;

(b) influences on parent's choice of involvement; (c) mechanisms (i.e., modeling, reinforcement, and instruction) through which parental involvement influences child outcomes; (d) tempering/mediating varianbles; and (e) child/student outcomes. The following review focuses on the first level of the model in order to investigate the factors which influence parents' decisions to become involved in their children's education. It is important to examine the factors which influence parent decision making in order to apply the information when designing and implementing a treatment plan or in order to evaluate whether a treatment model positively influences parental involvement in education. Clearly, the examination of specific parent variables related to children's school performance suggests a useful avenue towards understanding and improving parent-school relationships (Hoover-Dempsey, Bassler, & Brissie, 1992a).

Level 5 **Child/student outcomes**

Skills & knowledge

Personal sense of efficacy for doing well in school

Level 4 **Tempering/mediating variables**

Parent's use of developmentally appropriate involvement strategies	Fit between parents' involvement actions & School expectations

Level 3 **Mechanisms through which parental involvement influences child outcomes**

Modeling	Reinforcement	Instruction

Level 2 **Parent's choice of involvement forms, influenced by**

Specific domains of parent's skill & knowledge	Mix of demands on total parental time and energy (family, employment)	Specific invitations & demands for involvement from child & school

Level 1 **Parent's basic involvement decision, influenced by**

Parent's construction of the parent role	Parent's sense of efficacy for helping her/his children succeed in school	General invitations & demand for involvement from child & school

Figure 1: Model of the parental involvement process (Hoover-Dempsey & Sandler, 1995)

The first level of the model of the parental involvement process suggests that the majority of parents decide to become involved in their children's education as a function of three constructs: (a) parents construction of their role in the child's life; (b) parents sense of efficacy for helping their child succeed in school, and (c) the general invitations, demands, and opportunities for parent involvement as offered by the child and his/her school (Hoover-Dempsey & Sandler, 1995). Each construct comprising the first level of the model focuses primarily on the individual parent.

Roles may be defined as a set of expectations held by the group for the behavior of individual members or a set of behaviors characteristic of the individuals in the group (Hoover-Dempsey & Sandler, 1997). Hence, parents define their role in their children's life based on explicit and implicit expectations they hold regarding parent involvement and the behaviors they enact in relation to their children's schooling (Hoover-Dempsey & Sandler, 1997). Further, parents' ideas about child development, parenting, and school involvement influence a parent's decision of whether or not to become involved in their child's education. Hence, the decision about becoming involved in children's schooling is based on specific sets of beliefs. The beliefs relate to the person's perspectives about what children need from their parents in order to successfully grow and develop, his/her belief about advantageous childrearing outcomes, and his/her belief about the capability of specific childrearing practices in promoting and encouraging the desired outcomes (Hoover-Dempsey & Sandler, 1997).

Efficacy theory suggests that parents with a higher sense of efficacy for helping their children succeed will tend to perceive themselves as capable of making a positive difference for their children (Hoover-Dempsey & Sandler, 1997). Parents with a high sense of efficacy are likely to believe in their own ability to face challenges, and to persevere through difficult situations. On the other hand, parents low in efficacy are likely to avoid becoming involved in their children's schooling because they may have a fear of confronting their own inadequacies or they may doubt their abilities to make a positive difference for themselves or their children (Hoover-Dempsey & Sandler, 1997).

There is limited research in the area of parents' sense of efficacy as it relates to helping children succeed in school (Hoover-Dempsey & Sandler, 1997). Nevertheless, the existing research does suggest a positive relationship between the two constructs (Hoover-Dempsey et al., 1987). Hoover-Dempsey and her colleagues (1987) have grounded their research on parents' and teachers'sense of self-efficacy as it relates to children's success in school in Bandura's work on personal efficacy. Bandura (1977, 1984, 1986) examined the influence of the personal belief that one is capable of achieving a specific outcome based on his or her behavior choices. Bandura's work suggests that people with a greater sense of self-efficacy will generally be more goal directed and persistent when faced with obstacles than people with a lower sense of efficacy. Accordingly, Bandura's theory (1977, 1984, 1986) suggests that parents have self-efficacy beliefs about their ability to help their children learn which, in turn, influence their decision to become involved in their children's education (Hoover-Dempsey et al., 1992a). The premise follows that parents most likely to become involved in their children's education hold the belief that their involvement will "make a difference" for their children (Hoover-Dempsey et al., 1992a).

Hoover-Dempsey, Bassler, and Brissie (1992a) in a relevant study explored three different factors influencing parent-school relations. First, the researchers examined the relationship between parents' sense of efficacy and its relationship to specific indicators of parental involvement in the the elementary school child's education. Specific indicators were selected following Bandura's (1986) suggestion that self-efficacy be assessed within the domains of functioning that are under investigation. Second, the researchers examined the replicability of previous findings suggesting a positive relationship between teachers' sense of efficacy and parent involvement which follows that teachers who are more confident in their abilities will be more likely to welcome the involvement of parents in their classroom (Hoover-Dempsey et al., 1987). Third, the researchers investigated whether increased parent involvement would positively influence teachers' perceptions of parent efficacy.

Hoover-Dempsey and her colleagues (1992a) defined parent efficacy as parents' beliefs about their general ability to influence their child's developmental and educational outcomes, about their specific effectiveness in influencing the child's school learning, and about their own influence relative to that of peers and the child's teacher. The sample consisted of 390 parents of children from four elementary schools in a large school district and fifty teachers in the four schools. The parents and teachers completed questionnaires which included three components: (a) demographic items; (b) questions requesting estimates of participation in specific activities; and (c) questions assessing the respondents' perceptions of parent and teacher efficacy. Results of the study revealed significant correlations between parent efficacy and three indicators of parent involvement: (a) more hours spent volunteering in the classroom; (b) more hours involved in educational activities; and (c) fewer hours spent on telephone calls with the teacher. In addition, teacher efficacy and teacher perceptions of parents' efficacy were both positiviely associated with teacher reports of parent involvement in homework, educational activities, volunteering, and conference participation. In addition, teacher efficacy was positively related to teachers' reports of parent efficacy. Hence, the findings of this study suggest the usefulness of targeting parents' and teachers' feelings of efficacy as an avenue for improving parent-school relations, and ultimately, for improving children's school success (Hoover-Dempsey et al., 1987).

Although the assessment of perceived self-efficacy is believed to be a fundamentally important mechanism in the explanation of parents' decision to become involved in their children's education, it is, as previously explained by the model of the parental involvement process (Hoover-Dempsey, & Sandler, 1997), one of several contributors to parents' involvement decisions. The general invitations, demands, and opportunities for parental involvement is the third major construct influencing the decision for parents to become involved (Hoover-Dempsey, & Sandler, 1997). This construct relates to the parents' perception of whether or not the school or child wants them to be involved. Multiple invitations, opportunities, and requests made by both the children and schools seems to facilitate and encourage parent involvement. The degree to which parents believe themselves to be invited and welcomed to the educational process will influence the basic decision to become involved (Hoover-Dempsey, & Sandler, 1997). Clearly, a schoolwide effort is needed to create an inviting atmosphere for parent involvement which includes advocating for intervention and remedial programs for children that promote parent participation.

Predictions of the Present Study

The data examined in the present study are part of a larger longitudinal study comparing the effectiveness of videotape therapy and conjoint behavioral consultation for treating children with mild to moderate behavioral difficulties. In the following study, three experimental treatment conditions are tested with mothers and teachers: (a) conjoint behavioral consultation; (b) minimal consultation combined with videotape therapy; and (c) self-administered videotape therapy. The purpose of the present study is to evaluate the effectiveness of the three treatment conditions in treating children with specific behavior problems (i.e., internalizing and externalizing behavior) both at home and at school, and to evaluate whether mother involvement in their children's education increases as a result of the three treatment conditions. Several predictions are tested. Dependent variables are bolded as they appear in the following predictions.

I. Determining the Efficacy of CBC, GVT and VT

Prediction 1

It is predicted that each child in the CBC, GVT, and VT conditions will evidence significant improvement in their ***target behaviors*** *from pretreatment to posttreatment.*

The following study aims to ascertain the efficacy of conjoint behavioral consultation and videotape therapy in treating children with behavior problems (i.e, internalizing, externalizing, and a combination of both). The empirical effectiveness of conjoint behavioral consultation (Galloway & Sheridan, 1994; Kratochwill et al., 1999; Sheridan & Colton, 1994; Sheridan et al., 1990) and videotape therapy (Webster-Stratton, 1990, 1992a; Webster-Stratton, Kolpacoff, & Holinsworth, 1988; Webster-Stratton et al., 1989) has been documented in past research. The effectiveness of a self-administered treatment approach (i.e., self-help treatment manual) with minimal consultation has also been supported empirically (Sladeczek et al., 1996). Based on the above findings, it is predicted that the children from the three treatment conditions will evidence significant improvements in the behavior targeted for intervention.

Prediction 2

It is predicted that each child in the CBC, GVT, and VT conditions will evidence a decrease in ***internalizing difficulties****, a decrease in* ***externalizing difficulties****, a decrease in* ***problem behaviors****, or an increase in* ***social skills*** *from pretreatment to posttreatment.*

The efficacy of conjoint behavioral consultation and videotape therapy in treating children with behavior problems (i.e, internalizing, externalizing, or both) may be evaluated by comparing externalizing difficulties, internalizing difficulties, problem behaviors, and social skills at pretreatment as compared with posttreatment. It is predicted that the children from each of the three treatment methods will evidence significant improvements in behavior problems or social skills from pretreatment to posttreatment.

Prediction 3

It is predicted that there will be a significant improvement in ***parenting skills,*** *as defined by an increase in total effective skills (total praise + positive attending + direct commands), and a corresponding decrease in total ineffective skills (critical statements + no opportunity commands), and a decrease in* ***negative child behavior*** *(total child deviance + noncompliance to commands) from pretreatment to posttreatment*

In addition to evaluating treatment effectiveness via changes in target behavior and changes in internalizing behavior, externalizing behavior, problem behavior, and social skills, this study systematically evaluates the changes in mother and child interaction using an observational situation. It is predicted that there will be a significant improvement in parenting skills and child behavior from prettreatment to postreatment.

II. Effect of Treatment Type and Specific Problem Behavior on Treatment Outcome

Prediction 4

*It is predicted that the type of treatment delivered to children with problem behaviors will have a differential effect on the **behaviors targeted** for change.*

The following study allows for the direct comparison of the efficacy of three treatment approaches utilizing varying degrees of consultation ranging from direct behavioral consultation with mothers and teachers, to minimal consultation and videotape therapy, to self-administered videotape therapy only. This study is designed to isolate the treatment type that is most effective in reducing problem behaviors and increasing social behavior of children with behavioral difficulties.

Prediction 5

*It is predicted that children evidencing significant internalizing problem behaviors at pretreatment will evidence significant improvement in **internalizing behavior** and **social skills** at postreatment.*

Previous intervention researchers have shown that internalizing difficulties typically go unnoticed by teachers and caregivers therefore creating a population which is currently under-serviced (Rubin & Mills, 1991). In contrast, behavior problems of the externalizing nature receive considerable attention, representing an estimated one-third to one-half of child and adolescent cases referred to outpatient clinics (Achenbach & Howell, 1993; Gilbert, 1957; Robins, 1981; Kazdin, 1988). Moreover, researchers investigating treatment effectiveness have often grouped conduct-problem children with socially isolated and withdrawn children or children with other developmental problems, failing to acknowledge that children with internalizing difficulties may respond differently than children with externalizing difficulties to intervention (Webster-Stratton & Hammond, 1997). It is therefore necessary to deliberately examine the effectiveness of intervention for treating children evidencing internalizing type problems. It is predicted that there will be significant improvement in internalizing behavior as a result of CBC, GVT, and VT.

III. Examining Hoover-Dempsey and Sandler's Model (1995): Self-Efficacy and Involvement

Prediction 6

It is predicted that mothers and teachers participating in CBC, videotape therapy and minimal consultation, and self-administered videotape therapy will evidence a significant improvement in their ***perceived self-efficacy*** *and in* ***teacher perceptions of mother efficacy*** *from pretreatment to posttreatment.*

CBC and videotape therapy are designed to increase the competence of parents and teachers in effectively dealing with the behavior difficulties of children. In so doing, it is predicted that the perceived self-efficacy of mothers and teachers, and teachers' perceptions of mother efficacy, will improve as a result of treatment.

Prediction 7

It is predicted that mother and teacher perceptions of self-efficacy, and teacher perceptions of mother efficacy are associated with ***parent involvement****.*

Conjoint behavioral consultation was suggested by Sheridan and Kratochwill (1990) as one form of home-school service delivery that may improve parent and teacher collaboration by encouraging the active involvement of parents in their children's education. However, there is little research evaluating the actual strength of the parent/teacher partnership before consultation has begun and after consultation has terminated and only minimal research examining the effect of videotape therapy on parent and teacher collaboration. Based on the model developed by Hoover-Dempsey and Sandler (1995), the assessment of perceived self-efficacy is a fundamentally important mechanism in the explanation of parents' decision to become involved in their children's education. Hence, it is predicted that there will be a significant and positive relationship between perceived self-efficacy and parent involvement.

CHAPTER 3

Method

Research Design

The research study utilized a quasi-experimental research design involving both group and single-subject methodology. A repeated-measures group design was used to investigate the differences between treatment groups from pretreatment to posttreatment with respect to mother and teacher ratings of the target children's social skills, internalizing difficulties, externalizing difficulties, and problem behaviors, and with respect to mother and teacher ratings of perceived self-efficacy, and mother involvement. The repeated-measures design was selected because it controls for the variability among participants due to individual differences and require fewer participants for the study since the same individuals are being tested repeatedly (Stevens, 1996).

Given the individualized nature of consultation, the use of a small-n or single subject research design is recommended as the preferred means of documenting treatment outcomes (Gutkin, 1993, Busse, Kratochwill, & Elliott, 1995). Single-subject experiments are scientific investigations which examine the effects of a series of experimental manipulations on a single subject and the reasons for these effects (e.g., Hersen & Barlow, 1976; Kazdin, 1982; Kratochwill, 1978; Wilson, 1996). The underlying rationale of single-subject experimental designs, to compare the effects of different conditions on performance is similar to that of traditional between group experimentation (Kazdin, 1982).

The design of this study consisted of a baseline (A) period followed by a period of intervention (B). Behavioral observations collected during the baseline phase were compared with observations collected during the intervention phase in order to document treatment effectiveness (Barlow et al., 1984). Within this design, attempts were made to implement a multiple-baseline design across participants. A multiple baseline design involves the coordination of a series of simple phase changes (e.g., baseline to treatment) in order to strengthen the power of the research design to detect treatment effects (Barlow, Hayes, & Nelson, 1984). Attempts to stagger the start of the intervention phase across participants were not successful due to logistical reasons.

Baseline information was gathered for each participant until there was a satisfactory estimate of the frequency of the natural occurrence of the target behavior both at home and in the classroom. It was in this manner that each participant acted as his/her own control, as the baseline data collected for each participant served as a criterion to evaluate whether the intervention led to a change. Presumably, if the treatment program is effective, the participant's performance will differ from the projected level of the baseline (Kazdin, 1982). Hence, once baseline information was collected, treatment was introduced and information about the target behavior continued to be gathered throughout the treatment phase. Information was collected for all participants in the home and the classroom across baseline and treatment conditions. Continuous assessment is essential in order to investigate the effects of the intervention on the child's target behavior. Weekly contact with teachers and mothers was maintained in order to assess treatment progress. The A-B repeated measures design implemented in this study adequately controlled for threats to internal validity, and addressed threats to external validity by replicating treatment effects across multiple participants and settings.

Participants

Children

The study serviced 35 children (19 children in the CBC condition; 7 in the GVT condition; and 9 in the VT alone condition) between the ages of 3 and 10 years old who were experiencing social skill difficulties, problem behaviors, internalizing problem behaviors, or externalizing problem behaviors. Typical of the literature, the significant majority of children serviced were males (33 males, 2 females). The children were recruited from private preschools and three elementary schools affiliated to the Montreal English Speaking School Board via initial screening, teachers' referral, or via other staff in the schools.

Demographic information about the child sample was gathered using screening questionnaires and a history questionnaire. The history questionnaire asked relevant questions related to family composition, medical and psychiatric diagnoses, and previous interventions and medications (see Appendix A for the history questionnaire). The mean age of the children prior to treatment was 5.97 years. Nine of the children had been previously diagnosed with a medical or psychiatric condition or disorder, and of these, three were taking Ritalin on a daily basis during the consultation process. Four of the children and families reported that they had previously consulted with professionals for help with their children's behavior problems, although none of the children were receiving psychological services in addition to what was provided in the present study. Demographic data are outlined in Table 1.

Table 1

Child Demographic Data

Item	Number	Percentage of Sample
Average Age (in months)		
Prior to treatment	71.68 (SD = 20.9)	
Following treatment	76.70 (SD = 20.9)	
Previous/Comorbid Diagnoses		
Allergies	1	2.8%
Attention Deficit Hyperactivity Disorder	3	8.6%
Fine/Gross Motor Delay	1	2.8%
Global Developmental Delay	1	2.8%
Seizures	1	2.8%
Speech and Language Delay/Impairment	2	5.7%
Previous Professional Involvement		
Social Worker	2	5.7%
Psychiatrist	2	5.7%

Mothers and Teachers

Mothers interested in participating in this study were asked to complete the *Social Skills Rating System-Parent Form* (SSRS: Gresham & Elliott, 1990) and the *Child Behavior Checklist* (CBCL/4-16: Achenbach & Edelbrock, 1991). Interested teachers were asked to complete the *Social Skills Rating System-Teachers Form* (SSRS: Gresham & Elliott, 1990) and the *Teacher's Report Form-Revised* (Achenbach & Edelbrock, 1991). All of the teachers were female and taught in regular education classrooms. Mothers and teachers acted as either consultees within the CBC and GVT conditions, or as participants only in the VT condition. The demographic information is presented in Table 2.

Table 2

Mother Demographic Data

Item	Number	Percentage of Sample
Marital Status		
Married	20[a]	57.1%
Divorced	7	20.0%
Separated	2	5.7%
Number of Children		
1	6	17.1%
2	17	48.6%
3	4	11.4%
4	1	2.9%

[a] In three cases, the child's biological parents had divorced and the mother had remarried

Note. Mother occupation is provided in Table 4.

Some mothers reported major life events that may have impacted their children. Two children were adopted, one of the adopted children was sick at birth and adopted from a foreign country. Two of the married parents reported marital discord. One mother reported depression. In two cases, a recent death had occurred in the child's extended family.

Consultants

The consultants in the present study were 6 advanced graduate students from McGill University. The graduate students were trained in conjoint behavioral consultation. Training included: (a) reading relevant consultation literature (e.g., Bergan & Kratochwill, 1990; Sheridan et al., 1996); (b) attending workshops which reviewed the theory and process of behavioral consultation; (c) experience in conducting behavioral consultation with mothers and teachers; and (d) conducting mock interviews until a minimum of 85% proficiency was reached using the Consultation Objective Checklist (COC; Kratochwill & Bergan, 1990). Proficiency ratings were performed by Dr. Sladeczek, the Director of the McGill Behavioral Consultation Laboratory, in order to ensure the integrity of the consultation procedure. Conjoint behavioral consultation cases were randomly assigned to consultants. In addition, one consultant was responsible for all videotape therapy cases, and two consultants acted as facilitators for the group videotape therapy and minimal consultation (GVT) condition.

For every case, close supervision by Dr. Sladeczek was maintained throughout each phase of the consultation process. Each interview was audio taped and reviewed by Dr. Sladeczek using the COC. A minimum of 85% of the interview's objectives was met or the interview was repeated. In addition, regular meetings were held between Dr.

Sladeczek and the consultants, both individually and as a group, in order to discuss relevant consultation issues and to review the progress made in each case.

Measures

The section that follows presents an overview of the measures that were used in the study. A description and psychometric properties is provided for each measure.

Behavioral Observations

Direct observations were used to evaluate the impact of treatment on each participant's specific behavior targeted during the problem identification interview. Mothers and teachers collected data by directly observing the child and by quantifying the target behavior into a molecular measure (e.g., frequency count) immediately as it occurred. Observations of the target behavior were recorded during a baseline period and continued during a period of intervention for each child.

Behavioral Rating Systems

The following study evaluated the impact of treatment on the children's social skills, problem behaviors, and internalizing and externalizing problem behaviors. Social skills were operationalized using the standard score for Social Skills from the *Social Skills Rating System-Parent and Teacher Forms* (SSRS: Gresham & Elliott, 1990). Similarly, problem behaviors were operationally defined using the standard score for problem behaviors on the SSRS. The SSRS was selected because it provides norm-referenced scales that can be used to evaluate a child's social competence and adaptive functioning both at home and in school (Kratochwill & Elliott, 1991). Internalizing problem behaviors and externalizing problem behaviors were defined using the Internalizing T-score and the Externalizing T-score of the *Child Behavior Checklist-*

Revised (CBCL-R: Achenbach & Edelbrock, 1991) and the *Teacher's Report Form-Revised/4-18* (TRF-R: Achenbach & Edelbrock, 1991). The Total T-score from the CBCL and TRF was also used as a measure of problem behavior. The CBCL and the TRF were selected because they are empirically validated measures (Achenbach & Edelbrock, 1991; Achenbach, Howell, McConaughy, & Stanger, 1995). Furthermore, these measures provide a comprehensive evaluation, as mothers and teachers are usually the two most important sources of data regarding a child's competencies and problems (Achenbach & Edelbrock, 1991).

The Social Skills Rating System. The *Social Skills Rating System* is designed to assess the frequency (Never, Sometimes, Very Often) and importance (Not Important, Important, Critical) of social skills across five domains- Cooperation, Assertion, Self-Control, Responsibility, and Empathy. Scores across the five domains yield a standard social skills score. In addition, there are three scales measuring the frequency of potential Problem Behaviors-Externalizing problems, Internalizing problems, and Hyperactivity problems. Uniquely, the SSRS also provides different viewpoints of the student's social and adaptive functioning, as ratings can be obtained from the student, teacher, or mother (Gresham & Elliott, 1990). The SSRS-Teacher Form includes a nine-item scale evaluating Academic Competence, and the parent version of the *Social Skills Rating System* (SSRS-P) includes a Responsibility scale.

Studies have documented the reliability and validity of the *Social Skills Rating System-Teacher Form* (SSRS-T: Clark, Gresham, & Elliott, 1985; Elliott, Gresham, Freeman & McCloskey, 1988; Gresham & Elliott, 1990; Gresham, Reschly, & Carey, 1987). Elliott, Gresham, Freeman and McCloskey (1988) reported test-retest reliability coefficients of .90 for the total score and individual factor stability coefficients ranging from .60 to .93. High internal consistency of test items and factors was also reported, with a coefficient alpha of .96 at the first administration of the SSRS-T and .95 at a follow-up six weeks later. The coefficient alphas for the separate factors ranged from .80 to .93 at the first administration and ranged from .71 to .93 at a follow-up six weeks later (Elliott, Gresham, Freeman & McCloskey,1988).

Psychometric properties of the *Social Skills Rating System-Parent Form* (SSRS-P) have been reported by Gresham and Elliott (1990). The coefficient alpha was .87 for the Social Skills scale and above .74 for the three Problem Behavior subscales. Test-retest reliability was .87 for the Social Skills scale and ranged from .48 for the Internalizing subscale to .72 for the Hyperactivity subscale for Problem Behaviors.

<u>The Child Behavior Checklist.</u> The *Child Behavior Checklist-Revised* is a 118-item questionnaire designed to obtain parent's ratings on their child's problem behaviors and competencies on a 3-point ordinal scale; 0 ("not true"), 1 ("somewhat or sometimes true"), and 2 ("very true or often true"). It has been shown to discriminate clinic referred from non-referred children (Webster-Stratton & Lindsay, 1999). The CBCL-R is a global measure that provides a holistic view of the child being assessed. The items relate to specific maladaptive behaviors that are classified as internalizing (i.e., anxious/depressed, withdrawn, somatic complaints), externalizing (i.e., aggression and delinquent behavior), or other (i.e., social problems, thought problems, attention problems). Twenty items assessing the social competence of the child are also included. These items address the child's school performance, social relations, and leisure time (Achenbach & Edelbrock, 1991).

The *Child Behavior Checklist-Revised* was normed on a national sample that included 2, 479 referred and non-referred children between the ages of 4 to16. The normative sample yielded standardized T scores with a mean of 50 and a standard deviation of 10 (Achenbach & Edelbrock, 1991). T scores beyond 70 are considered to lie within the clinical range and are found in 5% of the population (Achenbach & Edelbrock, 1991). The distinction provides a useful marker for identifying the children who are more like the referred versus the non-referred children in the standardization sample (Achenbach & Edelbrock, 1991). T scores can be converted from the overall maladaptive behavior score. This score provides a general index comparing the results of a given child to the typical child of the same age (Achenbach & Edelbrock, 1991). Further, T scores are available separately for the internalizing and externalizing broad band scores.

<u>The Teacher Report Form-Revised.</u> The *Teacher Report Form-Revised* (Achenbach & Edelbrock, 1991), modeled on the *Child Behavior Checklist*/4-18, is a comprehensive questionnaire designed to obtain a teacher's ratings on a student's adaptive functioning and problems in a standardized format. The similarity between the items of the TRF and the CBCL facilitate comparisons between these two reports. Parents' ratings on the CBCL-R and teachers' ratings on the TRF have been found to discriminate between demographically matched referred and non-referred children, and are consistent with one another and the ratings of other professionals (Achenbach, Howell, McConaughy, & Stanger, 1995; Achenbach, Howell, Quay, & Conners, 1991). Interrater reliability averaging between .84 and.90 was found using the CBCL (Achenbach et al., 1995; Achenbach et al., 1991). Test-retest reliability, of differences

between teachers' ratings, averaged .90 for the adaptive scales and .92 for the problem scales using the TRF (Achenbach & Edelbrock, 1991).

The Parent Efficacy Scale. *The Parent Efficacy for Helping Children Succeed in School Scale/Thinking about Helping my Child Scale* (Hoover-Dempsey et al., 1992a) was developed for the purpose of evaluating the relationship between teacher and parent efficacy, and parent involvement in elementary schools (see Appendix B for scale). The Scale was administered to 390 parents from four public elementary schools, as one part of a larger Parent Questionnaire. The alpha reliability for the Scale in the above study was .81 (Hoover-Dempsey et al., 1992a). Subsequently, the Scale was used as a free-standing instrument in two studies. The first study consisted of a sample of 74 parents of public elementary school children in grade 2 to 5. The alpha reliability with this sample was .81 (Hoover-Dempsey, & Jones, 1997). In the second study, the instrument was modified to include a 6-point, as opposed to the previous 5-point, response scale and administered to 20 parents of public elementary school children. The alpha reliability for the Scale on this sample was .84.

The modified, free-standing scale consists of 15 items which are rated by parents on a 5-point response scale which range from agree strongly (5) to disagree strongly (1). The items are designed to assess parents' perception of their own efficacy. The scale incorporated items based on the teaching efficacy literature emphasizing parents' perception of their ability to influence children's school outcomes and learning (Hoover-Dempsey et al., 1992a). Hence, items such as "I know how to help my child do well in school" and "If I try hard, I can get through to my child even when he/she has trouble understanding something" are included in the scale. All items were scored on the 6-point scale, with negatively worded items rescored so higher scores reflect higher efficacy. Possible total scores for the scale range from 15, representing the lowest rating of self-efficacy, to 75, representing the highest rating of self-efficacy.

The Teacher Efficacy Scale. *The Teacher Efficacy Scale* was first reported in a study evaluating the contribution of teacher efficacy, school socioeconomic status, and other school characteristics on parent involvement (Hoover-Dempsey et al., 1987: see Appendix C for scale). This study evaluated data from 1, 003 public elementary school teachers (kindergarten through fourth grade) across 66 schools and eight school districts throughout a mid-southern state. Alpha reliability for the scale with this sample was .87 (Hoover-Dempsey et al., 1987). Subsequent analysis from the same sample was obtained and data of 1, 213 teachers analyzed. The alpha reliability for the scale was .76 (Brissie, Hoover-Dempsey, & Bassler, 1988). The Scale has been recently revised for a study exploring parent and teacher relations of 59 teachers in four elementary schools in a major mid-south metropolitan area. The alpha reliability for the Scale with this sample was .83.

The Teacher Efficacy Scale (Hoover-Dempsey et al., 1987) includes 15-items evaluating teacher perceptions of self-efficacy. Items include statements such as " If I try really hard, I can get through to even the most difficult and unmotivated students" and "I am successful with the students in my class". All items are scored on a 5-point scale ranging from strongly disagree (1) to strongly agree (5). Negatively worded items are re-scored so that higher numbers reflect higher efficacy. Total scores range from 15, lowest rating of self-efficacy, to 75, the highest rating of self-efficacy.

Adapted Teacher Perceptions of Parent Efficacy Scale. The *Teacher Perceptions of Parent Efficacy Scale* was developed during a study examining the relationships among teacher efficacy, parent efficacy, and parent involvement in elementary schools (see Appendix D for scale). The Scale, originally included as part of a larger Teacher Questionnaire, was administered to 50 teachers from four public elementary schools. The alpha reliability for the Scale with this sample was .79 (Hoover-Dempsey, Bassler, & Brissie, 1992b). The Scale was subsequently adapted for use by teachers with reference to individual parents. Teacher responses to the individual version of the Scale with this sample of 20 parents of public elementary school children were significantly correlated with a separately administered, single-item Teacher Rating of Individual Parent Effectiveness ($r = .82$, $p > .01$) (Hoover-Dempsey, Berreno, Reed, & Jones, 1998).

The *Teacher Perceptions of Parent Efficacy Scale* includes 7-items such as " If his parent(s) try really hard, they can help him learn even when he is unmotivated" and "her parent(s) help her with school work at home". All items are scored on a 6-point scale ranging from very strongly disagree (1) to very strongly agree (5). Negatively worded items are re-scored so that higher numbers reflect higher efficacy. The total possible score for the full scale ranges from 7 to 42, with higher scores representing more positive teacher perceptions of parental efficacy and lower scores representing more negative teacher perceptions of parental efficacy.

Parent Involvement Questionnaire. A parent questionnaire was attached to the Parent Scale (Parent Efficacy for Helping Children Succeed in School Scale/Thinking about Helping my Child) in order to assess mother involvement in parent-school activities (see Appendix E for involvement questionnaires). These activities include both home-based activities related to children's learning in school and school-based involvement. The home-based activities include reviewing the child's work, monitoring school progress, helping with homework, discussing school issues, providing enriched activities and talking to the teacher by phone. School-based activities include driving on a field trip, attending conferences, volunteering at school, and serving on an advisory board. Hence, ratings were requested in the following format:

Help with homework (estimated hours per average week);

Volunteer work at school (estimated hours per average week);

Telephone calls with teachers (estimated number in average month).

Similar estimates were asked in other studies (Hoover-Dempsey et al., 1987, 1992; Grolnick & Ryan, 1989; Hoover-Dempsey, Stevenson & Baker, 1987). Moreover, Conoley's (1987) four levels in which parents may become involved in their children's education and Becher's (1986) suggestions of several methods of involving parents in their children's education are included in the questionnaire. Conoley's (1987) and Becher's (1986) work was incorporated based on the suggestions of Sheridan and Kratochwill (1990), the first researchers to outline a rationale based on the parent involvement literature, for incorporating both parents and teachers into the behavioral consultation framework.

Teacher Perceptions of Parent Involvement Questionnaire. A questionnaire was attached to *The Teacher Efficacy Scale* in order to assess teachers' perception of parent involvement. Teachers were asked to rate parent involvement across home and school-based activities. Similar to the parent questionnaire, the activities include time spent monitoring school progress, helping with homework, discussing school issues, tallking to the teacher by phone, driving on a field trip, attending conferences, volunteering at school, and serving on an advisory board.

Parent Involvement Questionnaire (Teacher version). A teacher version of the parent questionnaire was also attached to *The Teacher Efficacy Scale* in order to assess teachers' ratings of parental involvement in school activities. Activities included time in which mother is volunteering in the classroom, time spent meeting with mother, and time spent involving mother in clasroom decision-making. Ratings were requested in the same format as shown for the parent version.

Observational Measure

The Dyadic Parent-Child Interaction Coding System. The Dyadic Parent-Child Interaction Coding System (DPICS; Eyberg & Robinson, 1992) was used as an observational measure of problem behavior and parenting skills and as a measure of treatment outcome. The DPICS, a multiple item coding system designed for children between the ages of 3 and 10 years, consists of 29 behavior categories. For this study, three separate summary variables were used from the parent behavior categories: total praise, total critical statements, and no opportunity commands. In addition, two summary child variables: total child deviance, and child responses to commands were examined.

The DPICS was initially standardized and validated on 42 families with and without children evidencing conduct problems (Robinson & Eyberg , 1981). Interrater reliability was assessed by correlating the frequency of each behavior recorded by two observers during 244 of the 276 five-minute observations. The mean reliability coefficient for parent behaviors was .91 and the coefficient for child behaviors was .92. The discriminate validity of the DPICS was also assessed by Robinson & Eyberg (1981).

Parents of children with conduct problems gave more critical statements and direct commands, and offered fewer descriptive questions than did parents of "normal" children ($p < .01$). In addition, the children with conduct problems evidenced more whining, yelling, and noncompliance than "normal" children ($p < .025$) (Robinson & Eyberg, 1981). The validity of the DPICS was supported by its ability to discriminate outcome between various treatments (Eyberg & Matarazzo, 1980). Results from discriminant function analyses of the DPICS observations showed that the coding system correctly classified 100% of the normal families, 85% of treatment families, and 94% of all families (Eyberg & Robinson, 1981). In addition, the DPICS predicted 61% of the variance in parental report of behavior problems within the home (Robinson & Eyberg, 1981).

The DPICS consists of three standard five-minute situations that vary in the degree of parent control required: *Child Directed Interaction* (CDI), *Parent Directed Interaction* (PDI), and *cleanup*. The three situations are each videotaped and later coded for 5 minutes. The following directions are given for the first situation:

> "In this situation, tell (child's name) that he/she may play what ever he/she chooses. Let him/her choose any activity he/she wishes. You just follow his/her lead and play along with him/her."

The CDI situation typically elicits positive behavior from the child, as the child chooses the activity or game and has the parent's undivided attention. The situation created by the CDI allows for the observation of parent and child interaction under optimal conditions (Hembree-Kigin & Bodiford McNeil, 1995). The PDI situation, in which the parent chooses the activity or game, and asks the child to play along, is more challenging for the child with behavior problems and for the parent. The situation allows for the observation of parent strategies used to engage the child's cooperation and compliance. Moreover, the situation facilitates the observation of the child's response to parental instructions, and the specific problem behaviors the child is evidencing. The instructions for the PDI are the following:

"That was fine. Now we'll switch to another situation. Tell (child's name) that it is your turn to choose the game. You may choose any activity. Keep him/her playing with you according to your rules."

The final situation, *Cleanup,* is the most difficult situation for the child with behavior problems as it requires the child to put away all the toys without help, even if the activity was not finished. The most significant noncompliant and disruptive behaviors are typically displayed in this final situation (Hembree-Kigin & Bodiford McNeil, 1995). For the third situation, the following directions are given:

"That was fine. Now I'd like you to tell (child's name) that it is time to leave and the toys must be put away. Tell him/her that you want him/her to put the toys away. Make sure you have him/her put them away."

Table 3

Repeated Measures Design

Participant	Treatment Condition	Consultants	Measures
1 to 19	CBC	Random assignment of cases to consultants	Mother/teacher observations CBCL TRF SSRS Parent Efficacy Parent Involvement Questionnaire (Parent and Teacher Version) Teacher Perceptions of Parent Efficacy Teacher Efficacy DPICS
20-28	VT	1 consultant	Mother/teacher observations CBCL TRF SSRS Parent Efficacy Parent Involvement Questionnaire (Parent and Teacher Version) Teacher Perceptions of Parent Efficacy Teacher Efficacy DPICS
29-35	GVT + minimal consultation	1 consultant (group facilitator) and assistant	Mother/teacher observations CBCL TRF SSRS Parent Efficacy Parent Involvement Questionnaire (Parent and Teacher Version) Teacher Perceptions of Parent Efficacy Teacher Efficacy DPICS

Procedure

Dr. Sladeczek and members of the Behavioral Consultation Laboratory conducted presentations explaining the nature of the study and services provided to interested mothers and teachers. In addition, brochures and an information sheet were used to inform mothers and teachers about the project.

Eligibility

In order to be eligible for this study, the mother or teacher rating of the child had to indicate poor social skills [a score of at least 1 standard deviation (15 points) below the mean of 100 on the SSRS] or problem behaviors [a score of at least 1 standard deviation above the mean on the SSRS or a score within the clinical range (Total T score beyond 63) on the CBCL-R or on the TRF-R] or maladaptive internalizing behavior [a score within the clinical range (T score beyond 63) on the CBCL-R or the TRF-R] or maladaptive extenalizing behavior [a score within the clinical range (T score beyond 63) on the CBCL-R or the TRF-R]. One parent rating or one teacher rating must have indicated a problem in order for a child to be eligible to participate in this study.

Children evidencing significant internalizing difficulties on the CBCL-R or TRF-R were considered to present with internalizing behavior problems. Children evidencing significant externalizing difficulties on the CBCL-R or TRF-R were considered to present with externalizing difficulties. Children evidencing significant problem behaviors or social skills difficulties, in the absence of significant internalizing or externalizing scores on the CBCL-R or TRF-R were characterized according to the behavior targeted for intervention.

Mothers and teachers of eligible children were offered one of the treatment conditions: Conjoint behavioral consultation (CBC), group videotape therapy combined with minimal consultation (GVT) and videotape therapy only (VT). Schools were randomly assigned to the treatment conditions.

Once a school had been assigned a treatment condition, a consultant was assigned to the case. The consultant contacted the mothers and teachers of the assigned case in order to obtain additional screening information, after parental consent had been given to do so. In addition, the consultant obtained consent from the mother and teacher to participate in treatment, and for the release of information between the school and mothers.

Pretreatment and Posttreatment Assessment

The *Social Skills Rating System-* Parent and Teacher Form (SSRS: Gresham & Elliott, 1990), the *Child Behavior Checklist* (CBCL/4-16: Achenbach & Edelbrock, 1991), and the *Teacher Report Form* (TRF: Achenbach & Edelbrock, 1991) were administered at two time points. They were first administered for screening purposes, in order to identify children experiencing externalizing or internalizing problem behavior, or social skills problems and then re-administered a second time following the termination of intervention, in order to evaluate treatment effectiveness.

The Parent Efficacy for Helping Children Succeed in School Scale/Thinking about Helping My Child (Hoover-Dempsey et al., 1992a) and *The Teacher Efficacy Scale-Revised* (Hoover-Dempsey et al., 1992a) were also administered at pretreatment and posttreatment to mothers and teachers of eligible participants in order to evaluate ratings of self-efficacy. Moreover, a questionnaire containing a series of questions requiring a

Likert-scale rating of mother involvement across a broad range of educational activities were given to participating mothers and teachers at pretreatment and posttreatment. These activities included both home-based activities related to children's learning in school and school-based involvement. The home-based activities included reviewing the child's work, monitoring school progress, helping with homework, discussing school issues, providing enriched activities and talking to the teacher by phone. School-based activities included driving on a field trip, attending conferences, volunteering at school, and serving on an advisory board.

Observational data from the DPICS were collected at pretreatment and posttreatment by videotaping the three standard five-minute situations in a clinic playroom. The playroom was equipped with a table, two chairs, and a large toy box. The toy box was filled with constructional toys that included Duplo, Tinkertoys, a Mr. Potato Head, puzzles, and a toy farm. In order to initiate the play situations, a behavioral consultant knocked on the door of the clinic playroom, entered, and provided the mother with verbal instructions prior to each situation.

Four observers were trained in the DPICS coding system. Training involved reading the coding manual (Eyberg & Robinson, 1992), and coding role-played DPICS situations until a minimum of 80% reliability was obtained on the practice videotapes. All observers were blind to whether the session was recorded at pretreatment or posttreatment and to the treatment condition of the participants.

Direct Observations

Direct observations were used to evaluate the impact of treatment on each participant's specific behavior targeted during the conjoint problem identification interview. Services across each condition were initiated via the CPI interview, at which point the consultant assisted mothers and teachers in identifying and defining the problem of concern in behavioral terms and in developing the procedures to measure the frequency of the client's target behavior.

Following the first interview, baseline information was obtained as mothers and teachers collected the frequency data by directly observing the participant and by quantifying the observed behavior immediately as it occurred. The behavior was documented on a frequency chart that depicted the number of times the target behavior was emitted per each day of observation.

Experimental Treatment Conditions

There were three treatment conditions under investigation: the highly individualized conjoint behavioral consultation (CBC), group videotape therapy combined with minimal consultation (GVT), and the self-administered videotape therapy (VT). Across each treatment condition, weekly telephone contact was maintained during treatment implementation. The purpose of maintaining contact was to monitor the progress and effectiveness of the treatment condition and to implement modifications when needed.

Conjoint behavioral consultation condition. Within the CBC condition, mothers and teachers served as consultees and implemented the intervention. Conjoint behavioral consultation occurred through 3 interviews (Sheridan et al., 1993: see Appendix F for the interview manuals). The Conjoint Problem Identification Interview (CPII) was conducted in order to initiate consultation services. The purpose of this interview was to ascertain the problem being addressed and to discuss the procedures to be used in collecting baseline data. Shortly after the CPII, a second interview was held, the Conjoint Problem Analysis Interview (CPAI). The goal of the second interview was to validate the problem based on the data the mothers and teachers collected and to develop and discuss a treatment plan. The environmental conditions that influence the behavior were discussed, as a complete functional analysis of behavior was conducted prior to designing the treatment plan. Eight to twelve weeks were allotted for mothers and teachers to implement the treatment both at home and at school. Following treatment implementation, a Conjoint Treatment Evaluation Interview (CTEI) was held in order to determine the effectiveness of the plan and to discuss plan modifications.

Videotape therapy-only condition. Mothers and teachers participating in this condition received, on average, one video from Webster-Stratton's (1988) videotape therapy program per week for a total of 10 to 12 weeks. The same order of presentation was maintained across all participants. The mothers and teachers were encouraged to carefully view the videotape through the week and implement the strategies with their children. Weekly homework assignments in the form of short reading assignments and brief exercises were provided for mothers and teachers to complete. Moreover, suggestions, tips, and reminders were given to mothers and teachers to reinforce the strategies being illustrated on the videos. Further details pertaining to the content of the Webster-Stratton treatment package (1988) are provided in the intervention section to follow.

Group Videotape Therapy. This condition consisted of two components: a group viewing and discussion of the Webster-Stratton (1982; 1992b) videotapes series as well as access to a behavioral consultant for specific assistance regarding their child. Each week, small groups of 3-6 mothers gathered at their child's school to watch a videotape and participate in a group discussion led by the consultant who functioned as a group facilitator. Mothers were encouraged to share and explore ideas, and problem-solve within a collaborative context. Consultants led discussions by providing questions and topics outlined in the guide accompanying Webster-Stratton's videotape series. Consultants were also available to answer any questions or concerns they had regarding their child.

Intervention

Conjoint behavioral consultation condition. The skills to be taught and used as part of the CBC treatment intervention were based on problems identified during the Problem Analysis Interview. During the interview, the results of the pretreatment assessment and the observational data collected in the home and the classroom were reviewed by the teacher, mother, and consultant and the treatment package was outlined and strategies reviewed. The treatment package was individualized and personalized for each case (Kratochwill & Elliott, 1991a).

The treatment package was based on treatment manuals that have been used successfully with parents and teachers who have participated in CBC (Sladeczek et. al, 1996). Separate parent and teacher manuals have been developed for children with externalizing versus children with internalizing difficulties. The consultant and consultees collaborated and decided on the elements from both programs that best addressed the needs of each particular child.

The treatment manual devised for children with internalizing difficulties consists of four components: skill selection, goal setting, peer activity, and positive reinforcement.

Similarly, the manual devised for children that externalizing difficulties consists of skill selection, goal setting procedures and peer activities. However, in replacement of the section on positive reinforcement found in the internalizing manual is a section on child management.

Skill selection. Information pertaining to the child's social skills problems and internalizing problem behaviors was assessed in order to identify the most significant problem(s) contributing to the child's socially withdrawn behavior. Focusing on one problem at a time, the mother, teacher, and consultant worked collaboratively to develop goals and to form a plan to meet these goals.

Goal setting. The goal was to help the student learn the selected skill (e.g., initiating conversation). Four steps were used to guide the child's learning of the skill: Tell, Show, Do, and Practice.

1. Tell: The teacher and parent talk about the skill to the child and explain why the skill is important.
2. Show: The parent and teacher model and practice the skill for the student.
3. Do: The child practices the skill both at home and in the classroom.
4. Set a goal and Practice: Set a specific goal of having the child acquire the skill and on a daily basis, have the child practice the skill in different situations, with different children.

Goal setting procedures allowed children to develop appropriate personal goals for improving social competence. It was important that the child had control over the goal and was capable of meeting the goal that had been set. Moreover, the goal directed the child's actions and was specific to the child.

Peer activity. The importance of early, healthy peer relationships has been well documented (e.g., Rubin et al., 1989; Rubin & Ross, 1982). Hence, opportunity is needed for children who are socially withdrawn to practice interacting with peers. Teachers and parents were encouraged to provide children with time to play with a peer(s) at least once a week. There were eight steps that mothers and teachers followed in order to initiate peer activities:

1. With consultant, decide on type of activity;
2. Selects materials needed for the activity;
3. Bring child and friend together in an appropriate environment;
4. Explain activity and give directions;
5. Tell child what behaviors are expected of him/her;
6. Praise child and friend for positive behavior;
7. End activity after 10-15 minutes;
8. Provide feedback.

Positive reinforcement. Positive reinforcement or a "special reward" was provided after the child reached the target goal. Selecting and planning appropriate reinforcement techniques occurred in connection with the goal-setting procedures. The child was involved in selecting the particular reward that he/she worked towards. A reinforcement "menu" or "survey" was used in order to provide the mothers and teacher with additional ideas and activities that can be provided in response to appropriate behavior.

Prompting is a necessary component of a reinforcement program. Prompts, such as a teacher saying, "Jimmy may like a chance to roll the dice first," were used as a means of promoting the appropriate behavior, while cueing the child on what needed to be done to reach the goal. In some cases several prompts were necessary in order for the child to reach the goal. Once the behavior occurred, it was reinforced.

Child management. Child management, the third section of the externalizing manual, consists of differential attention, instruction giving, and time away. Differential attention, which involves attending, rewarding, and ignoring, was used when the child was behaving inappropriately. This strategy involves consistently attending and rewarding good behavior, while ignoring inappropriate behavior whenever possible. Instruction-giving skills, in combination with differential skills were used to help mothers and teachers be more effective in issuing instructions, and encouraging compliant behavior. Finally, the time away procedure, or removing the child from a negative situation for three to five minutes, was used to discourage specific inappropriate behavior.

Praising the child's social behaviors was especially important at the beginning of intervention. Praise provides the child with feedback that his/her behavior has been noticed and approved. Praising was typically used less frequently as social behaviors became more established.

Videotape treatment conditions. The treatment package developed by Webster-Stratton (1988) consists of nine videotapes and a parent manual. The package is divided into four programs: (a) Play; (b) Praise and Rewards; (c) Effective Limit Setting; and (d) Handling Misbehavior.

The play program consists of two videotapes. The first videotape consists of 25 short vignettes that intend to teach parents how to play with their children. The first videotape emphasizes the importance for parents to recognize the individual needs and abilities of their children, to encourage the process of creative play, to promote their children's self-concept and to handle boredom. The second video of the play program consists of 22 vignettes that teach parents how to help their children learn through play. Skills emphasizing problem solving, dealing with frustration, and language development are encouraged.

Play and Rewards, the second program of the series, also consists of two videotapes. The first videotape consists of 26 vignettes that teach parents how to praise their children. Moreover, this videotape illustrates the correct use of rewards for appropriate behavior. The second videotape of this series consists of 15 vignettes that are designed to help parents use tangible rewards, such as number charts and stickers, to monitor and promote desirable behavior.

The third program, Effective Limit Setting, consists of three videotapes which focus on setting household rules and following through with commands. The first of the three videotapes consists of 34 vignettes that help parents identify important rules and clearly explain these rules and issue unambiguous commands. The second of the videotapes consists of 19 vignettes that help parents set effective limits for their children by providing examples of strategies for dealing with children who are noncompliant. The last of the videotapes in this program consists of nine vignettes that teach effective strategies for handling noncompliance. The strategies emphasized are time-out and ignoring.

Finally, the last series of videotapes comprise the program entitled Handling Misbehavior. This program consists of three videotapes. The first videotape consists of 14 vignettes that cover how to avoid and ignore inappropriate behavior, such as tantrums, while redirecting children to positive behavior. The second videotape consists of 31 vignettes that deal with issuing punishment, such as time-away and penalties, such as loss of privilege, for unacceptable behavior. The final videotape to be viewed consists of seven vignettes that highlight preventive techniques such as promoting sharing and cooperation, with young children.

Treatment Termination

As previously mentioned, upon completion of the treatment services, mothers from each condition completed the CBCL/4-18 and the SSRS-P and teachers completed the TRF and the SSRS-T. Mother efficacy was assessed using the *Parent Efficacy for Helping Children Succeed in School Scale* and teacher's perception of mother efficacy was assessed using *The Teacher Efficacy Scale*. Mother involvement in their children's education was evaluated using the questionnaire that accompanied the parent and teacher scales. Finally, problem behavior and parenting skills were evaluated using the DPICS.

CHAPTER 4

Results

In this study, statistical analyses of the data involved both group and single-n analyses to assess the efficacy of conjoint behavioral consultation versus videotape therapy, and to examine the relationship between intervention efficacy and mother-teacher collaboration. The predictions are divided into three subgroups. The first subgroup of predictions investigate the efficacy of CBC, GVT, and VT; the second subgroup of predictions evaluate the effect of intervention type and specific problem behaviors on treatment outcome, and the third subgroup of predictions examine Hoover-Dempsey and Sandler's Model (1995) of self-efficacy and involvement.

I. Determining the Efficacy of CBC, GVT and VT

Prediction 1

It is predicted that each child in the CBC, GVT, and VT conditions will evidence significant improvement in their target behaviors from pretreatment to postttreatment. An effect size appropriate for single-n data was used to test this prediction.

The effect size measure. The effect size measure (Busk & Serlin, 1992) takes into account the lack of independence in the data typical of successive observations of the same individual. The effect size measure can be calculated by dividing the difference between the baseline and treatment phase means by the standard deviation for the baseline phase Busk & Serlin, 1992). This is expressed in the following formula:

$$ES = \frac{\overline{X}_{treatment} - \overline{X}_{baseline}}{SD_{baseline}} \qquad (1)$$

where $$SD = \sqrt{\frac{N\sum x^2 - (\sum x)^2}{N(N-1)}} \qquad (2)$$

However, in circumstances where the standard deviation for baseline data cannot be computed due to a lack of variance during this phase, an aggregate measure of the standard deviation is recommended by pooling the data from the baseline and treatment phases (Busk & Serlin, 1992).

The effect size statistic may be interpreted as standard deviations units expressed in the form of z scores (Gresham & Noell, 1993). Consequently, the meaning of the ES can be translated into notions of overlapping distributions and comparable percentiles (Kavale & Glass, 1984). Effect sizes are positive when the mean frequency of the target behavior is greater during the treatment phase than during the baseline phase, and the effect sizes are negative when the frequency of the target behavior decreases from baseline to treatment (Gresham & Noell, 1993). Hence, an ES of +1.00 would indicate an increase in target behavior from baseline to treatment of one standard deviation (Kavale & Glass, 1984; Gresham & Noell, 1993). Conventionally, effect sizes of ± .40 are considered to be significant (Forness, Kavale, Blum, & Lloyd, 1997).

There were thirty-one complete cases in which an effect size could be computed using mother baseline and treatment data. The effect size in 90% of the cases was in the expected direction. In 55% of cases, the computed effect size, indicating positive change, was greater than .40. The effect size in 45% of cases indicated more than half a standard deviation of positive change in target behavior from baseline to treatment (effect size of >.5). In 19% of cases, the effect size was larger than 1.0 indicating greater than one standard deviation of change in the expected direction over the course of treatment.

There were twenty-two complete cases in which an effect size could be computed using teacher baseline and treatment data. The effect-size in 82% of cases was in the expected direction indicating positive change in the target behavior from baseline to treatment. In 72% of the cases, the effect size indicating positive change was greater than .40. In 60% of the cases, the effect size was greater than .5 indicating more than half a standard deviation of positive change from baseline to treatment. In 36% of cases, the effect size was larger than 1.0 indicating above one standard deviation of positive change over the course of treatment.

Table 4 presents case description data (i.e., age of the child, target behaviors, and intervention condition) and the effect sizes across home and school for each participant.

Table 4

Summary of Consultation Case Descriptors and Effect Sizes Across Home and School

Case	Age	Target Behavior	Intervention	Mother Occupation	ES Home	ES School
1	43	Noncompliance	CBC	Nurse	-.30	.04
2	86	Aggression	CBC	Lunch monitor	-.02	-1.10
3	75	Socially Inappropriate	VT	NA	NA	-.28
4	77	Attention Getting	VT	Registered nurse ass.	-.21	NA
5	110	Noncompliance	VT	Student	-.24	1.32
6	67	Prosocial skills	CBC	Special ed. Teacher	.45	-.06
7	71	Aggression	GVT	Clerk	-.78	NA
8	71	Noncompliance	GVT	Home-maker	.01	NA
9	64	Aggression	GVT	Labourer	-1.16	NA
10	74	Tantrumming	VT	Home-maker	-.58	-1.06
11	69	Tantrumming	VT	Home-maker	-.46	NA
12	42	Noncompliance	CBC	NA	-.73	-1.75
13	35	Noncompliance	CBC	Pharmacist	-.56	-1.98
14	76	Noncompliance	CBC	NA	-.84	-5.15
15	67	Noncompliance	GVT	Line attendant	-.13	NA
16	80	Inattention	CBC	NA	NA	NA
17	67	Aggression	CBC	Home-maker	-.56	-.19
18	43	Noncompliance	CBC	NA	-2.10	-.18
19	63	Tantrumming	CBC	Home-maker	1.77	1.16

20	74	Socially Inappropriate	CBC	Home-maker	-5.31	-1.97
21	78	Socially Inappropriate	CBC	Home-maker	-.12	-.40
22	66	Noncompliance	CBC	Home-maker	-.51	-1.24
23	52	Aggression	CBC	NA	NA	NA
24	63	Noncompliance	GVT	NA	NA	-.61
25	88	Noncompliance	VT	Sales manager	-.45	NA
26	55	Noncompliance	VT	NA	-.10	-1.46
27	109	Noncompliance	VT	House cleaner	-3.27	-.03
28	72	Aggression	GVT	NA	2.85	NA
29	93	Aggression	GVT	Home-maker	-1.04	NA
30	36	Aggression	CBC	Receptionist	-.68	-.66
31	117	Off-task	CBC	Secretary	-.24	-.53
32	70	Aggression	CBC	Secretary	-.10	-.80
33	96	Impulsivity	CBC	Home-maker	-.39	-.52
34	88	Noncompliance	VT	Home-maker	-1.21	NA
35	57	Noncompliance	CBC	Home-maker	-.04	NA

	N	Minimum	Maximum	M	SD
ES (mother)	31	-2.85	5.31	.5819	1.3239
ES (teacher)	22	-1.32	5.15	.7877	1.2935

Note. Pretreatment age expressed in months. CBC = Conjoint Behavioral Consultation; GVT = Group videotape therapy; VT = Videotape therapy

Prediction 2

It is predicted that each child in the CBC, GVT, and VT conditions will evidence a decrease in internalizing difficulties, a decrease in externalizing difficulties, a decrease in problem behaviors, or an increase in social skills from pretreatment to postreatment.

The reliable change index. The reliable change index (RC) was used to determine whether the magnitude of change for a given participant was statistically and clinically reliable (Jacobson & Truax, 1991). Clinically significant change, using the RC index is defined in terms of the client's functioning after treatment and in terms of how much change has occurred (Jacobson & Truax, 1991). The reliable change index was used because it provides a clear criterion for evaluating improvement. The participant's pretreatment score was subtracted from the posttreatment score and divided by the standard error of difference between the two observation scores. This formula is written as:

$$RC = \frac{X_{posttreatment} - X_{pretreatment}}{S_{diff}} \qquad (3)$$

where

$$S_{diff} = \sqrt{2(S_E)^2} \qquad (4)$$

The standard error of measurement (S_E) was computed using the standard deviation and the reliability of the measure. This formula is expressed as:

$$S_E = s_1\sqrt{1 - r_{xx}} \qquad (5)$$

where

s_1 = the standard deviation across pretreatment scores and r = the reliability of the measure.

A RC is considered to be statistically significant ($p<.05$) when the value obtained is $\geq$ 1.96 (Jacobson et al., 1984). Hence, a RC equal to or greater than this cut off value was used to ascertain that a reliable degree of change occurred as a result of the intervention.

There were twenty-eight cases in which mothers completed both pretreatment and posttreatment questionnaires pertaining to their child's social skills and problem behaviors. In 71% of cases, the target child evidenced an improvement in social skills from pretreatment to posttreatment. Thirty-six percent of children evidenced statistically significant improvements. Seventy-nine percent of children evidenced a decrease in problem behavior from pretreatment to posttreatment, 14% were statistically significant.

Changes in each child's externalizing behavior, internalizing behavior, and overall behavior problems were also assessed using questionnaires completed by the child's mother. In 81% of cases in which pretreatment and posttreatment data was obtained, children evidenced a decrease in externalizing behavior at the time of the second assessment, 32% were statistically significant. In 72% of cases, the target child evidenced a decrease in internalizing behaivour from pretreatment to posttreatment, 44% were statistically significant. In 88% of cases, the target child evidenced a decrease in overall behavior problems at the time of the second assessment, 52% were statistically significant.

Teacher data indicated that in 68% of cases, teachers documented increases in social skills from pretreatment to posttreatment, 32% were statistically significant. Similarly, in 68% of cases, teachers documented decreases in problem behavior at posttreatment, 26% were statistically significant. Also according to teachers, 64% of children evidenced a decrease in internalizing behavior, 50% were statistically significant and 50% of children evidenced a decrease in externalizing behavior, 36% were statistically significant. Fifty-eight percent of children evidenced a decrease in behavior problems from pretreatment to posttreatment, 50% were statistically significant.

Table 5

Summary of Consultation Case Descriptions and Reliable Change Indices for the SSRS Social Skills Scale and Problem Behavior Scale and for the CBCL and TRF Total Scores, Externalizing Scale and Internalizing Scale

Case	Age	Target Behavior	Intervention	RCI SSRS SS–M	RCI SSRS PB–M	RCI SSRS SS-T	RCI SSRS PB-T	RCI CBCL Total-M	RCI CBCL Ext. M	RCI CBCL Int. M	RCI TRF Total-T	RCI TRF Ext-T	RCI TRF Int-T
1	43	Noncompliance	CBC	-.39	-1.04	-.78	-.32	-3.76	-1.34	-4.61	1.61	1.61	1.68
2	86	Aggression	CBC	NA	NA	.97	-2.24	-1.45	-2.14	-2.61	NA	NA	NA
3	75	Socially Inappropriate	VT	NA	NA	-1.05	-.24	NA	NA	NA	-.27	.27	-2.69
4	77	Attention Getting	VT	.39	-.16	-3.01	.80	-2.02	-1.07	-1.20	4.28	3.21	4.04
5	110	Noncompliance	VT	-.65	-.40	NA	NA	-.29	-.80	.20	NA	NA	NA
6	67	Prosocial skills	CBC	3.27	.00	-.26	-.08	-2.89	-2.68	-1.80	.54	.80	1.68
7	71	Aggression	GVT	3.14	-.48	NA	NA	-.87	-.80	NA	NA	NA	NA
8	71	Noncompliance	GVT	.00	-.64	NA	NA	NA	NA	NA	NA	NA	NA
9	64	Aggression	GVT	4.18	2.15	NA	NA	NA	4.82	NA	NA	NA	NA
10	74	Tantrumming	VT	-.26	-.88	1.05	.08	-2.02	-1.61	-2.00	.54	-.27	1.68

11	69	Tantrumming	VT	3.01	-1.43	4.57	-2.15	-2.02	-1.34	-1.80	-4.28	-4.28	-5.72
12	42	Noncompliance	CBC	4.44	-2.79	1.18	1.04	-8.10	-6.42	-3.81	-4.28	-4.01	-2.36
13	35	Noncompliance	CBC	1.31	.00	NA	NA	-1.73	-.54	-1.40	NA	NA	NA
14	76	Noncompliance	CBC	NA	NA	-.61	-1.53	NA	NA	NA	NA	NA	NA
15	67	Noncompliance	GVT	.39	-1.20	NA	NA	-2.60	-2.68	-3.81	NA	NA	NA
16	80	Inattention	CBC	NA	NA	1.57.	.16	NA	NA	NA	-2.68	-1.07	-3.37
17	67	Aggression	CBC	-.26	-.24	-.13	.32	-4.92	-3.75	-3.81	1.07	.54	3.03
18	43	Noncompliance	CBC	.13	-1.67	1.83	-.56	-1.16	-1.61	.40	NA	NA	NA
19	63	Tantrumming	CBC	NA	NA	5.10	-.64	NA	NA	NA	-2.94	-2.68	-.67
20	74	Socially Inappropriate	CBC	-3.66	-.64	2.74	-1.83	-.29	-1.61	.00	-4.82	-5.35	-6.40
21	78	Socially Inappropriate	CBC	-2.35	1.67	1.05	-.96	2.60	2.14	2.00	NA	NA	NA
22	66	Noncompliance	CBC	1.17	-2.47	NA	NA	-2.60	.00	-4.01	NA	NA	NA
23	52	Aggression	CBC	NA	NA	2.74	-2.47	NA	NA	NA	-4.28	-4.01	-3.70
24	63	Noncompliance	GVT	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
25	88	Noncompliance	VT	1.31	-.80	.49	-2.83	NA	NA	NA	NA	.50	-1.68

26	55	Noncompliance	VT	3.01	2.79	2.44	.00	-1.16	.53	-2.00	.27	.75	-4.71
27	109	Noncompliance	VT	-.39	-.80	NA	NA	.29	-.27	.1.20	NA	.NA	NA
28	72	Aggression	GVT	.39	-.32	NA	NA	-.29	-.53	.60	NA	NA	NA
29	93	Aggression	GVT	9.15	-3.58	NA	NA	-2.31	-.53	-2.20	NA	NA	NA
30	36	Aggression	CBC	3.26	-1.28	4.63	-3.18	-3.47	-3.74	-.40	NA	NA	NA
31	117	Off-task	CBC	.78	-.23	NA	NA	.29	-.27	.00	NA	NA	NA
32	70	Aggression	CBC	2.35	-.56	NA	NA	-2.02	-1.87	-2.20	NA	NA	NA
33	96	Impulsivity	CBC	1.83	.72	NA	NA	NA	1.34	-.80	NA	NA	NA
34	88	Noncompliance	VT	3.27	-.64	NA	NA	-3.76	-2.67	-2.00	NA	NA	NA
35	57	Noncompliance	CBC	.92	-2.87	NA	NA	-.29	-1.07	-.40	NA	NA	NA
M				1.42	-.63	1.29	-.88	-1.87	-1.13	-1.46	-1.29	-1.00	**-1.37**

Note. Pretreatment age expressed in months. RCI = Reliable Change Index; SSRS SS = Social Skills Rating System, Social Skills Scale; SSRS PB = Social Skills Rating System, Problem Behaviors Scale; CBCL = Child Behavior Checklist – Total Scale, Externalizing Scale, and Internalizing Scale; TRF = Teacher's Report Form, Total Scale, Externalizing Scale, and Internalizing Scale.

<u>Prediction 3</u>

It is predicted that there will be a significant improvement in parenting skills and child behavior from pretreatment to postreatment.

Reliable change indices were calculated in order to determine whether each child evidenced a significant decrease in Total Child Deviance from pretreatment to posttreatment, and in order to determine whether each mother evidenced a significant increase in parenting skills. Fifty-seven RCI's were calculated of which 46% were in the expected direction, only 14% of which were statistically and clinically significant. Table 6 presents the parent skills scores, child behavior scores and reliable change indices for the DPICS.

Paired Sample t-tests were used to examine significant differences in overall parenting skills and child behavior from pretreatment to postreatment. Although findings were in the expected direction, with an increase in parenting skills from pretreatment to posttreatment and a decrease in negative child behaviors from pretreatment to posttreatment, the differences were not significant. Mean parenting skills and child behavior scores are presented in Table 7 and the results of the Paired Sample t-tests are presented in Table 8.

Table 6

Parent Skills Scores, Child Behavior Scores and Reliable Change Indices for the DPICS

	Parenting Skills						Child Behaviors		
Case	Eff. Pre	Eff. Post	RCI	Ineff. Pre	Ineff. Post	RCI	Child Dev. Pre	Child Dev. Post	RCI
2	12	12	.00	7	2	-.65	10	6	-.74
3	71	NA	NA	24	NA	NA	2	NA	NA
4	5	18	1.51	2	3	.13	3	6	.55
6	27	28	.12	16	6	-1.29	13	13	.00
8	17	NA	NA	8	NA	NA	1	NA	NA
12	19	29	1.16	3	6	.39	1	0	-.18
13	64	27	-4.29	31	30	-.13	8	22	2.58
15	13	10	-.35	4	10	.78	0	4	.74
17	20	18	-.23	11	6	-.65	14	19	.92
18	38	85	5.45	44	10	-.52	19	14	-.92
19	19	17	-.23	20	6	-1.81	7	15	1.48
20	14	35	2.43	5	12	.90	7	6	-.18
21	15	NA	NA	7	NA	NA	7	NA	NA
22	82	82	.00	11	7	-.52	9	12	.55
25	35	30	-.58	11	9	-.26	4	2	-.37
26	22	15	-.81	10	17	.90	6	9	.55
28	NA	24	NA	NA	13	NA	NA	10	NA
29	9	20	1.27	12	13	.13	30	10	-3.69
30	55	54	-.12	50	24	-3.36	17	10	-1.29
32	11	10	-.12	82	51	-4.01	64	17	-8.67

33	17	15	-.23	8	14	.78	2	7	.92
34	15	12	-.35	9	9	0	10	1	-1.66
35	29	25	-.46	21	14	-.90	28	43	2.77
Mean	26.48	26.78	.17	16.68	13.13	-.52	11.24	10.52	-.33

Note. Eff. = Effective Parenting Skills; Ineff = Ineffective parenting Skills; Child Dev. = Child Deviance

Table 7

Mean Parenting Skills Scores and Child Behaviors Scores at Pretreatment and Posttreatment

	M	N	SD	Std. Error
Parent Skills				
Effective Skills Pretreatment	25.41	22	19.12	4.08
Effective Skills Posttreatment	26.91	22	20.89	4.45
Ineffective Parenting Pretreatment	17.18	22	19.22	4.10
Ineffective Parenting Posttreatment	13.14	22	12.70	2.71
Child Behaviors				
Total Child Deviance Pretreatment	12.32	22	14.08	3.00
Total Child Deviance Posttreatment	10.55	22	9.65	2.06

Table 8

Paired Sample T-Test Comparing Parenting Skills and Child Behaviors at Pretreatment and Posttreatment

				95% Confidence Interval of the Difference				
	M Diff	SD Diff.	Std. Err Diff.	Lower Diff.	Upper Diff.	t	df	Sig.
Parenting Skills								
Effective Parenting Skills	1.50	14.62	3.12	-4.98	7.98	.048	21	.64
Ineffective Parenting Skills	-4.05	9.64	2.06	-8.32	.23	-1.97	21	.06
Child Behaviors								
Child Deviance Behaviors	-1.77	12.58	2.68	-7.35	3.81	-0.66	21	.52

Note. Diff = paired differences using pretreatment and posttreatment data

II. Effect of Treatment Type and Specific Problem Behavior on Treatment Outcome

Prediction 4

It is predicted that the type of treatment delivered to children with problem behaviors will have a differential effect on the behaviors targeted for change.

In order to enable group comparisons, a mean effect size for each treatment condition was computed by combining the effect sizes across each individual in each of the three treatment conditions (Busse et al., 1995). In the present study, a mean effect size for each intervention condition was calculated across home and school. In the CBC condition, home effect sizes ranged from 1.77 to –5.31 (M = -.66, SD = 1.40, n = 17) and school effect sizes ranged from 1.16 to –5.15 (M = -.95, SD = 1.39, n = 16). In the GVT condition, home effect sizes ranged from 2.85 to –1.16, with the largest effect size in the unexpected direction (ES = 2.85) considerably lowering the overall mean (M = .03, SD = 1.49, N = 6). The overall mean for the GVT condition was substantially greater when this effect size was considered an outlier and removed (M = -.62, SD = .53, N = 5). The single effect size obtained at school was .61. In the VT condition, home effect sizes ranged from -.10 to –3.27 (M = .-82, SD = 1.05, N = 8) and school effects ranged from 1.32 to -1.46 (M = -31, SD = 1.07, N = 5). The mean effect size for school was substantially greater when the largest effect size in the unexpected direction was removed (M = -.71. SD = .67, N = 4). Mean effect sizes for each treatment condition are presented in Table 9.

It is necessary to address the very small effect size obtained from the mother data within the GVT condition. There were only 6 mothers and their children involved in the GVT condition. A large effect size (ES = 2.85) obtained from mother data for one of these six children was in the unexpected direction suggesting an increase in aggression at posttreament. If this case is considered an outlier to be examined independently from the other cases, and a mean effect size for the GVT condition is recalculated using the remaining 5 cases, the resulting ES is a respectable -.62, suggesting significant behavior change in the expected direction. As for the "outlier", it is interesting to note that although this child's mother documented an increase in aggression from pretreatment to posttreatment, she did indicate improvement in social skills, problem behavior, and even externalizing behavior on the questionnaires given at posttreatment. A similar pattern was obtained for the mean effect across teacher data within the VT treatment condition. A mean effect of .30 is increased to .71 with the removal of one case.

Table 9

Mean Effect Sizes for Each Treatment Condition

Treatment	N	Maximum Unexpected Direction	Maximum Expected Direction	M	SD
CBC mother	17	1.77	-5.31	-.6629	1.40
CBC teacher	16	1.16	-5.15	-.9506	1.39
GVT mother	6	2.85	-1.16	-.03	1.49
GVT mother	5	.01	-1.16	-.62	.53
GVT teacher	1		-.61	-.61	
VT mother	8	-.10*	-3.27	-.8150	1.05
VT teacher	5	1.32	-1.46	-.3020	1.07
VT teacher	4	-.03*	-1.46	-.71	.67

NOTE. * = Minimum effect size was provided in cases when there were no effect sizes in the unexpected direction

Similarly, mean RC indices were calculated for each intervention condition using mother and teacher ratings on the CBCL, TRF, and SSRS. Mothers and teachers within all three conditions reported significant behavioral change on at least one of the three scales. For example, a significant RCI was reported by teachers in overall behavior problems within the CBC treatment condition (M = –1.97, SD = 2.63, N = 8). Similarly, a significant RCI in social skills was obtained by mothers within the GVT treatment condition (M = 2.87, SD = 3.51, N = 6). In the VT condition, a significant RCI was reported by mothers for problem behaviors (M = -2.90, SD = 1.30, N = 8). The mean RC indices for each condition are presented in Table 10.

Table 10

Mean Reliable Change Indices Across Rating Scales, Raters, and Intervention Conditions

Mother Variables	N	Maximum Unexpected Direction	Maximum Expected Direction	M	SD
CBC					
CBCL Total	14	2.60	-8.10	-2.13	2.56
External	15	2.14	-6.42	-1.57	2.11
Internal	15	2.83	-6.52	-2.21	2.72
SSRS (SS)	14	-3.66	4.44	.91	2.18
SSRS (PB)	14	1.67	-2.87	-.81	1.32
GVT					
CBCL Total	4	-.29*	-2.60	-1.52	1.12
External	5	4.82	-2.68	.06	2.81
Internal	3	.85	-5.38	-2.55	3.15
SSRS (SS)	6	.00*	9.15	2.87	3.51
SSRS (PB)	6	2.15	-3.58	-.68	1.84
VT					
CBCL Total	7	.29	-3.76	-1.57	1.33
External	7	.53	-2.67	-1.03	1.01
Internal	7	1.70	-2.83	-1.54	1.82
SSRS (SS)	8	-.65	3.27	1.21	1.67
SSRS (PB)	8	2.79	-1.43	-2.90	1.30
Teacher Variables					
CBC					
TRF Total	8	1.61	-4.82	-1.97	2.63
External	8	1.61	-5.35	-1.77	2.61
Internal	8	4.29	-9.05	-1.79	4.60
SSRS (SS)	13	-.78	5.10	1.54	1.87
SSRS (PB)	13	1.04	-3.18	-.95	1.23
GVT					
(no teachers data)	NA				
VT					
TRF Total	4	4.28	-4.28	.14	3.51
External	6	3.21	-4.28	0.03	2.43
Internal	6	5.71	-8.10	-2.14	5.31
SSRS (SS)	6	-3.01	4.57	.75	2.64
SSRS (BP)	6	.80	-2.83	-.72	1.43

Note. CBCL Total, External, Internal = Child Behavior Checklist Total Scale, Externalizing Scales, and Internalizing Scale; SSRS (SS), (PB) = Social Skills Rating System, Social Skills Scale, Problem Behavior Scale; * = Minimum effect size.

Prediction 5

It is predicted that children evidencing significant internalizing problem behaviors at prettreatment will evidence significant improvement at postreatment.

The behavior targeted for intervention in 89% of cases addressed externalizing behavior problems. Using these cases, Paired Sample t-tests were used to examine significant differences in internalizing behavior problems from pretreatment to posttreatment. There was a significant difference ($t = -3.998$, $p < .05$) between mother rated internalizing scores from pretreatment to posttreatment. Teacher ratings of differences in internalizing behavior were not significant at the .01 level ($t = -1.537$, $p = .148$). Similarly, a Paired Sample t-test was used to determine whether there was a significant difference in social skills from pretreatment to posttreatment. There was a significant difference ($t = 3.089$, $p < .01$) between mother rated social skills scores and a significant difference in teacher rated social skills scores ($t = 2.692$, $p < .05$) from pretreatment to posttreatment. Mean Internalizing T Scores and Social Skills Scores of the full sample are presented in Table 11 and the results of the Paired Sample t-tests are presented in Table 12.

Table 11

Mean Internalizing T Scores and Social Skills Scores at Pretreatment and Posttreatment

	Mean	N	SD	Std.Error
Mother				
Pre Internalizing T	60.35	26	10.15	1.99
Post Internalizing T	51.69	26	15.72	3.08
Pre Social Skills Score	84.61	28	13.98	2.64
Post Social Skills Score	95.46	28	17.44	3.30
Teacher				
Pre Internalizing T	59.64	14	7.28	1.95
Post Internalizing T	55.57	14	10.92	2.92
Pre Social Skills Score	80.42	19	12.16	2.79
Post Social Skills Score	90.53	19	13.63	3.13

Table 12

Paired Sample T-Test Comparing Pretreatment and Posttreatment Internalizing Behavior and Social Skills

				95% Confidence Interval of the Difference				
	M Diff	SD Diff.	Std. Err Diff.	Lower Diff.	Upper Diff.	t	df	Sig.
Mother Internalizing	-8.66	11.04	2.16	-13.11	-4.20	-3.00	25	.000
Teacher Internalizing	-4.04	9.911	2.65	-9.79	1.65	-1.54	13	.148
Mother Social Skills	10.86	18.62	3.52	3.64	18.08	3.09	27	.005
Teacher Social Skills	10.11	16.36	3.75	2.22	17.99	2.69	18	.015

Note. Diff = paired differences using pretreatment and posttreatment data

In addition to carrying out Paired Sample t-tests across all participants, descriptive statistics were carried out using the data obtained from only those participants with a significant Internalizing T score or Social Skills Scale Score at pretreatment. Within this restricted sample, it is possible to examine more closely the effects of intervention for children evidencing significant internalizing problems at pretreatment. Significant improvements in internalizing problems and social skills were obtained across home and school. Specifically, mothers who rated their children as evidencing significant internalizing problems at pretreatment (M = 68.70, SD = 3.68) no longer perceived their children as having significant internalizing problems at posttreatment (M = 60.70, SD = 10.55). Teachers also rated significant improvements in internalizing problems from pretreatment (M = 66.92; SD = 3.94) to posttreatment (M = 62.57, SD = 10.39). Similarly, mothers and teachers who rated their children/students as having significant social skills problems at pretreatment ($\underline{M}$ = 75.31, $\underline{SD}$ = 17.34; $\underline{M}$ =75.07, $\underline{SD}$ = 8.07) no longer perceived significant social skills problems at posttreatment ($\underline{M}$ = 92.5, $\underline{SD}$ = 6.92; $\underline{M}$ = 88.14, $\underline{SD}$ = 11.83). Table 13 presents case information with mother and teacher pretreatment and posttreatment scores.

Table 13

Summary of Consultation Case Descriptions and Mothers' and Teachers' Internalizing T- Scores and Social Skills Ratings at Pretreatment and Postreatment

Case	Age	Group	Target Behavior	Interv.	Int-T Pre (M)	Int-T Post (M)	Int-T Pre (T)	Int- T Post (T)	SS Pre (M)	SS Post (M)	SS Pre (T)	SS Post (T)
1	43	E/I	Noncompliance	CBC	**66**	**43**	43	48	87	**81**	**100**	94
2	86	E/I	Aggression	CBC	**73**	**60**	56	NA	73	NA	91	99
3	75	E/I	Socially Inappropriate	VT	71	NA	**64**	**56**	73	NA	82	74
4	77	E/I	Attention Getting	VT	**69**	**63**	**63**	**75**	**65**	**68**	108	85
5	110	E/I	Noncompliance	VT	**73**	**74**	69	NA	**75**	**70**	86	NA
6	67	E/I	Prosocial skills	CBC	60	51	**67**	**72**	**67**	**92**	**66**	**64**
7	71	E	Aggression	GVT	43	NA	53	NA	106	130	80	NA
8	71	E	Noncompliance	GVT	NA	NA	56	NA	101	101	79	NA
9	64	E/I	Aggression	GVT	46	NA	64	NA	**74**	**106**	91	NA
10	74	E/I	Tantrumming	VT	**68**	**58**	**64**	**69**	**80**	**78**	**69**	**77**
11	69	E	Tantrumming	VT	55	46	60	43	**78**	**101**	88	123
12	42	E	Noncompliance	CBC	53	34	53	46	91	125	**82**	**91**

13	35	E	Noncompliance	CBC	56	49	NA	NA	**81**	**91**	58	NA
14	76	E/I	Noncompliance	CBC	66	NA	66	NA	68	NA	90	85
15	67	E/I	Noncompliance	GVT	**72**	**53**	57	NA	95	98	NA	NA
16	80	E/I	Inattention	CBC	51	NA	**66**	**56**	76	NA	**79**	**91**
17	67	E	Aggression	CBC	53	34	48	57	89	87	**82**	**81**
18	43	E	Noncompliance	CBC	51	53	NA	56	87	88	**70**	**84**
19	63	E/I	Tantrumming	CBC	49	NA	**66**	**64**	64	NA	**56**	**95**
20	74	E/I	Socially Inappropriate	CBC	34	34	**65**	**46**	120	92	**76**	**97**
21	78	E/I	Socially Inappropriate	CBC	**64**	**74**	76	NA	87	69	**79**	**87**
22	66	E/I	Noncompliance	CBC	**66**	**46**	61	NA	87	96	86	NA
23	52	E	Aggression	CBC	46	NA	57	46	81	NA	86	107
24	63	E	Noncompliance	GVT	44	NA	54	NA	106	NA	82	NA
25	88	E	Noncompliance	VT	NA	53	62	57	**79**	**89**	**80**	**84**
26	55	E/I	Noncompliance	VT	**70**	**60**	57	43	**67**	**90**	**70**	**90**
27	109	E/I	Noncompliance	VT	55	61	73	NA	93	90	76	NA
28	72	E/I	Aggression	GVT	**76**	**79**	NA	NA	**66**	**69**	NA	NA

29	93	E	Aggression	GVT	57	46	NA	NA	**61**	**131**	NA	NA
30	36	E	Aggression	CBC	51	49	NA	46	**81**	**106**	**74**	**112**
31	117	E	Off-task	CBC	49	49	NA	NA	**78**	**84**	NA	NA
32	70	E/I	Aggression	CBC	**66**	**55**	NA	NA	**82**	**100**	NA	NA
33	96	E/I	Impulsivity	CBC	**64**	**60**	NA	NA	104	118	NA	NA
34	88	E	Noncompliance	VT	59	49	NA	NA	**84**	**109**	NA	NA
35	57	E/I	Noncompliance	CBC	**66**	**64**	61	NA	104	111	103	NA
_M_	**72.5**	**E/I**		**CBC, GVT, VT**	**68.70**	**60.70**	**66.92**	**62.57**	**75.31**	**92.50**	**75.07**	**88.14**

NOTE. E = Externalizing; I = Internalizing; E/I = Externalizing and Internalizing; Interv. = Intervention; Int-_T_ Pre (_M_) = Mother's Internalizing _T_ Score at pretest; Int-_T_ Post (_M_) = Mother's Internalizing _T_ Score at posttest; Int-T Pre (T) = Teacher's Internalizing _T_ Score at pretest; Int-_T_ Post (_T_) = Teacher's Internalizing _T_ Score at posttest; SS Pre (_M_) = Mother's Social Skills Rating System, Social Skills Scale Score at Pretest; SS Post (_M_) = Mother's Social Skills Rating System, Social Skills Scale Score at Posttest; SS Pre (_T_) = Teacher's Social Skills Rating System, Social Skills Scale Score at Pretest; SS Post (_T_) = Teacher's Social Skills Rating System, Social Skills Scale Score at Posttest. Bolded numbers represent significant scores at pretest. Mean scores were obtained using bolded numbers only.

III. Examining Hoover-Dempsey and Sandler's Model (1995): Self-Efficacy and Involvement

Prediction 6

It is predicted that mothers and teachers participating in CBC and videotape therapy will evidence a significant improvement in their perceived self-efficacy and in teacher perceptions of parent efficacy from pretreatment to posttreatment.

Reliable change indices were calculated in order to evaluate the magnitude of change in mother and teacher perceptions of self-efficacy, and teacher perceptions of parent efficacy for each case. Efficacy ratings and RCI's are presented in Table 14. There were 18 RCI's calculated, of which 56% indicated positive change in perceived efficacy, however only 17% of these improvements were statistically and clinically significant. In 33% percent of cases, efficacy ratings went down from pretreatment to posttreatment and in 11% of cases efficacy ratings remained the same.

In addition to evaluating the changes in perceived efficacy for each case, Paired Sample t-tests were computed in order to ascertain whether pretreatment means were significantly different from the posttreatment means of mother and teacher self-efficacy ratings and teacher perceptions of mother efficacy. Indeed, posttreatment means were consistently higher than pretreatment means for ratings of mother efficacy, teacher efficacy, and teacher perceptions of mother efficacy. Mean scores are presented in Table 15. However, results of the t-tests indicate no significant differences between the pairs suggesting that perceived self-efficacy did not significantly improve from pretreatment to posttreatment. Results of the t-tests are presented in Table 16.

Table 14

Mother and Teacher Efficacy Scores and Reliable Change Indices

Case	M Eff. Pre	M Eff. Post	RCI	T Eff. Pre	T Eff. Post	RCI	T Perc. M. Eff. Pre	T Perc. M. Eff. Post	RCI
2	61	68	1.81	51	58	1.69	12	42	4.73
10	NA	50	NA	NA	53	NA	NA	25	NA
14	53	NA	NA	53	56	.72	23	23	00
22	NA	53	NA	NA	NA	NA	NA	NA	NA
25	63	59	-1.04	51	54	.72	36	33	-.47
26	53	43	-2.59	58	56	-.48	18	20	.32
27	44	58	3.63	NA	NA	NA	NA	NA	NA
28	47	55	2.07	NA	NA	NA	NA	NA	NA
29	53	57	1.04	NA	NA	NA	NA	NA	NA
32	59	51	-2.07	65	NA	NA	27	NA	NA
33	57	64	1.81	69	69	00	40	37	-.47

Note. M = Mother; T = Teacher; Pre = Pretreatment; Post = Posttreatment; Eff. = efficacy; T. Perc. M. Eff. = Teacher perceptions of mother's efficacy

Table 15

Mean of Mother and Teacher Pair Efficacy Scores

		N	M	S.D.	Std. Error M
Pair 1	M.Eff-Pre	8	54.63	6.67	2.36
	M. Eff-Post	8	56.88	7.66	2.71
Pair 2	T. Eff.-Pre	5	56.40	7.60	3.40
	T. Eff.-Post	5	58.60	5.98	2.68
Pair 3	Teacher Perception M. Eff-Pre	5	25.80	11.88	5.31
	Teacher Perception M. Eff-Post	5	31.00	9.30	4.16

Note: M = Mother; T = Teacher; Pre = Pretreatment; Post = Posttreatment;

M. Eff. = Mother Efficacy; T. Eff. = Teacher Efficacy

Table 16

Paired Sample T-Tests Comparing Pretreatment and Posttreatment Efficacy Scores

				95% Confidence Interval of the Difference				
	M Diff	SD Diff.	Std. Err Diff.	Lower Diff.	Upper Diff.	t	df	Sig.
Mother Efficacy	2.3	8.56	3.03	-4.91	9.41	.74	7	.48
Teacher Efficacy	2.2	3.42	1.53	-2.05	6.45	1.44	4	.22
Teacher Perception M. Efficacy	5.2	14.02	6.27	-12.21	22.61	.83	4	.45

Note. Diff = paired differences using pretreatment and posttreatment data; Teacher Perception

M. Efficacy = Teacher perception of mother's efficacy

Prediction 7

It is predicted that mother and teacher perceptions of self-efficacy, and teacher perceptions of mother efficacy are associated with parent involvement.

Pearson-Zero Product Moment correlations were computed between mother and teacher perceptions of self-efficacy and teacher perceptions of mother efficacy, and mother involvement to determine their relationship at posttreatment (See Table 17). The strength of the correlations were assessed based on the guidelines recommended by Juniper, Guyatt, and Jaeschke (1996):

0.00 to 0.19 -- negligible or not correlated,
0.20 to 0.34 -- weakly correlated,
0.35 to 0.50 -- moderately correlated,
> 0.50 -- strongly correlated.

Mother involvement at posttreatment was strongly correlated with mother's perception of self-efficacy (r = .767, p <.05); teacher perception of self-efficacy (r = .71); and teacher perception of mother efficacy (r = .9.14, p <.05). Specifically, higher efficacy ratings were associated with more hours of mother involvement in educational activities per week. Efficacy ratings and hours of mother involvement are presented in Table 18.

Table 17

Correlations between Efficacy Ratings and Mother Involvement

	Mother Involvement	Mother Efficacy	Teacher Efficacy	Teacher Perception of Mother Efficacy
Mother Involvement	1.0	.767*	.710	.914*
Mother Efficacy	.767*	1.0	.501	.997**
Teacher Efficacy	.710	.501	1.0	.491
T Perception M. Efficacy	.914*	.997**	.491	1.0

Note. T. Perception. M. Efficacy = Teacher perception of mother's efficacy

Table 18

Efficacy Scores and Mother Involvement at Posttreatment

Case	M Efficacy Post Total of 75	T Efficacy Post Total of 75	T Percep. M. Efficacy Post Total of 42	Mother Involvement Post (hrs per/week)
2	68	58	42	21.25
10	50	53	25	2.75
14	NA	56	23	4.75
22	53	NA	NA	3.00
25	59	54	33	17.5
26	43	56	20	5.00
27	58	NA	NA	2.00
28	55	NA	NA	7.00
29	57	NA	NA	7.00
32	51	NA	NA	7.00
33	64	69	37	25.50

Note. M = Mother; T = Teacher; Pre = Pretreatment; Post = Posttreatment;

T. Percep. M. Efficacy = Teacher perception of mother's efficacy

CHAPTER 5

Discussion

The findings of the present study provide support for the effectiveness of a highly individualized behavioral consultation model, minimal consultation with videotape therapy, and self-administered videotape therapy for children with behavior problems. In addition, this study documents the effectiveness of these three approaches for children with specific behavior problems, with particular consideration of internalizing-type problems. This study also supports the positive relationship between perceived self-efficacy and mothers' involvement in their children's education. In the following section, these results are organized and discussed according to the three main predictions addressed in the present study. In addition, the implications of the present investigation are presented and the original contributions to the existing literature are discussed. Finally, limitations and directions for future research are proposed.

Efficacy of CBC, GVT and VT

Observational data collected by mothers and teachers support the prediction that the children from the three treatment conditions evidenced significant improvements in their target behaviors. In over 85% of the cases, mothers and teachers documented improvements in the specific behaviors targeted for intervention, such as noncompliance and attention getting behavior, during the intervention phase as compared to baseline behaviors recorded prior to the implementation of treatment. In more than half of these cases, a moderate to large effect size was reported suggesting a significant degree of behavior change across home and school settings.

In addition to documented improvements in specific behaviors targeted for intervention, every child evidenced fewer internalizing problems, externalizing problems, or general problem behaviors, or improved social skills following intervention. In approximately three-quarters of the cases, a meaningful and clinically significant degree of behavior change was obtained in at least one domain (i.e., internalizing behavior or social skills) by at least one rater (i.e., mother or teacher). These results clearly indicate that the interventions were effective in facilitating behavior change for the large majority of children.

One interesting finding in the present investigation was that teachers, overall, documented greater improvements in specific target behaviors than did mothers. Based on this finding, one may conclude that teachers documented larger overall treatment gains in the classroom than mothers documented at home. However, mothers actually documented greater improvements in internalizing behavior, externalizing behavior, general problem behavior, and social skills than did teachers. It can be argued, based on these findings, that mothers reported more general behavioral change, whereas teachers documented more specific behavior change. It is unclear why teachers documented larger improvements in the specific behaviors targeted for intervention, but reported smaller improvements in internalizing behavior, externalizing behavior, general problem behaviors, and social skills than did mothers. Perhaps teachers are more skilled than mothers in documenting specific behavior change as a result of their training and experience in systematic observations and therefore are more likely than mothers to focus on specific changes in target behavior. In contrast, mothers may not be as skilled in recognizing specific behavior changes, but recognize more general behavior improvements. Nevertheless, both mothers and teachers clearly documented improvement in behavior following treatment.

The positive treatment gains obtained in the present study corroborate the findings of other researchers who have documented the efficacy of conjoint behavioral consultation (e.g., Colton & Sheridan, 1999; Sheridan et al., 1999; Sladeczek, 1996) and videotape therapy (e.g., Webster-Stratton, 1993; Webster-Stratton & Hammond, 1997; Webster-Stratton & Lindsay, 1999) in treating children with behavioral problems. In addition to supporting existing research, this study also extends the literature beyond case studies and small-n methodologies that are typical of the majority of behavioral consultation research studies (Gresham & Noell, 1993). Although such research methodologies provide valuable information about consultation, there is a need for studies to evaluate the effectiveness of behavioral consultation on a larger scale (Gresham & Noell, 1993). The present investigation is one of only three studies to date that has examined the efficacy of conjoint behavioral consultation with a large number of children. The findings in this study are generally consistent with the results reported by Sheridan and her colleagues (1999) and Kratochwill and his associates (1999).

Sheridan and her colleagues (1999) are investigating the usefulness of CBC in facilitating inclusion practices for children with disabilities into regular classrooms in the United States. Similar to the present findings, preliminary treatment data obtained from parents and teachers indicate positive changes in children's behavior. Similarly, Kratochwill and his associates (1999), in their study examining the use of conjoint behavioral consultation for children with internalizing and externalizing problems, have also demonstrated positive behavior changes in both home and school settings from pretreatment to posttreament.

Unique to the present investigation was the use of videotaped observations of mother and child interactions to evaluate changes in the children's problem behavior and mother's parenting skills following intervention. Videotaping standard play situations provided an additional context by which to observe and evaluate behavior change for each child, and also provided a context for the evaluation of parenting skills prior to treatment and after treatment. However, the results obtained from the videotaped mother and child interactions did not provide any additional evidence that children's negative behaviors improved as a result of the interventions. Although, in general, the target children evidenced an improvement in child deviance behaviors following treatment, the improvement was not statistically significant. The absence of significant behavior change during the semi-structured observations was surprising based on the positive behavior changes reported by mothers and teachers via their observations of target behavior and their reports of decreased externalizing behavior and problem behaviors.

Similarly, videotaped interactions did not provide evidence that mothers' parenting skills improved over the course of treatment. Mothers' uses of direct commands, labeled, and unlabeled praise and descriptive statements did not significantly increase as a result of the interventions. In addition, mothers did not reduce their use of ineffective commands and critical statements following intervention. Again, it was surprising that the videotaped interactions did not provide evidence of improved parenting skills following intervention. Videotape therapy, by definition is a behavioral parent-training program (Webster-Stratton, 1987) and conjoint behavioral consultation is a framework which emphasizes the skill development of parents and teachers (Sheridan, 1993). These indirect service delivery models, in which services are provided to the parents and subsequently to the respective child, have received support based on their premise that by improving parental skills, the consultant increases the probability that a parent will work effectively with a child (Shiver, Kramer, & Garnett, 1993). Hence, it is likely that the children's deviant behavior and mothers' parenting skills did improve over the course of treatment, but the observational measure was not sensitive enough to detect the changes. Such reasoning may help explain why child deviance did not improve following treatment based on the videotaped interactions, while mothers and teachers documented positive behavior changes via observations and reports.

Effect of Treatment Type and Specific Problem Behavior on Treatment Outcome

Consistent with previous research documenting the effectiveness of CBC and videotape therapy in treating children with behavior problems (i.e., Kratochwill et al., 1999; Sheridan et al., 1990; Sheridan et al., 1996;Webster-Stratton, 1992a), mothers and teachers documented improvements in children's problem behaviors across the three treatment conditions. Intending to bring the present investigation one step further than previous investigations, the study compared the efficacy of the three consultation approaches with the goal of isolating the treatment type that was most effective in improving the problem behaviors and social skills of children with specific behavioral difficulties.

The CBC condition was the only treatment condition to obtain significant mean effect sizes across home and school. Also noteworthy, the VT condition obtained the largest mean effect size using mother data, while the CBC condition obtained the largest mean effect size using teacher data. Hence, it seems reasonable to consider that the setting in which an intervention program is implemented may relate to treatment efficacy. This line of reasoning suggests that a minimal consultation approach using videotape therapy would need to be implemented concurrently across home and school in order to obtain consistent treatment effects across both settings. In addition, this reasoning reinforces the importance of "conjoint" parent and teacher participation in the behavioral consultation model. Clearly, more comparative research is needed in order to determine the level of consultation that is most effective for parents and teachers. This type of research is necessary in order to address the call made by scholars and researchers in the field of consultation to compare the usefulness of behavioral consultation and other cost effective treatment models (Kratochwill et al., 1998; Noel & Witt, 1996).

The present study sought to examine the impact of the three treatment models on a continuum of behavior problems by including children who evidenced internalizing problems (i.e., withdrawn, depressed), a combination of internalizing and externalizing problems (i.e., anxious-aggressive), and externalizing behavior problems (i.e., noncompliance, aggression). It was particularly important to include children with internalizing problems, as previous findings have indicated that children with internalizing difficulties typically go unnoticed by teachers and caregivers therefore creating a population which is currently under-served (Rubin & Mills, 1991). Moreover, there is little research that has specifically and systematically examined the effectiveness of videotape therapy and CBC on reducing children's internalizing behavior problems.

In the current study, there was not one case in which a child presented with internalizing difficulties alone. Moreover, typical of the literature, an externalizing type problem, such as aggression, was targeted for intervention in the large majority of cases, despite the fact that in most cases the targeted children were evidencing coexisting internalizing problems. Yet, with few exceptions, the consultants and consultees aimed to decrease a specific externalizing behavior rather than increase social skills or decrease internalizing behavior. Of particular interest however, was that despite this emphasis on externalizing behavior problems, there was significant improvement in children's internalizing behavior from pretreatment to posttreatment. This finding provides support for the conceptualization of behavior problems along a continuum and highlights the importance for researchers to study the full spectrum of behavior problems, ranging from problems of undercontrol, categorized as externalizing difficulties, to problems of overcontrol, categorized as internalizing difficulties.

In the present study, mothers targeted externalizing-type problems, yet they perceived their children to be less internalizing (i.e., socially withdrawn, introverted), and more socially appropriate (i.e., improved social skills, more appropriate with other children and adults) after treatment. Teachers also perceived the children as having improved social skills following treatment. Moreover, considering only the children who evidenced significant internalizing problem behaviors before treatment, it was determined that, on average, mothers and teachers no longer perceived significant internalizing problems following treatment. Similar findings were obtained for mothers and teachers who rated their children/students as having significant social skill problems prior to treatment. On average these mothers and teachers no longer perceived significant social skills problems following treatment. These results provide solid support for the use of indirect models of service delivery in treating children with internalizing behavior problems. Although few researchers have examined the efficacy of CBC or VT with children who evidence internalizing behavior problems, the present findings are generally consistent with the studies conducted to date.

The findings in the present study are consistent with the findings of Sheridan, Kratochwill and Elliott (1990) in their study comparing conjoint and traditional behavioral consultation for four children who evidenced social withdrawal. Sheridan and her colleagues were the first to document the utility of using CBC to deliver treatment for specific internalizing problems (i.e., social skill deficiencies of children who were socially withdrawn). Findings from the present study were also consistent with the positive results obtained by Sheridan and Colton (1994) in their study documenting the effectiveness of CBC in treating irrational fears and childhood phobias, both specific examples of internalizing difficulties.

Most recently, Kratochwill and his associates (1999) completed a five-year study examining the use of CBC for children with internalizing and externalizing problems. Similar to the present study, a self-help manual-based approach to behavioral consultation was compared to videotape therapy. Also similar to the present investigation, children in the Kratochwill study demonstrated overall behavioral improvements following treatment. However, Kratochwill and his colleagues did not examine behavioral changes specific to internalizing problems. In short, the evidence thus far suggests that indirect behavioral interventions provide an effective framework within which to treat children with internalizing difficulties, however further research of this nature is needed.

Self-Efficacy and Involvement

According to Hoover-Dempsey and Sandler's model of the parental involvement process (1995) a major construct influencing parents' decision to become involved in their child's education is their sense of efficacy for helping their children succeed in school. A strong sense of efficacy enables parents to assume that their involvement in school activities will positively influence their children's learning and school performance (Hoover-Dempsey & Sandler, 1997). This assumption is linked closely to the rationale endorsed throughout the present study that CBC, GVT, and VT provide avenues to improve skills and empower parents and teachers, thereby strengthening their contribution to their children's/students learning and development. In the current study, positive changes in perceived efficacy were obtained in 56% of cases from pretreatment to posttreatment, however only 17% of these improvements were statistically and clinically significant. Although posttreatment means were consistently higher than pretreatment means, perceived mother efficacy, teacher efficacy, and teacher perceptions of mother efficacy did not significantly improve from pretreatment to posttreatment.

Mothers and teachers did not agree with most efficacy statements that suggested a perception of effectiveness in helping their child/student be successful in the classroom. Following treatment, mothers and teachers continued to indicate that they did not agree with most efficacy statements. Teacher perceptions of mother efficacy also indicated that, on average, teachers did not agree with the majority of mother efficacy statements prior to treatment. Interesting, however, was that, following treatment, teachers agreed with the majority of the mother efficacy statements, suggesting that at least qualitatively, the teachers perceived an increase in mother effectiveness after treatment. It is important to recognize that self-efficacy beliefs are not related to actual skills, but rather to the beliefs about what one can do with the subskills they possess (Hoover-Dempsey, 1997). Hence, it is perhaps reasonable that the mothers' and teachers' personal belief systems were ingrained and resistant to change, therefore explaining the absence of a significant increase in perceived self-efficacy at posttreatment. Therefore, it is possible that mothers' and teachers' skill level improved as a result of the three interventions, but that their self-efficacy beliefs remained the same. It is also reasonable that the teachers' beliefs pertaining to mother efficacy were less resistant to change than were their beliefs about themselves.

Despite the fact that efficacy beliefs did not significantly improve over the course of intervention, efficacy scores were strongly associated with mother involvement at the end of treatment. Specifically, mother involvement following treatment was strongly correlated with mother's perception of self-efficacy, teacher perception of self-efficacy, and teacher perception of mother efficacy. Consistent with Hoover-Demspsey's model and research, efficacy ratings were associated with more hours of mother involvement in educational activities per week.

Overall, the results seem to suggest that perceived self-efficacy represents a set of beliefs that tend to be resistant to change. Therefore it would appear to be an uphill battle to try to increase parent involvement in school activities for those parents' holding negative beliefs about their ability to make effective changes in their child's life. In a more positive light, the results may serve as a positive reminder to researchers and consultants of the individual nature of consultation services, and that there are no blanket assumptions that can be made without careful consideration of the multiple variables that impact service delivery. Hence, it may be inappropriate to blankly state that consultation services increase parent and teacher collaboration. Further research is clearly needed in order to discern the conditions under which collaboration can be facilitated. The findings seem to suggest that consultation services may be considered an optimal method to increase parent and teacher collaboration for families and teachers who feel empowered to make positive changes in the lives of their children and students.

Original Contributions

The present study has advanced the conceptual understanding of conjoint behavioral consultation and videotape therapy, and has provided information that may be used to inform the clinical application of the intervention models. The present study is one of only three large-scale studies of CBC ever conducted. Typically, studies investigating the effectiveness of CBC have used small sample sizes, thereby limiting the generalizability of the findings (e.g., Colton & Sheridan, 1998; Sheridan & Colton, 1994; Sladeczek, 1996). The inclusion of single-n analyses within a group design methodology in this investigation facilitated a more detailed exploration of the consultation process. Although the conjoint behavioral consultation framework has been used as a model for the provisions of consultation services in the United States, it is glaringly absent from the Canadian school psychology literature and has inevitably received little attention in the field (Sladeczek & Heath, 1997). Hence, the present investigation has initiated the large-scale analysis of CBC within a Canadian context.

In both Canada and the United States there is a striking absence of empirical data comparing behavioral consultation with other methods of service delivery in order to determine whether behavioral consultation is more effective or efficient than other models of intervention (Noell & Witt, 1996). Hence, the present study sought to systematically investigate the efficacy of CBC as a service delivery as compared with other cost-efficient models of intervention (i.e., videotape therapy). This study was unique in its investigation and comparison of three cost-efficient models of intervention that vary along a continuum of indirect service delivery.

The study also enhanced the existing research base by including participants who exhibited externalizing and internalizing difficulties. Children presenting with various difficulties along the continuum of behavior problems were targeted, thus facilitating the investigation of a range of behavior problems. Specifically, the study was unique in its examination of internalizing behavior problems pretreatment and posttreatment. Kratochwill and his colleagues (1999) recently included children with internalizing and externalizing challenging behavior problems in their recent study. However, their study did not include an outcome measure specific to internalizing problems. Hence, the present study is unique in its investigation of treatment effects for both internalizing and externalizing behavior problems using outcome measures specific to both types of problem behavior.

Another significant contribution of this study was the focus on parent and teacher collaboration. Although Sheridan and Kratochwill (1990) suggest that CBC is one form of home-school service delivery that may improve parent and teacher collaboration, there is little research evaluating the strength of the parent/teacher partnership before and after consultation. Moreover, there is minimal research examining the effect of videotape therapy on parent and teacher collaboration. The present study incorporated research from the parent involvement literature, focusing on a model developed by Hoover-Dempsey and Sandler (1995) that illustrates the influence of specific variables on the parent involvement process. The study specifically examined the influence of perceived self-efficacy, which, according to Hoover-Dempsey and Sandler (1995), is a fundamental mechanism in the explanation of parents' decision to become involved in their children's education. The examination of perceived self-efficacy as it relates to parents' decision to become involved in their children's education was a unique contribution of the present study and provides a useful first step towards understanding parent-school relationships within the consultation framework.

Implications of Findings

There are a number of theoretical and practical implications that can be drawn from this investigation. First, the high prevalence of children with significant internalizing and externalizing difficulties targeted reinforces the conceptualization of behavior problems along a behavioral continuum and highlights the need to investigate the range of behavior difficulties along this continuum. Second, the results of this study suggest that reducing consultant involvement may not compromise treatment success. Finally, the present study speaks to the importance in empowering parents and teachers in order to facilitate change. Each of these implications is discussed.

The combination of externalizing and internalizing behavior is considered to have particularly negative implications for future psychosocial functioning (Somersalo et al., 1999). In the present study, a large number of children presented with both internalizing and externalizing problem behaviors, and therefore represent a population of children at high risk for poor occupational success, low social status, and unsuccessful social relationships (Moskowitz & Schwartzman, 1989). The high prevalence of children with significant internalizing and externalizing problems who were targeted in the present study reinforces the conceptualization of behavior problems along a behavioral continuum and suggests the importance of investigating the range of behavior difficulties along this continuum.

The prevalence of children evidencing various behavior problems considerably exceeds the personnel and resources available. Consequently, there is a need for cost-effective interventions for these children (Brestan & Eyberg, 1998). The significant improvements in children's behavior problems and increases in prosocial behaviors that were obtained in the present study suggest that conjoint behavioral consultation and videotape therapy are effective models by which to service young children with behavioral difficulties. The three treatment conditions investigated in the present study each emphasized parent training and early intervention, but varied in the degree of consultant involvement. All three of the intervention approaches were demonstrated to be effective in addressing children's behavior problems at home and in the classroom. Hence, in a time of budgetary cutbacks, and high prevalence rates of behavior problems, the results of this study suggest that reducing consultant involvement may not compromise treatment success.

The present study speaks to the importance in empowering parents and teachers in order to mobilize change. The parent involvement literature and the results obtained in this study highlight the importance of perceived self-efficacy in facilitating parent and teacher collaboration. This finding provides psychologists and consultants with important information that can be used to involve parents in their children's education. In addition, it may provide a feasible explanation as to why so many parents are resistant to becoming involved in their children's school activities.

Limitations and Future Directions for Research

The limitations of this study are discussed within the context of proposals for future research. One of the limitations of the present study is the small sample size. Although not a consideration for small-n research, the small sample size limited the types of group analyses that could be conducted. The small sample made it particularly difficult to draw definitive conclusions regarding the efficacy of the CBC versus GVT, and VT conditions. In addition, logistic challenges inherent in clinical research interfered with the use of rigid experimental procedures. Certainly the use of either a wait-list control group or a multiple baseline design would have strengthened the reliability of the findings. These methodological controls would have allowed for a stronger test of the three interventions. It is necessary for future consultation researchers to continue to employ group and single-n methodology in combination with either a wait-list control group or a multiple baseline design to compare the effectiveness of conjoint behavioral consultation with other cost-effective models of intervention. In addition, it is necessary to consider the influence of SES and culture on treatment outcome within both group and single-n methodology. The findings of the present study are limited by the exclusion of cultural, social and economic considerations.

Further investigation should be conducted examining the usefulness of videotape therapy for children with internalizing behavior problems. Although this was an intended goal of this study, the lack of identified participants with pure internalizing disorders, and the disproportionate number of externalizing problems targeted for intervention limited the generalizability of the results. The examination of mother and teacher efficacy in the present study represents a first step towards the investigation of relevant variables associated with parent and teacher collaboration. Further research is necessary to further evaluate the effect of CBC and videotape therapy on parent and teacher collaboration. Specifically, systematic assessment of the actual strength of the parent and teacher partnership before consultation has begun and after consultation has terminated is needed in order to obtain a better understanding of the effects of behavioral consultation on parent/teacher collaboration. To improve on the methodology of the present study, it is suggested that future researchers not only examine the frequency of involvement by summing time spent on school related activities but also ascertain the quality of parents' involvement with their children's education at home and at school both before and after treatment.

Consultation researchers need to continue in their endeavor to determine the most effective intervention programs for children with internalizing and externalizing behavior problems. Upon this venture, one thing seems certain, the collaboration of parents and teachers will be central to the process of behavioral change.

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Appendix A

History Questionnaire

HISTORY QUESTIONNAIRE

Name of child: ____________

Name of parent guardian completing this questionnaire: ____________

Your relationship to this child: Mother Father

Guardian Other ________

1. Who is currently living in the home?

Name	*Indicate whether brother/sister; father, mother, grandparent, etc.*
____________	____________
____________	____________
____________	____________
____________	____________
____________	____________
____________	____________
____________	____________

2. Have there been any recent major events in the home (e.g., birth of a child, divorce, a move to another town)?

NO YES

If so, please explain:

____

____

____

____

____

____

3. Is your child currently taking medication prescribed by a physician? No Yes

If so, name the medication: ______________________________

Why was the medication prescribed?

____

____

____

____

____

4. Is your child currently receiving other services for his/her behavioral or social difficulties?
No Yes If so, please describe:

____

____

____

____

____

5. Is there any other information regarding your child or family history that you would like to share?

____

____

____

____

____

Appendix B

The Parent Efficacy Scale

Parent Efficacy for Helping Children Succeed in School Scale
Thinking About Helping My Child

We would like you to think about your child __________, in Ms./Mr.________'s class. Please circle the number that most closely matches your response to each question. (There are no right or wrong answers here; we just want to know what you think).

	Strongly agree	Agree	Neither agree nor	Disagree	Strongly disagree
1. I know how to help my child do well in school.	5	4	3	2	1
2. My child is so complex. I never know if I am getting through to him/her.	5	4	3	2	1
3. I don't know how to help my child make good grades in school.	5	4	3	2	1
4. A student's motivation to do well in school depends on the parents.	5	4	3	2	1
5. I feel successful about my efforts to help my child learn.	5	4	3	2	1
6. Other children have more influence on my child's grades than I do.	5	4	3	2	1
7. Most of a student's success in school depends on the classroom teacher, so I have only limited influence.	5	4	3	2	1
8. I don't know how to help my child learn.	5	4	3	2	1
9. If I try hard, I can get through to my child child even when he/she has difficulty understanding something.	5	4	3	2	1
10. I make a significant difference in my my child's school performance.	5	4	3	2	1
11. Other children have more influence on my child's motivation to do well in school that I do.	5	4	3	2	1
12. My efforts to help my child learn are successful.	5	4	3	2	1
13. Other children have more influence on my child's behavior than I do	5	4	3	2	1
14. I don't know how to help my child make friends in school.	5	4	3	2	1
15. I can make a significant difference in my child's behavior at school.	5	4	3	2	1

Appendix C

Teacher Efficacy Scale

Teacher Efficacy Scale

<u>Please circle the number that most closely matches your response to each question</u>. (There are no right or wrong answers here; we just want to know what you think).

	Strongly agree	Agree	Neither agree nor	Disagree disagree	Strongly
1. I feel that I am making a significant educational difference in the lives of my students.	5	4	3	2	1
2. If I try really hard, I can get through to even the most unmotivated students.	5	4	3	2	1
3. Children are so private and complex. I never know if I am getting through to them.	5	4	3	2	1
4. I usually know to get through to students.	5	4	3	2	1
5. Most of a student's school motivation depends on the home environment, so I have a limited influence..	5	4	3	2	1
6.There is a limited amount that I can do to the basic performance level of students.	5	4	3	2	1
7. I am successful with the students in my class	5	4	3	2	1
8. I am uncertain how to teach some of my students.	5	4	3	2	1
9. I feel as though some of my student's are not making any academic progress.	5	4	3	2	1
10. My student's peer s influence their motivation more than I do.	5	4	3	2	1
11. Most of a student's performance depends on the home environment, so I have a limited influence.	5	4	3	2	1
12. My student's peers influence their academic performance more than I do.	5	4	3	2	1
13. My student's peers influence their behavior more than I do.	5	4	3	2	1
14. If I try really hard, I can get through to the students with behavior difficulties.	5	4	3	2	1
15. I am uncertain how to help some of my students with problem behaviors.	5	4	3	2	1

Appendix D

Adapted Teacher Perceptions of Parent Efficacy Scale

Adapted Teacher Perceptions of Parent Efficacy Scale:

We would like to know more about your perceptions of __________'s parents' influence on student learning. Specifically, we would like to know what you think about _________'s parents' influence on his/her learning.

	Agree Very Strongly	Agree Somewhat	Agree	Disagree	Disagree Somewhat	Disagree Very Strongly
1. His/her parent(s) help him/her learn.	6	5	4	3	2	1
2. His/her parent(s) have little influence on his/her motivation to do well in school.	6	5	4	3	2	1
3. If his/her parent(s) try really hard they can help him/her learn even when he/she is unmotivated.	6	5	4	3	2	1
4. His/her parent(s) feel successful about helping him/her learn.	6	5	4	3	2	1
5. His/her parent(s) don't know how to help him/her make educational progress.	6	5	4	3	2	1
6. His/her parent(s) help him/her with school work at home.	6	5	4	3	2	1
7. His/her parent(s) make a significant, positive educational difference in his/her life.	6	5	4	3	2	1

Appendix E

Involvement Questionnaires

Parent Name:_______________ Date: _______________

Parent Involvement Questionnaire

Helpful Information Related to Home and School Collaboration- Parent Form

Please provide an accurate estimate of your estimate of your participation in the following forms of parent-school activities: (hours per average week)

1. Time spent volunteering in classroom ______

2. Time spent in educational activities ______

3. Time spent helping your child with homework ______

4. Time spent engaged in written communication with teacher ______

5. Time spent meeting with the teacher ______

6. Time spent visiting the classroom ______

7. Time spent involved in classroom decision-making (hours per month) ______

Is there a system in place by which basic information is shared across home and school?

____

____

____

Are you presently involved in a program that facilitates the collaboration between home and school? Please describe.

____

____

____

Teacher's Name:_______________ Date: _________________

Teacher Involvement Questionnaire

Helpful Information Related to Home and School Collaboration- Teacher Form

Thinking of ___________ 's parent, please provide an accurate estimate of participation in the following activities: (in hours per week)

1. Time in which parent is volunteering in your classroom ______
2. Time spent engaged in written and personal communication with parent ______
3. Time spent meeting with parent ______
4. Time spent involving parent in classroom decision-making ______

Thinking of your class in general, please provide an accurate estimate for following activities:

5. Number of students in the classes whose parents participated in scheduled conferences ______
6. Number of students in the classes whose parents participate in volunteer work at school ______
7. Number of students in the classes whose parents participate in regular assistance in homework ______
8. Number of students in the classes whose parents participate in educational activities with children (e.g., reading and playing games) ______
9. Number of students in the classes whose parents participate in telephone calls with the teacher ______

Is there a system in place by which basic information is shared across home and school?

____

____

____

____

Appendix F

Overview of Conjoint Behavioral Consultation Manual

Behavioral Consultation:
Problem Identification Interview (PII)

OBJECTIVES AND DEFINITIONS

PII Goals

* Provide an overview of the consultation and the consultation process.
* Establish a working relationship between parents and teacher.
* Confirm teacher and parent permission for participation.
* Collect information about formal composition, receptivity, involvement, home problems, special needs, etc.
* Establish primary language of parent
* Present the results of the screening (if applicable)
* Define the problem(s) in behavioral terms (i e., provide an operational definition)
* Provide a tentative identification of behavior in terms of antecedent, situation, and consequent conditions across settings
* Provide a tentative strength of the behavior across settings (ie., how often or severe)
* Discuss and reach agreement on a goal for behavior change across settings
* Establish a procedure for collection of baseline data across settings in terms of sampling plan, what, who, and how the behavior is to be recorded

Interview Objectives:

OPENING SALUTATION

PROJECT SUMMARY: Summarize what will be covered during the meeting.

GENERAL STATEMENT: General statement to begin discussion related to referral concerns. Specifically discuss the general results of the screening process.

Examples: What seems to be the problem?
What is it that you are concerned about?

Establish Primary Language of Parent: Ask, "What is the primary language of the home?"

BEHAVIOR SPECIFICATION: Elicit behavioral descriptions of client functioning Focus on specific behaviors, Provide as many examples of the problem as possible Prioritize the problems from the most to the least severe (problems across settings should be prioritized).

a. Behavioral description:

What does Jamie do when he's angry?
Tell me what you mean when you say, "he gets upset with himself easily".
Give me some examples of what you mean by, "self-abusive behaviors"

b. Elicit examples:

What are some more examples of Jamie's "self-abusive" behaviors at home/at school?

c. Prioritize behavior:

We've discussed several behaviors, such as head-slapping, kicking objects, ripping up papers, and screaming.
Which of these is most problematic across settings?
Do you both agree?

BEHAVIOR SETTING: A precise description of the settings in which the problem behavior occurs.

a. General setting description:

Where is Jamie usually when he hits himself?
Give me some examples of where Jamie does this at school.
Where does the head-slapping occur at home?

b. Elicit examples

What are some more examples of where this occurs?

c. Prioritize settings:

Which of the settings at school is most problematic?
Which of the settings at home is most problematic?

IDENTIFY ANTECEDENTS: Events which precede the child's behavior. These events can immediately precede the behavior, or they may be removed in time (eg. events at home in the morning that impact the child's behavior at school, etc.).

Examples: What typically happens at home/at school before Jamie starts to hit himself?

What things do you notice before he starts that might be contributing to its occurrence?

What is a typical morning like before Jamie goes to school?

SEQUENTIAL CONDITIONS ANALYSIS: Situational events or environmental conditions occurring when the behavior occurs. A pattern or trend of antecedent/consequent conditions across a series of occasions (e.g. time of day, day of week).

Examples: What else is typically happening in the classroom/playground/home when Jamie is observed hitting himself?

What patterns do you notice in Jamie's head slapping behavior?

What time of day or day of week seems to be most problematic at home/at school?

IDENTIFY CONSEQUENT CONDITIONS: Events which occur immediately following the behavior These can be reactions of parents, teachers, or peers, and they can occur immediately following the behavior or at a later point in time (e.g. at home after school).

Examples. What typically happens after Jamie hits himself at home/at school?
What types of things do you notice at home/at school after that might be maintaining its occurrence?

How are school-related problems handled at home?

BEHAVIOR STRENGH: The level or incidence of the behavior how often (frequency) or how long (duration) the behavior occurs The question format will depend on the specific behavior and focus on consultation.

Examples. How often does Jamie hit himself at home/at school?
How long does it last?
On a scale O -10. how severe is the behavior at home/at school?

GOAL OF CPNSULTATION: Appropriate or acceptable level of behavior

Examples: What would be an acceptable level of head-slapping at home/at school?

Is any head-slapping OK?

Is there general agreement for Jamie across home and school?

CHILD'S STRENGTHS/ASSESTS: Strengths, abilities, or other positive features of the child.

Examples: What are some of the things that Jamie is good at?

What are some of Jamie's strengths?

EXISTING PROCEDURES: Procedures or rules in force that are external to the child and to the behavior

Examples: What are some programs or procedures that are currently operating in the classroom?

How are problems currently dealt with when they occur at home/at school?

PROVIDE A RATIONALE FOR DATA COLLECTION: A purpose or rationale for data collection is provided. At this time also note that observers will also be used to gather data in the home and classroom setting.

Examples: It would be very helpful to watch Jamie for a week or so and monitor how often he hits himself in the head This will help us key in on some important facts that we may have missed, and also help us document the progress that Jamie makes.

DISCUSS DATA COLLECTION PROCEDURES: Specify the target responses to record, including the kind of measure, what is to be recorded, and how to record. Consistent data collection procedures across should be encouraged. Specific details of data recording should be emphasized. A written plan and format for parents and teachers is often helpful.

Examples: What would be a simple way for you to keep track of Jamie's head-slapping at home/at school?

DATE TO BEGIN DATA COLLECTION: Procedural details regarding when to begin collection data.

Examples: When can you begin to collect data at home/at school?

NEXT APPOINTMENT: Establish meeting time for PAI. Note that the P AI could occur at different times for teacher and parent.

Examples: When can we all get together again to discuss the data and determine where to go from here?

CLOSING SALUTATION

Behavioral Consultation:
Problem Analysis Interview (PAI)

Objectives and Definitions

<u>PAI Goals</u>

* Secure teacher and parent permission for treatment program.
* Evaluate and obtain agreement on the sufficiency and adequacy of baseline data across settings.
* Conduct a tentative functional analysis of the behavior across settings (ie, discuss antecedent, consequent, and sequential conditions).
* Identify setting events (events that are functionally related, but temporally or contextually distal to the target behavior), ecological conditions, and other cross-setting variables that may impact the target behaviors.
* Implement an intervention plan including specification of conditions to be changed.
* Reaffirm record-keeping procedures.

<u>Interview Objective</u>

OPENING SALUTATION

GENERAL STATEMENT RE: DATA AND PROBLEM

<u>Example:</u> Were you able to keep a record of... ?

BEHAVIOR STRENGH: Question or statement regarding behaviors, specific to the baseline data collected

<u>Example:</u> According to the data. it looks like Jamie hit himself in the head at least 4 times at home and 5 times at school each day.

ANTECEDENT CONDITIONS: Information regarding events which precede the child's behavior. These events may have immediately preceded the behavior, or they may have been removed in time (e.g. events at home in the morning that impact the child's behaviors at school, etc.) Refer to baseline data in this discussion.

Examples: What did you notice before Jamie began to hit himself at home/at school? What things may have led up to its occurrence?

CONSEQUENT CONDITIONS: Events which occurred following the behavior. These can be reactions of parents, teachers, or peers, and they can occur immediately following the behavior or at a later point in time (e.g. at home after school) Refer to baseline data in this discussion.

Examples: What typically happened after Jamie hit himself at home/at school?

What types of things did you notice afterwards that may have maintained its occurrence?

SEQUENTIAL CONDITIONS: Situational events or environmental conditions occurring when the behavior occurs. A pattern or trend of antecedent/ consequent conditions across a series of occasions (e.g. time of day, day of week).

Examples: What else was happening in the classroom! playground/home when you observed Jamie hitting himself?

What time of day, or day of week seemed most problematic?

What patterns did you notice in Jamie's behavior at home/at school?

INTERPRETATION OF BEHAVIOR: Parents' and teachers' perceptions regarding the purpose or function of the behavior. Consultant may also suggest hypotheses regarding the behavior if other explanations are plausible.

Examples: Why do you think Jamie hits himself?

It sounds like it might also be related to a very low frustration tolerance level.

Conjoint Behavioral Consultation
Treatment Evaluation Interview (TEI)

Objectives and Definitions

TEI Goals:

* Determine if the goals of consultation have been obtained across settings.
* Evaluate the effectiveness of the treatment plan across settings.
* Discuss strategies and tactics regarding the continuation, modification, or termination of the treatment plan.
* Schedule additional interviews if necessary, or terminate consultation.

Interview Objectives

OPENING SALUTATION

EVALUATE GENERAL PROCEDURES AND OUTCOME: Question or statement regarding general procedures and outcome.

Example: How did things go with the plan?

QUESTIONS ABOUT GOAL A TRAINMENT: Determine specifically if the goals of consultation have been attained. Refer to treatment data collected, and the goal statement specifies in the PII.

Example: Has our goal of 1 "head slap" per day been met at home/at school?

ESTABLISHING A PLAN: Plan strategies are established with the intention of implementing the intervention across settings (when you are working with both teacher and parent) The tentative goal stated in the PII, the interpretation of the behavior, and the child's strengths should be considered in the plan.

<u>Examples:</u> It seems that we need to try something different

What can be done at both home and school to stop Jamie from hitting himself and to teach him alternative, more appropriate ways to cope with frustration?

CONTINUE DATA RECORDING PROCEDURES: Data recording procedures to be used in treatment implementation. Should be identical to or consistent with baseline data collection procedures.

<u>Examples:</u> It would be very helpful if we could continue to collect data on the number of times that Jamie hits himself each day at home and school.

Can we continue the same recording procedures as before?

NEXT APPOINTMENT: Establish a meeting time for the TEI.

CLOSING SALUTATION

If goals have been attained:

EVALUATE PLAN EFFECTIVENESS:
Determine the effectiveness of the plan for the specific child. Was the specific plan effective in producing behavior change, or are there other competing explanations? What is the internal validity of the plan?

> Example: Do you think that the behavior program was responsible for Jamie's decrease in head-slapping?

EVALUATE EXTERNAL VALIDITY OF PLAN:
Determine the potential effectiveness of the plan for another setting where the child has a similar problem. This tactic may also increase the potential for consultees to generalize the plan to other clients.

> Example: Do you think this plan would work with another child with similar difficulties?

CONDUCT POST-IMPLEMENTATION PLANNING:
Decision is made regarding the advisability of leaving the plan in effect, removing the plan, or constructing a new plan. Selecting a post-treatment alternative to implement across settings may occur.

> Example: Should we leave the plan in effect for a while longer?

PROCEDURES FOR GENERALIZATION/MAINTENANCE:
Procedures to encourage continued progress are discussed. The goal is to encourage generalization to other behaviors, persons, or situations, or to maintain behavior over a long period of time. If the goals of consultation are not met, this question may not be non-applicable.

> Example: How can we encourage ________to display these behavior changes in other problem settings?
>
> What procedures should we use to make sure that the behavior change continues over time?

If goals have not been attained:

QUESTIONS RE: PLAN MODIFICATION:
Establish new plan strategies to increase plan effectiveness across settings. Consultant may suggest a change or question the need for change. If plan is successful and goals are met, this question may be nonapplicable.

Examples: How can we modify the procedures so that the plan is more effective?

FOLLOW-UP ASSESSMENT: Discuss regarding follow-up recording procedures to monitor the behavior over time and over settings.

Examples: How can we monitor Jamie's progress to ensure that these positive changes continue?

QUESTIONS RE: NEED FOR FUTURE INTERVIEWS

Examples: When can we meet again to discuss the effectiveness of our modifies plan?
Would you like to meet again to check on __________'s progress?

TERMINATION OF CONSULTATION (if goals have been met)

CLOSING SALUTATION

Appendix G

Ethics Approval Form

MCGILL UNIVERSITY
FACULTY OF EDUCATION

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Faculty of Ed. Assoc. Dean

CERTIFICATE OF ETHICAL ACCEPTABILITY FOR FUNDED AND NON FUNDED RESEARCH INVOLVING HUMANS

The Faculty of Education Ethics Review Committee consists of 6 members appointed by the Faculty of Education Nominating Committee, an appointed member from the community and the Associate Dean (Academic Programs, Graduate Studies and Research) who is the Chair of this Ethics Review Board.

The undersigned considered the application for certification of the ethical acceptability of the project entitled:

Treatment of Children with Problem Behaviours: The Efficacy of Conjoint Behavioural Consultation versus Videotape Therapy and the Impact on Parent-Teacher Collaboration

as proposed by:

Applicant's Name Leigh Ann Wayland

Applicant's Signature LA Wayland

Degree / Program / Course Ph.D / School Psychology

Supervisor's Name Ingrid E. Sladeczek, Ph.D.

Supervisor's Signature Ingrid E. Sladeczek

Granting Agency ____________

The application is considered to be:
A Full Review ____________

An Expedited Review X (based on the fact that my research is part of a larger study which has received approval)

A Renewal for an Approved Project ____________

A Departmental Level Review ____________
Signature of Chair / Designate

The review committee considers the research procedures and practices as explained by the applicant in this application, to be acceptable on ethical grounds.

1. Prof. Evelyn Lusthaus
Department of Educational and Counselling Psychology
Evelyn Lusthaus Dec 15, 2000
Signature / date

2. Prof. John Leide
Graduate School of Library and Information Studies
John Leide 001215
Signature / date

3. Prof. René Turcotte
Department of Physical Education
Dec 14/00
Signature / date

4. Prof. Lise Winer
Department of Second Language Education
____
Signature / date

5. Prof. Claudia Mitchell
Department of Educational Studies
____
Signature / date

6. Prof. Kevin McDonough
Department of Culture and Values in Education
____
Signature / date

7. Member of the Community
____
Signature / date

Mary H. Maguire Ph. D.
Chair of the Faculty of Education Ethics Review Committee
Associate Dean (Academic Programs, Graduate Studies and Research)
Faculty of Education, Room 230
Tels: (514) 398-7039/398-2183 Fax: (514) 398-1527

Mary Maguire Jan 3/2001
Signature / date

(Updated January 2000)

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Determination, mobilization and dechlorination of polychlorinated biphenyl (PCB) compounds in contaminated soils

By

Qixiang Wu

Department of Food Science and Agricultural Chemistry
Faculty of Agricultural and Environmental Sciences
McGill University, Montreal

June 2001

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Doctor of Philosophy

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Abstract

Polychlorinated biphenyls (PCBs) are a group of 209 chemical congeners that are toxic and persistent organic contaminants that have been present in the environment for several decades. It has been estimated that some 11 million tons of PCBs have contaminated soil, sediments, vegetation and animals. About 300 million tons of PCBs, that remain in use in North America, represent a potential source of contamination that can further deteriorate the environment.

Due to their toxicity, physical and chemical stability and environmental persistence, PCBs have attracted a great deal of attention and have encouraged researchers to develop new techniques/approaches to detoxify PCBs and PCB contaminated matrices in a rapid, efficient and environmentally friendly manner. In 2000, the market for PCB treatment technologies is estimated to be \$300–\$600 million (Canadian) dollars.

This study investigated novel approaches/techniques for PCB dechlorination with zero-valent metals or bimetallic mixtures; optimised a method for PCB determination within contaminated soil/sediments and PCB washing/flushing from contaminated soil. Soil washing/flushing was combined with supercritical carbon dioxide ($scCO_2$) mobilization dechlorination *on-line* using zero-valent metals. Studies have demonstrated that PCB can be dechlorinated efficiently by heated columns of zero-valent metal or bimetallic mixtures. The limit of detection for PCBs within contaminated soil was estimated to be 0.15 mg/kg for a simple procedure that converted PCB residues to biphenyl. PCBs were flushed efficiently from polluted soils into surfactant suspension and then back-extracted into supercritical CO_2. Finally, they were dechlorinated virtually quantitatively in a continuous *on-line* process using heated columns of zero-valent bimetallic mixtures. The dechlorination yield for PCB extracts from contaminated soil or from PCB surfactant mixture was greater than 99.5%. The treated surfactant suspensions could be recycled to extract more PCBs from the contaminated soil. The techniques/approaches developed in this study would seem to have a broad application in PCB dechlorination/detoxification and in the remediation of historically contaminated soil/sediments.

Résumé

Les diphéniles polychlorés (DPC) sont un groupe de 209 molécules chimiques qui sont des contaminants organiques toxiques et persistants qui ont été présents dans l'environnement pendant plusieurs décennies. On estime qu'environ 11 millions de tonnes de DPC ont contaminés les sols, les sédiments, la végétation et les animaux. Environ 300 millions de tonnes de DPC sont toujours utilisés en Amérique du Nord, ce qui représente une source potentielle pour détériorer l'environnement. En raison de leur toxicité, leur stabilité physique et chimique, et leur persistance dans l'environnement, les DPC ont attirés l'attention de nombreux chercheurs à développer de nouvelles techniques/approches pour déchlorurer des matrices contaminées de DPC d'une façon efficace et rapide. En l'an 2000, on estime que le marché pour traiter les DPC est de \$300~\$600 millions (dollars canadiens). La présente étude démontre l'utilisation de nouvelles approches/techniques pour la déchloruration de DPC en utilisant des métaux de valence zéro ou des composés bimétalliques. L'optimisation d'une méthode pour déterminer les DPC de sols/sédiments contaminés fut développer de même que le 'lavage/purgage' de DPC de sols contaminés. Le 'lavage/purgage' de sols contaminés fut combiné avec l'extraction par fluide supercritique au dioxide de carbone (SC-CO_2) et les métaux de valence zéro. Ces études ont démontrées que les DPC peuvent être déchlorurés avec efficacité en chauffant des colonnes de métaux de valence zéro ou des composés bimétalliques. La limite de détection des DPC pour les sols contaminés fut estimée à 0.15 mg/kg pour la conversion de résidus de DPC au composé de diphénile. Les DPC de sols pollués furent purgés efficacement dans une suspension d'agent tensio-actif pour être par la suite extrait avec SC-CO_2. Finalement, les DPC furent déchlorurés quantitativement dans un procédé en continu utilisant des métaux bimétalliques de valence zéro. Le rendement de déchloruration fut de 99.5% et plus pour les extraits de DPC de sols contaminés ou les mélanges d'agent tensio-actif de DPC. Les suspensions d'agent tensio-actif furent recyclées de nouveau pour extraire de plus amples DPC de sols contaminés. Les techniques/approches développées dans cette étude ouvre de nombreuses perspectives d'applications pour la déchloruration/ détoxification de DPC et pour la remédiation de sols/sédiments contaminés.

Contribution of Co-authors

The present work has been *supported by* Strategic grants from the Natural Science and Engineering Research Council of Canada (NSERC). The research has been supervised by Dr. William D. Marshall from McGill University (Montreal, Canada). Dr. William D. Marshall is co-author for all the materials that have been published and will be co-author for the publications that have been submitted / accepted for publication.

Dr. Abdul Majid from the Institute for Chemical Process and Environmental Technology, National Research Council of Canada contributed to part of this work by supplying some PCB extract that had been isolated from contaminated soil using a patent technique and by providing supervisory assistance. He is a co-author for part of the project.

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Qixiang Wu and William D. Marshall. Extractions of Polychlorinated biphenyl (PCB) compounds from surfactant suspension/soil extracts with dechlorinations on line (Chapter 5). Accepted for Publication in Journal of Environmental Monitoring, 2001, 3

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Abbreviations and Glossary

Abbreviation	
AcA	Acetic Anhydride
ANOVA	Analysis of Variance
CAS	Chemical Abstract Service. CAS registry numbers are unique chemical identifiers
CB	Chlorobiphenyl
CEPA	Canadian Environmental Protection Agency
Cl	Chlorine
DME	Ethylene glycol dimethyl ether
ECD	Electron Capture Detector
FID	Flame Ionization Detector
GC	Gas Chromatograph, an analytical instrument
GC-MS	Gas Chromatograph Mass Spectrometry
HPLC	High performance liquid chromatograph
IBMK	Isobutyl methyl ketone
IUPAC	International Union of Pure and Applied Chemistry, IUPAC numbers are unique Chemical identifiers
kg	Kilogram (1000 g)
L	Litre
LOD	Limit of Detection
LOQ	Limit of Quantitation
mg	Milligram (0.001g)
mg/kg	Milligrams per kilogram
ml	Millilitre (0.001 litre)
MS	Mass Spectrometry
MW	Molecular weight
ng	Nanogram (0.000000001 g)
PCBs	Polychlorinated biphenyls

pg	Picogram (0.000000000001 g)
$scCO_2$	Supercritical carbon dioxide
μg	Microgram (0.000001 g)
μg/kg	Micrograms per kilogram (part per billion parts)
μl	Microlitre (0.000001 l)
US EPA	United States Environmental Protection Agency

Glossary of terms

Aroclor	Commercial PCB formulation containing many different PCB congeners in a mineral-oil carrier
CEPA	Canada Environmental Protection Agency
Congener	An individual PCB
Coplanar	A PCB having zero or one chlorine in an ortho position
Dechlorination	The process that replaces one or more chlorine atom from chlorinated compounds to make the substrate less toxic and/or virtually non-toxic
Ex-situ	Above ground (outside of ground)
Homolog	Group of PCBs having the same degree of chlorination
In-situ	In the ground (within ground)
Internal Standard	Known amount of chemical added to a sample prior to measurement, to control for the sample quantity or instrument variability
Isomers	Chemicals having the same molecular formula, but different arrangements of their constituent atoms
Micelle	Self-aggregated surfactant molecules, having either hydrophobic ends out, or vice versa
Ortho	When referring to PCBs, ortho refers to the binding sites adjacent to the bridge between the two phenyl rings
Remediation	The removal of contaminants from environmental media to achieve regulatory or risk-based goals
Solution	Homogeneous mixture of two or more substances

Surfactant	Molecules with polar and non-polar regions that self-aggregate into micelles
Surrogate	Chemicals added to a sample prior to sample preparation to monitor for the loss of analyte during processing

Introduction

Rationale

Polychlorinated biphenyls (PCBs) are toxic, persistent organic contaminants that have been present in the environment for several decades (Erickson, 1997). According to studies (Rantanen *et al.*, 1975; Hester and Harrison, 1996), the global burden of PCBs is about 374,000 tons (31% of the cumulative world PCB production), of which 39 % is concentrated within the terrestrial and coastal environments. Although the total amount of PCBs produced annually has declined (on a worldwide basis) since the 1970s, the toxicological threat posed by these compounds has not decreased appreciably (U S Agency for toxic substance and disease registry, 1993). In fact, their persistence in the environment has been of growing concern due to their toxicity, low degradability, mutagenicity, and tendency to bioaccumulate (US EPA, 1996). Environmental cycling is suspected of being the current, major source of PCBs to soil outside of disposal and spill sites (U S Agency for toxic substance and disease registry, 1993). When PCBs are introduced into a soil medium they can become sorbed strongly and may remain there for many years. They are unlikely to be taken up by plants and therefore they are not readily mobilized from soil systems. The principal transportation route for PCBs through aquatic systems is from waste streams into receiving waters, with further downstream movement occurring by solution and readsorption onto particles as well as by the movement of sediments (Rantanen *et al.*, 1975). The widespread occurrence of PCBs in the environment and the apparent link to carcinogenesis has promoted an increasing world concern since the early 1970s, that has resulted in restrictions in using PCB in most countries.

According to information from Environmental Canada, approximately 40,000 tons of PCBs were imported into Canada prior to 1977, and there remains about 15,100 tons of PCBs still in use across the country. They were the first substances to be regulated and originally prohibited for certain applications under the Canada

Environmental Contaminants Act (1976). Several regulations have been developed in Canada for PCB compounds since 1988. Under these newer regulations, several standards, recommendations, guidelines and criteria for PCBs in the Canada environment have been established. The restriction for PCB application has increased the amount of PCB waste. By 1990, more than 150,000 tons of PCB wastes involving PCB contaminated soil, mineral oil, and other metallic components of electrical equipment had been stockpiled across Canada. Between 1989 and 1995, the federal government allocated $6 million for PCB destruction projects in Atlantic Canada, Quebec, and Ontario. With the implementation of PCB related regulations, more PCB waste will be produced and more financial resources will have to be allocated to the destruction and remediation of PCB contaminated media (Environment Canada, 1998).

Remediation of PCB matrices is a comprehensive process involving PCB extraction/ mobilization, PCB destruction and the restoration of cleaned materials. During the last two decades, more than 80 techniques have been developed for PCB destruction and decontamination (U S Agency for toxic substance and disease registry, 1993; US EPA 1996). However, the majority of these processes remain theoretical or they have been optimized only for small-scale destruction (US EPA, 1996). When used in the real-world, many methods still face challenges. The disadvantage of most methods for PCB remediation/destruction make it necessary to continue to develop increasingly efficient, rapid, and simple processes to destroy PCBs.

Objectives of theses studies

Due to the increasing concerns of PCB contamination and the potential deterioration of the environment, the strategy of these studies was focused on PCB dechlorination /detoxification and remediation of PCB contaminated soils. The major objectives were:

1) to apply the supercritical fluid technologies as an alternate method to conventional procedures for PCB mobilization from contaminated soils.

2) to explore novel techniques that use zero-valent metal/bimetallic particles as

accelerants that might rapidly and efficiently dechlorinate/detoxify PCBs and PCB contaminated materials.

3) to develop a quantitative analytical method that can accurately determine PCB concentrations within contaminated soils/sediments.

4) to investigate the feasibility of PCB extraction from contaminated soils using surfactant suspensions in combination with supercritical carbon dioxide ($scCO_2$).

5) to develop/optimize a process that combines PCB extraction with on-line dechlorination to make the PCB clean up procedure a continuous operation while recycling the surfactant back to the contaminated soil to mobilize more toxicant.

Organization of this thesis

This thesis is organized into 8 Sections. Section 1 provides a brief overview of the problem and lists the overall project objectives. Chapter 1 reviews background information on a range of topics that relate to PCB uses, environmental contamination and remediation/destruction processes. Chapter 2 describes the development and validation of a quantitative analytical method for the determination of PCB concentration in contaminated soils. Chapter 3 presents a novel approach/technique for PCB dechlorination under reducing conditions. Chapter 4 investigates PCB mobilization from contaminated soils with back-extraction from the soil extract. Chapter 5 evaluates the efficiency of PCB extraction from surfactant suspension and/or soil extracts with *on-line* dechlorination. Chapter 6 is the project summary and overall conclusions. The final section of this thesis contains the references.

Chapter 1

Literature review

1.1 Structure and nomenclature

Polychlorinated biphenyl (PCB) compounds are a group of 209 chemical congeners, each of which consists of two benzene rings joined head to head with one to ten possible chlorine substituents. PCB nomenclature is based on the location of chlorine substituents on the biphenyl ring, as illustrated in Figure 1.1. There are no known PCB that occur naturally. They were first synthesized some 100 years ago and have been available commercially available worldwide since 1929 (Erickson, 1997). All PCB mixtures were synthesized by chlorinating biphenyl with chlorine gas. The empirical formula of PCBs is $C_{12}H_{10-x}Cl_x$ (x = 1-10). The average degree of chlorination was controlled by the reaction conditions in order to yield the desired chemical and physical properties (Erickson, 1997; Rantanen *et al.*, 1975). When PCBs are grouped according to the degree of chlorination, the groups are called homologs. A given PCB homolog with different chlorine substituted at different positions are referred as to isomers. Individual PCB congeners are conventionally given a systematic name that identifies the position of chlorine substitution and the degree of chlorination.

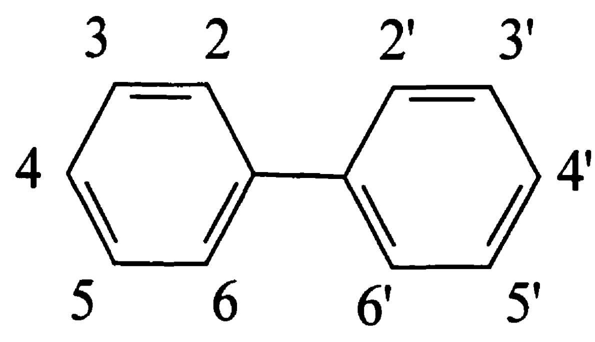


Figure 1.1 The General molecular structure of PCBs

Two different numbering systems continue to be used for PCB congener identification, each arranges all the congeners in order and assigns to them a number from 1 to 209. The first numbering system is the Ballschmiter system and was proposed by Ballschmiter and Zell in 1980 (Erickson, 1997). The second numbering system in common use is the International Union of Pure and Applied Chemistry (IUPAC) system of nomenclature. The differences appeared for eleven congeners. The 209 PCB congeners are grouped according to the degree of chlorination of the molecule. The mono-, di-, tri-, tetra-, penta-hexa-, hepta-, octa-, nona- and decachlorobiphenyl congeners can exist in 3, 12, 24, 46, 42, 24, 12, 3 and 1 isomeric forms respectively. There are several registered trademarks in use for commercial PCB mixtures such as Aroclor, Therminol, Askarel and Pydraul. This thesis uses the trademarks of Aroclor (Monsanto, Corp., USA) and the IUPAC numbering system.

1.2 The properties and use of PCBs

It was estimated that some 1.2 million tons of PCBs was manufactured in the world from 1929 until the late 1970s, when their production ceased in most western countries (Hester and Harrison, 1996). Polychlorinated biphenyls occur as liquids or solids, and they are clear to light yellow in color. PCBs have no odor or taste, and are insoluble in water, but are soluble in organic or hydrocarbon solvents, oils and fats (Table 1.1). PCBs are nonvolatile, chemically inert and do not undergo oxidation, reduction, addition, elimination or electrophillic substitution reactions except under extreme conditions. Most PCBs are oily liquids in which colour darkens and viscosity increases with increasing chlorine content. These characteristics, combined with their chemical stability, have made PCBs valuable for industrial applications such as in insulating liquids, capacitors and transformers and as additives in plastics, adhesives, paints, pesticides, carbonless copy paper, newsprint, fluoresence light ballasts, dyes and waxes (Table 1.2). PCBs do not degrade readily in the environment, and can bioaccumulate up the food chain with the possible adverse effects on wildlife and human health (Galveston-Houston Association for Smog Prevention, 1996). As increasing attention was turned to

Table 1.1 Characteristics of PCB mixtures

Aroclor	Density	Solubility in water at 25°C (μg/L)	Average number Cl/molecule	Approximate wt. Cl (%)
1221	1.18	15,000	1.15	21
1232	1.26	1,450	2	32-33
1016	1.37	420	3	40-42
1242	1.38	240	3	40-42
1248	1.44	52	4	48
1254	1.54	12	5	52-54
1260	1.62	3	6-6.3	60
1262	1.64		6.8	62
1268	1.81		8.7	68
1270	1.95		10	71

Source: from Erickson, 1997.

Table 1.2 Industrial uses of PCBs (1929-1975)

PCB use	Ton (millions)	Percentage of Total
World wide		
Capacitors	235	50.3
Transformers	123	26.7
Placticizers uses	42.8	9.2
Hydraulics and lubricants	30	6.4
Carbonless copy paper	16.8	3.6
Heat transfer fluids	7.5	1.6
Petroleum additives	0.4	0.1
Miscellaneous industrial uses	10.1	2.2
Total	467.4	100

Source: from US EPA Report, 1997.

PCBs, it became clearer that these compounds were causing a negative impact on many biological systems. When evidence of their toxicity began to be reported in the early 1970s, the use of PCBs became increasingly restricted and was being phased out (United Nations Environment Program, 1988; Galveston-Houston Association for Smog Prevention, 1996).

1.3 Environmental impact and health effects of PCBs

1.3.1 Pathways for PCB entry into the environment

The discharge of polychlorinated biphenyl compounds represents a serious threat to the environment and the biosphere (Galveston-Houston Association for Smog Prevention, 1996). PCBs have been discharged into the environment exclusively from anthropogenic activities. In the past, the release of PCB wastes into rivers, streams and open landfills was considered to be acceptable, and was thought to be hazard-free practices (American Council on Science and Health, 1997). Therefore, PCBs were able to enter into the environment from all of these activities, as well as from the incineration of waste, industrial discharges and sewage effluents (US EPA, 1997). There have also been accidental releases of PCBs and associated contaminants into the environment via the leaking of sealed PCB fluid compartments during use of transformers and capacitors, and as a result of improper disposal of PCB-containing equipment or chemical products (American Council on Science and Health, 1997).

1.3.2 PCBs in soil systems

PCBs are widespread contaminants in the environment primarily in soil systems (Erickson, 1997). According to studies (Rantanen *et al.*, 1975; Hester and Harrison, 1996), the global burden of PCBs is about 374,000 tons (31% of total world PCB production), of which 39 % burdened the terrestrial and coastal environment. Although the total amount of PCBs produced annually has declined (on a worldwide basis) since the 1970s, the toxicological threat posed by these compounds has not decreased appreciably (U.S. Agency for toxic substance and disease registry, 1993). In fact, their persistence in the environment has been of increasing concern due to their toxicity, low degradability, mutagenicity and tendency to bioaccumulate (US EPA, 1996). Environmental cycling is suspected of being the current, major source of PCBs in soil outside of disposal and spill sites (U.S. Agency for toxic substance and disease registry, 1993). Once introduced into a soil medium, PCBs can become sorbed strongly and can remain there for many years. They are unlikely to be taken up by plants, and therefore they are not readily mobilized from soil systems. In 1991, the cumulative burden at U.S. sites, that had been identified as having excessive PCB levels, was estimated at 382 million tons (US EPA 1994; 1996). PCB concentrations in soils at contaminated sites can be many-fold higher than background levels (Table 1.3).

1.3.3 PCBs in water systems

Open oceans contain about 228,140 tons of PCBs, of which 66,000 tons was held in North America basins (Rantanen *et al.*, 1975; Hester and Harrison, 1996). PCB concentrations are generally higher in waters near human activity and near shorelines. Currently, the major input of PCBs into surface waters is from environmental cycling (Hester and Harrison, 1996). Approximately 98% of the PCBs entering the ocean are currently deposited from the atmosphere. The principal transport route for PCBs through aquatic systems is from waste streams into receiving waters, with further downstream movement occurring by solubilization and readsorption onto particles as well as by the movement of sediments (Rantanen *et al.*, 1975). The release of PCBs from sediments to overlying waters can occur by slow desorption. Translocation can also occur through biological activity (US EPA, 1997). Desorption of PCBs from particulate is more likely to occur from lower chlorinated, more water-soluble PCB congeners. As a result, the marine environment becomes one of the terminal sinks for PCBs, and the concentration of PCBs in fish can be many-fold higher than that in the surrounding water due to the bioaccumulation (U.S. Agency for toxic substance and disease registry, 1993).

1.3.4 PCBs in the air

Traces of PCBs have been detected in the air far remote from their point of release (U.S. Agency for toxic substance and disease registry, 1993). Municipal waste combustion, hazardous waste incineration and medical waste incineration account for an appreciable portion of reported national PCB emissions to the air (US EPA,1996). Additional sources of PCB emissions included treatment, storage

Table 1.3 The occurrence of PCBs in representative environments

Country	Location	Air(ng/M^3)	Water(ng/l)	Soil(μg/g)
Canada	Great Lakes	0.03-0.04	0.11-0.64	~0.2
	Montreal		0.18-0.55	
U.S./Canada	Arctic(81°N)	0.1-0.3		
U.S.	Great Lakes			0.03-0.2
	Lake Michigan		100-450	
Japan	Tokyo			
	Agricultural land	20		<1,000

Source: Hester, 1996; Pham,1999; Erickson, 1996.

disposal facilities and landfills; hazardous waste sites; steel and iron reclamation facilities; accidental releases; and environmental sinks of past PCB contamination (US EPA, 1996). The most recent compilation of PCB concentrations in the air of the Great Lake area ranged from 30 to 400 picograms/m^3, and it is generally highest in the summer and lowest in the winter (The Royal Society of Chemistry, 1996). According to a report of World Health Organization (WHO, 1987), in Bangkok, Thailand, the average PCB concentration was 570-820 ng/m^3.

These levels are 1000 times greater than those measured in urban air in the United Kingdom (WHO, 1987). About 25% of airborne PCBs was attributed to volatilization from capacitors and the remainder from volatilization of PCBs spilled on the surrounding soil.

1.3.5 Co-Planar PCBs and their health effect

Attention to the environmental presence of PCBs began in early 1960s when PCBs were reported in soil and water (Galveston-Houston Association for Smog Prevention, 1996). In 1968, an incident of widespread human poisoning in western Japan was attributed to the consumption of rice bran oil that had become contaminated with PCBs during processing (Busert *et al.*, 1978). Global concerns grew over the potential deleterious health effects of PCBs and were spurred on by human poisoning episodes that were similar to the incident of PCB-contaminated rice bran oil consumption in Taiwan (Rogan *et al.*, 1988).

PCBs are divided into 2 groups of isomers based on differences in structure:

i) Coplanar PCBs - these compounds have chlorinated substituents in both para positions, and any/all meta positions (Parkinson & Safe,1987). Meta or para chlorine substituents have, by their structures, low steric hinderance with neighbouring hydrogens, which allows free rotation about the phenyl-phenyl bond (Parkinson & Safe,1987).

ii) Mono-ortho chlorinated PCBs - all molecules have 1 or more chloro substitutions in the ortho positions only (Parkinson & Safe,1987). Ortho-substituents tends to create rigid bonds due to the large steric interference between the Cl and H atoms (Parkinson & Safe,1987).

PCB isomers react with different receptors. For example, co-planar molecules are more toxic than ortho isomers in the development of thymic atrophy, caused by a loss in cortical lymphocytes (Parkinson & Safe,1987). In comparison, ortho isomers have a higher affinity for estrogen receptors as compared to co-planar isomers; estrogenic hormonal activity was therefore increased (Korach *et al.*,1987).

Halogenated compounds tend to bind to estrogen receptors, resulting in abnormal estrogenic activity (Korach *et al.*,1987). Uterotropic activity has been studied in the rat using mixtures of either two isomer types of PCB, as well pure individual chlorobiphenyls (Korach *et al.*,1987). Only mixtures with 1 or more degree of ortho substitutions were active in estrogen-receptor binding, behaving as competitive inhibitors of estradiol (Korach *et al.*,1987). The ortho-chlorine substituents also forced conformational restrictions, which may have improved the estrogen receptor-binding activity through increased homology between estradiol and PCBs (Korach *et al.*,1987). Regions of homology include a hydrophobic area, the conformational inflexibility, and the phenolic ring between the biphenyl and the A-ring of estradiol (Korach *et al.*,1987).

However, while here may be a strong correlation between toxicity and structure, where ortho-para-meta- substituents can reliably predict or explain differences in toxicities, PCB carcinogenesis has little or nothing to do with PCB structure (Parkinson & Safe,1987). The latter depends primarily on the actions of cytochrome P-450 located primarily in the liver.

Within the liver endoplasmic reticulum, there is a mechanism used by most vertebrates to remove harmful lipophilic xenobiotics. Through biotransformation by at least 12 cytochrome P-450 isozymes, xenobiotics are nullified (Parkinson & Safe,1987). The cytochrome P-450 isoenzymes hydroxylate, epoxidate, dealkylate and oxygenate many compounds such as drugs, environmental pollutants and carcinogens, as well compounds found within the body such as fatty acids, sterols, steroid hormones and vitamins (Parkinson & Safe,1987). Cytochrome P-450 converts lipophilic compounds to metabolites that are more easily eliminated from the body, and thus works to defend the cells from PCB intoxication (Parkinson & Safe,1987). However, the PCB-metabolites that this cytochrome P-450 produces are often more toxic than the parent molecule itself (Parkinson & Safe,1987).

Some specific P-450 isozymes prefer to metabolize co-planar chlorophenyls, others prefer to act on non-coplanar PCBs (Parkinson & Safe,1987). Toxicity depends on the amount of conversion to reactive intermediates by monooxygenases, produced by cytochrome P-450. The greater the preference for metabolism, the more reactive intermediates that are produced, the more toxic the isomer. The co-planar molecules are the more toxic isomers, which induces cytochrome P-450 more powerfully than the ortho-substituents (Parkinson & Safe,1987). TPCBs, PCDFs, PCDDs, PCNs, PBBs, bromobenzenes, hexachlorobenzenes, DDT and others all induce cytochrome P450 isozymes (Parkinson & Safe,1987). Other xenobiotic metabolizing enzymes are also induced that may not be related to cytochrome P-450. For example, benzo(a)-pyrene hydroxylase is an enzyme that has similar functions to that of cytochrome P-450 (AHH activity). AHH activity results in the hydroxylization of benzo(a)-pyrene, a reactive intermediate of cytochrome P-450. PCBs can also be hydroxylated to stable molecules (eg. methlsulfonyl metabolites) and not just reactive intermediates (Schellman Sipes,1987). Accumulation of stable metabolites in bronchi caused "respiratory distress" in rodents (Schellman Sipes,1987).

PCBs can enter the human body by inhalation, ingestion, or by direct dermal contact. The trace quantities present in most people are the result of ingestion through food. As recorded in Table 1.4, the daily average intake of PCBs has been estimated to be as much as 60 μg per person. PCBs accumulate in fatty tissues, their half-life has been estimated to be 38 years (The Royal Society of Chemistry, 1996). PCB residues in adipose tissue and milk samples from the general population in industrialized countries range from less than 1 to 5 ppm (fat basis). Plasma PCB residues in the general population have been found to range from 5 to 50 ng/g (Table 1.5). Studies (American Council on Science and Health, 1997) have suggested that certain mixtures of PCBs are carcinogenic. The potential health effects associated with exposure to PCBs include carcinomas, reproductive and development toxicities, impaired immune function, effects on the central nervous system and deleterious liver changes. Other non-cancerous, short-term effects of PCBs in humans include body-weight loss, headaches, dizziness, depression, nervousness and fatigue. Chronic exposure may also result in changes of enzyme activities (U.S. Agency for toxic substance and disease registry, 1993).

Table 1.4 Estimated dietary intake of PCBs in Canada

Food	Food intake (g/person/day)	Maximum residual level (μg/g)	PCB intake (μg/person/day)
Dairy	32.8	0.2	6.6
Meat	48	0.2	9.6
Poultry	3.6	0.5	1.8
Eggs	34	0.1	3.4
Fish	20	2	40
Total			61.4

Source: from report EPS 4/HA/1, Environment Canada.

Table 1.5 PCBs content in food and the human body

Area	Year collected	Adipose (mg/kg)	Eggshell (mg/kg)	Cheese (mg/kg)
Canada	1970s	0.91 ± 0.82		
(All regions)	1980s	0.94 ± 0.90		
Ottawa	1980-1981	2.0 ± 0.87		
Kingston	1971-1981	3.0 ± 3.6	550	250

Source: from Erickson, 1996.

1.4 PCB analysis and quantification

1.4.1 Qualitative analysis of PCB congeners

Qualitative analysis of PCB is to precisely identify each of the 209 PCB congeners, especially the identities of the coplanar PCBs because these compounds are more acutely toxic in terms of the environment impact. The analysis of PCBs in environmental and biological sample is a multi-step process (Ashok *et al.*, 1998) and includes steps of extraction, cleanup, removal of sulfur, column fractionation and gas chromatographic separation (Medes and Boer, 1997). The PCB congener separation in environmental matrices is based not only on the degree of chlorination but also on their structure and on the analytical protocal adopted. Most of the commercial mixtures and environmental samples exhibit a multitude of peaks. High-resolution isomer-specific analysis is now a feasible option for the identification and quantitation of individual PCBs present in commercial mixtures and in environmental samples (Mullin and Pochini, 1984). Identification of PCB congeners is made more difficult with the variation in composition of the environmental PCB mixtures among the sample types. Errors in the analysis of PCBs are further compounded by wide variations in the response of each congener for GC-ECD, the most common method of analysis. Environmental aging, varying degrees of volatility for each congener, and confounding factors due to of matrix also add to the uncertainty of PCB analysis. Until now, there is not a standard method for the qualitative analysis of PCB congeners. The optimal conditions are still being investigation, although the major congener mass spectral patterns are available (Figure 1.2).

Several attempts have been made in recent years to separate PCB mixtures. One of the two seminal works involved the synthesis of all 209 PCBs combined with their determination on a SE-54 column. Mullin and co-workers (1984) studied the retention times of 209 PCB congeners and response factors relative to the standard, octachloro- naphthalene, using a 50-m fused silica capillary column coated with SE-54 and equipped with a ^{63}Ni electron capture detector. They summarized a plot of relative retention times (RRT) vs. PCB isomer groups and illustrated the overall increase with increasing chlorine content of the congeners.

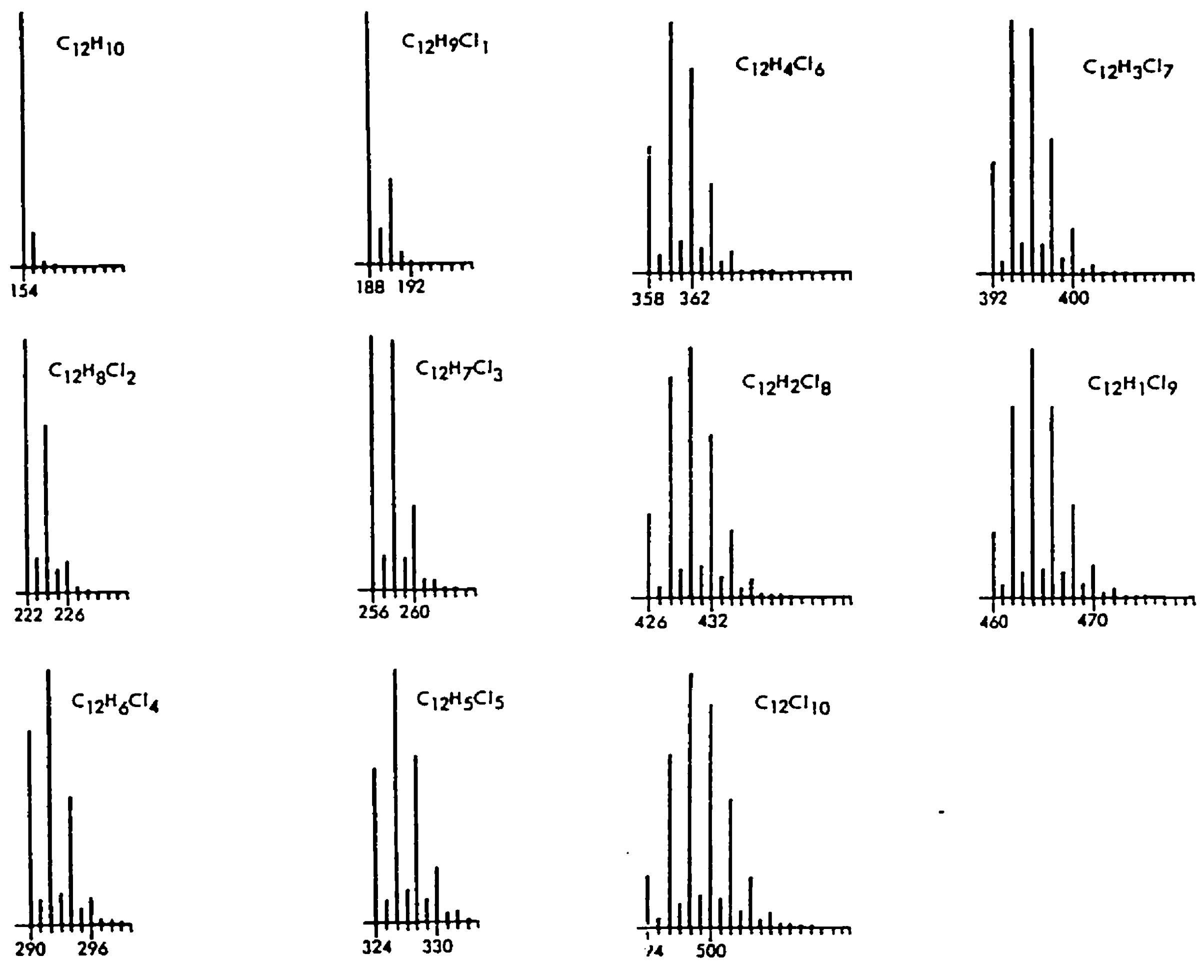


Figure 1.2 Molecular ion clusters of mass spectral patterns of PCB congeners (Source: from Erickson, 1997)

Vetter *et al.* (1998) investigated all 209 PCB congeners using GC-electron ionization mass spectrometry equipped with a high temperature capillary column coated with Thermocap A phase. They separated and identified all of the 209 congeners and listed the unique retention times of different congeners. Recently, Bolgar *et al.* (1995) analyzed 209 PCB congeners by high resolution GC and low resolution MS and demonstrated the physical and spectral properties of all 209 PCB congeners.

When compared with the determination of individual PCB congener, the analysis of commercial mixtures is more difficult to identify because the multiple components of each mixture produce a characteristic chromatographic pattern that changes with exposure time in the field. Although by comparing the pattern for an unknown PCB mixture with patterns for standard Aroclor PCB mixtures, the unknown often can be identified. By contrast, the peak pattern for a chemically or biologically degraded Aroclor mixture can differ appreciably from that of the manufactured mixture. Problems also arise when a sample contains two or more Aroclor mixtures, or non-Aroclor mixtures of PCBs. Frame *et al.* (1998) studied 6 commercial Aroclors on 20 different high-resolution GC columns and demonstrated the variability in the numbers of congeners that each system could quantify. Their results indicated that the greater congener count in some GC-systems was due to difference in detector sensitivity and not to peak resolution. According to the bulletin 817C (Supelco report, 1996), ECD is more sensitive to PCB congeners, but mass spectrometric detection is more selective and enhances the chromatographic separation.

1.4.2 Quantitative analysis of total PCBs

The convential PCB quantitation methods include the calculation of the total integrated area of calibrated individual PCB congener/isomer peak by GC-ECD and/or GC-MS with the use of individual reference standards (Dowdall *et al.*, 1995). More frequently, some researchers use a set of PCB congeners with a complex calibration procedure to quantify the PCB content in routine analyses. The results of this method can deviate up to 100% from the true value for single CBs although the total amount could be determined correctly (Buthe and Denker, 1995).

For the determination of the correct amount of total PCBs, there are two principle approaches which are straightforward (Schuetz *et al.*, 1999). One is the complete hydrodechlorination of pure PCBs to biphenyl. Analysis of biphenyl may then be conducted by GC-FID and/or petentiometric detection of Cl^- post reaction. Doyle *et al.* (1998) demonstrated that dechlorination of PCBs to biphenyl can be effected within ten min under mild conditions in the presence of Mg and K_2PdCl_6 powders. For a given commercial Aroclor product, the chlorine and/or biphenyl content are fixed within the sample. When the chlorine atoms are displaced into solution, the liberated chloride ions can be determined by titration with silver nitrate. The disadvantage of this method is the requirement to determinine either the chloride ion or the biphenyl in the sample. Another approach for total PCB determination is perchlorination, in which all the PCB congeners are converted to decachlorobiphenyl. Although the conversion of PCBs to one species would be of great benefit, especially to the techniques employing chromatographic separations of complex matrices, perchlorination has been selected only infrequently due to its disadvantages involving harsh reaction condition, toxic reagents and a more demanding derivatization procedures (Schuetz *et al.*, 1999).

1.5 PCB regulations

The widespread occurrence of PCB in the environment and the apparent link to carcinogenesis has promoted an increasing concern throughout the world since 1970s, that has resulted in the increased restrictions on the use of PCB in most countries. In 1976, the U.S. congress imposed the Toxic Substance Control Act, which specifically regulates manufacture, processing, distribution in commerce and use of PCBs. The EPA subsequently promulgated a series of rules on the various aspects of the law, and many other PCB related federal, state, and local laws have been established (Erickson, 1997). Similar PCB related regulations were also imposed in South America, Australia, and most European countries (Erickson, 1997).

PCBs were never manufactured in Canada (Environment Canada, 1997). According to Environment Canada, approximately 40,000 tons of PCB was imported into

Canada prior to 1977, and there remain about 15,100 tons of PCBs still in use across the country. PCBs are substances specified on the list of Toxic Substances in Schedule I to CEPA. They were the first substances to be regulated and originally prohibited for certain uses under the Canada Environmental Contaminants Act (1976). Four regulations have been developed in Canada for PCB compounds since 1988. They include the Federal Mobile PCB Treatment and Destruction Regulations; PCB Waste Export Regulations; Chlorobiphenyl Regulations; and Storage of PCB Material Regulation (Environment Canada, 1997). Under these regulations, several standards, recommendations, guidelines and criteria for PCBs in the Canadian environment have been established (Table 1.6). To date, there continues to be a great amount of PCB compounds in use across Canada (Table 1.7) and removal of PCBs from service has increased the quantities of PCB waste. By 1990, more than 150,000 tons of PCB waste involving PCB contaminated soil, mineral oil, and other metallic components of electrical equipment were stockpiled across Canada. Between 1989 and 1995, the federal government allocated $6 million for PCB destruction projects in Atlantic Canada, Quebec, and Ontario. With the implementation of PCB related regulations, more PCB waste will be produced and more investment will have to be allocated to the destruction of PCBs and the remediation of PCB contaminated media (Environment Canada, 1998).

1.6 Remediation and destruction of PCBs

Remediation of PCB contaminated matrices is a comprehensive process involving PCB extraction/mobilization, PCB destruction and the restoration of cleaned materials. During the last two decades, more than 80 techniques have been developed for PCB destruction and decontamination (U.S. Agency for toxic substance and disease registry, 1993; US EPA 1996). However, the majority of these processes remain theoretical or they have been optimized only for small-scale destructions (US EPA, 1996). When used in the real-world, many methods still face challenges. As summarized in Table 1.8, commercially available methods for PCB remediation and destruction can be divided into physical, chemical, biochemical, photolytic and more comprehensive combined methods. The disadvantage of most methods make it necessary to develop increasingly efficient, rapid and simple processes to destroy PCBs.

Table 1.6 Standards, recommendations, guidelines and criteria concerning PCBs in the Canada environment.

Environmental medium	Region	Concentration	Comments
Air	Ontario	35ng/m^3	Ambient air quality criteria
Drinking water	Ontario	3 µg/l	Recommended standard
	Quebec	0.1 µg/l	Recommended standard
Soil contaminated	Quebec	>5 mg/kg	Level considered
	Quebec	≤1 mg/kg	Target level for cleanup
Liquid waste Considered Hazardous	Canada	≥50 mg/kg	Regulated under the ECA*
Dangerous waste	Quebec	≥0.3 mg/kg	Considered dangerous under Quebec's Waste Regulation
Eggs	Canada	0.1mg/kg	Administrative guideline established by HC **
Poultry	Canada	0.5mg/kg	Administrative guideline established by HC
Beef	Canada	0.5mg/kg	Administrative guideline established by HC

Source: from Environment Canada,1987.

*: Environmental Contaminants Act.

**: Health Canada.

Table 1.7 Quantity of PCBs in use in Canada.

Province	Type of unit	Quantity of PCBs (ton)
British Columbia	transformers	1350
	capacitors	656
	non-electric	30.8
Alberta	transformers	324
	capacitors	46
	electromagetets	1.1
Saskatchewan	transformers	204
	capacitors	14.5
Manitoba	transformers	94.9
	capacitors	12.6
	electromagets	1.8
Ontario	transformers	6980
	capacitors	473.4
Quebec	transformer	2980
	capacitors	875
	electromagetets	12.4
New Brunswick	transformers	339
	capacitors	52.5
Nova Scotia	transformers	294
	capacitors	60
Prince Edward Island	transformers	1.5
	capacitors	0.2
Newfoundland	transformers	297.8
	capacitors	11.1
Nunavut	transformers	8.9
	capacitors	0.9
Total		15,100

Source: from Environmental Canada, Report EPS 3-Ec-83-1.

Table 1.8 The methods used for PCB remediation and destruction

Treatment Tech	**Type**	**Process**
Incineration	Destruction	Thermal
Thermal desorption	Separation	Thermal
Solidification/Stabilization	Isolation	Physical
Soil washing/flushing	Separation	Physical
Solvent extraction	Separation	Chemical
Reduction/oxidation	Destruction	Chemical
Bioremediation	Destruction	Biological
Soil vapour extraction	Separation	Physical
Landfilling	Isolation	Physical
Photoremediation	Destruction	Chemical
Supercritical extraction	Separation	Physical

Sources: from Erickson (1997) and Rantanen *et al.*(1975).

1.6.1 Physical dechlorination of PCBs

1.6.1.1 Incineration

Incineration remains the pre-eminant disposal option for the destruction of PCBs because of increased concerns about the potential impact of PCB disposal into the environment (Mullin *et al.*, 1984). This situation has not changed appreciably in the last two decades. PCBs can be destroyed by incineration under adequate operating conditions (Georges, 1987). When incinerated, PCBs are combusted at facilities that purportedly can achieve a 99.99% destruction removal equivalence (Mullin *et al.*, 1984; Yezzi *et al.*, 1984; Yu *et al.*, 1991; US EPA, 1996).

In North America, PCBs have been disposed of primarily by incineration (Galveston- Houston Association for Smog Prevention, 1996). However, the capacity of incinerators for PCB destruction is limited. With the thermal breakdown of PCBs occurring at high temperatures, both chlorinated furans and dioxins can be produced under inadequately controlled conditions (Hutzinger *et al.*, 1985; Georges, 1987). These products are more acutely toxic than the PCBs themselves. Furthermore, the incineration process can cause fugitive emissions from leaking valves, vented storage tanks, tank transfers and spills. According to a report (Galveston-Houston Association for Smog Prevention, 1996) in Canada one PCB incineration facility was estimated to have released 75 pounds of PCBs into the environment during 1994.

1.6.1.2 Solvent extraction

This process uses an organic solvent to physically separate hazardous contaminants from soil and sediment, and to reduce the volume of hazardous waste that must be treated (US EPA, 1996). Several extraction methods have been proposed and applied in laboratory research including Soxhlet extraction, microwave assisted solvent extraction, sub-critical water extraction and surfactant suspension extraction. The overall extraction efficiency depends on the number of extraction cycles used (Meckes *et al.*, 1997). Solvent extraction of PCBs and PCDD/Fs from lake and harbor sediments using microwave-assisted and Soxhlet extraction was investigated by Chiu *et al.* (1997). Recovery and precision of both methods were comparable, but microwave-assisted extraction reduced the extraction time from 20 h to 20 min and solvent quantity was reduced from 350 ml of toluene to only 20 ml of hexane/acetone.

Bandh *et al.* (1998) evaluated an accelerated-solvent extraction (ASE) technique to determine PCBs in sediments of the Baltic Sea and compared the results with conventional Soxhlet extraction. The ASE method was characterized by equal or even improved precision relative to the Soxhlet extraction and was completed with less solvent consumption. Szostek *et al.* (1999) demonstrated the quantitative extraction of PCBs from environmental solids by using a microscale adaptation of pressurized fluid extraction (μPFE). Recoveries were measured for eight PCB congeners spiked into two soil types. The extraction process with hexane at 300°C provided significantly increased recoveries for several representative PCB congeners than had been reported for a duplicate 16 h Soxhlet extraction with a mixture of acetone/hexane.

1.6.1.3 Thermal desorption

Thermal desorption (TD) is a process that has been targeted to remediate hazardous waste from soils/sediments and sludges by removing sufficient PCBs, Hg and volatile organics to satisfy the criteria of waste disposal (Krabill *et al.*, 1996). Nardini *et al.* (1998) studied the thermal desorption of soils contaminated with numerous compounds involving low levels of PCBs and chlorinated solvents. The results indicated that all soils contaminated with low level PCBs (<50 ppm) were remediated to below the treatment standard of 1 ppm with removal efficiencies ranging from 90.11 to 99.47%. Soils contaminated with chlorinated solvents were treated successfully with removal efficiencies of 95.8 to 99.98% for trichloroethylene (TCE) and 93.5 to 99.98% for perchloroethylene (PCE). Norris *et al.* (1998) reported on an effective remediation of PCB contaminated soil using low temperature thermal desorption. Thermal treatment has been demonstrated to remove sufficient PCBs from a contaminated soil matrix to pass stringent residual contamination values, without any unacceptable impacts on the environment and at a cost per ton appreciably lower than that of high temperature incineration. The method, that used low temperature thermal desorption, could save 75% of the remediation cost (Brown *et al.*,1987). Osborn *et al.* (1984) investigated the extractive removal of PCBs from mineral oil dielectric fluids by using polyethylene glycol solvents as the primary extraction medium, followed by re-extraction of the polar liquids, using a volatile secondary solvent from which the primary solvent can be recovered for reuse and the PCBs concentrated for ultimate disposal by incineration or chemical destruction.

1.6.1.4 Soil washing/flushing

There are two approaches for soil PCB removal. Soil washing (*ex-situ*) involves an organic solvent and/or surfactant suspension to rinse the contaminated soil and to transfer contaminants into the liquid phase (American Council on Science and Health, 1997). The second approach, soil flushing (*in-situ*), involves infiltrating an aqueous solution into a zone of contaminated soil, followed by down gradient extraction of ground water, elutriate, above-ground treatment and re-injection of the cleaned aqueous fraction. Abdul *et al.* (1991) evaluated the extent of washing of PCBs from soil using an alcohol ethoxylate surfactant to mobilize contaminants and demonstrated that PCBs could be washed efficiently from sand using surfactant solutions. To date the majority of pilot-scale demonstrations of *in-situ* flushing have involved the use of surfactant and co-solvents. In the U.S., several full-scale site remediations have utilized *in-situ* flushing.

1.6.1.5 Stabilization/Solidification

Waste stabilization is a process that adds a binding agent to the waste to convert contaminants into a less soluble, less mobile phase. By contrast, waste solidification adds a binding agent to the waste to encapsulate the contaminants within a solid material. Both of these technologies reduce the mobility of PCB, but do not concentrate or destroy them (US EPA, 1996). Therefore, further treatments must be employed.

Sawyer *et al.* (1989) demonstrated an *in-situ* stabilization/solidification process using deep-soil-mixing equipment. The solidified material displayed satisfactory physical properties, with high, unconfined compressive strengths, moderately low permeabilities and satisfactory integrity for the wet/dry samples. The microstructural results indicated a dense, low-porosity, homogeneous mass, indicating a potential for long-term durability.

1.6.1.6 Vitrification

Vitrification technologies use melting, induced by electrode heating of contaminated soil or sediment containing organic and inorganic contaminants, to form a rigid, glassy product when cooled (Erickson, 1997). Temperatures in the process are in the range of 1,000-2,000 °C. PCBs can be destroyed by the high temperatures during the process. In the 1990s, the vitrification system was authorized by U.S. EPA to treat PCBs in soil and sediment (U.S. Agency for toxic substance and disease registry, 1993; US EPA, 1996).

1.6.1.7 Photolytic dechlorination of PCBs

Photolysis is a popular means of both physical and chemical degradation of PCBs. This process uses free radicals, produced from sunlight or generated artificially, to remove the chlorine atoms from the biphenyl ring. Nishiwaki *et al.* (1981) concluded from their study that photo- or radiation-induced chain dechlorination of PCBs in alcohol proceeded by a homolytic fission of C-Cl bond in a photoexcited state to give substituted H^+ radicals and Cl^- (by decomposition of radical anion of PCB). Mincher (1995) studied the ability to degrade PCBs by exposure to gamma radiation from spent nuclear fuel in a number of solvents, including hydraulic oils. The results demonstrated that the photodechlorination mechanism was a reductive dechlorination, associated with the capture of solvated electrons by the PCBs. The more highly chlorinated PCB congeners were generally more reactive toward photodechlorination.

In the presence of TiO_2, chlorinated methanes, 2,4-dichlorophenoxyacetic acid (2,4-D), *p*-dichlorobenzene and PCBs were degraded through photodegradation both in organic solution and in water (Carey *et al.*, 1976; Menassa *et al.*, 1988; Rao *et al.*, 1993; Choi *et al.*, 1995). Lin *et al.* (1996), using simulated sunlight and a photosensitizer (diethylamine), studied the photodegradation of Aroclor 1254. The degradation rate of Aroclor 1254 congeners was $4.74 \pm 1.51\times10^{-9}$ mol/l/h. The half-lives of 5 major congeners of Aroclor 1254 (66, 101, 110, 118, and 138) ranged from 30.31 to 52.11 h. Chu and co-workers (1994) suggested that photoreduction, through photodechlorination, was the main decay pathway in which lesser chlorinated congeners and benzene were formed as intermediates. In addition, some minor pathways were observed including photochlorination, photoisomerization, and photohydrolysis, in which phenol was formed.

For most of the PCB destruction approaches, the cost is prohibitive and the processes are time consuming. An overall cost comparison of chemical and physical PCB destruction and disposal is povided in Figure 1.3.

1.6.2 Chemical dechlorination

Evidence of the environmental and public health impacts of incinerators and other combustion systems has created strong public opposition to incineration. This factor as well as increased infrastructural requirements, particularly those associated with the management of air emissions and other residues, has encouraged the development of alternative destruction technologies. Some of the more recently developed technologies offer appreciable advantages in both performance and costs over combustion using dedicated incinerators. Chemical degradation represents one of these technologies.

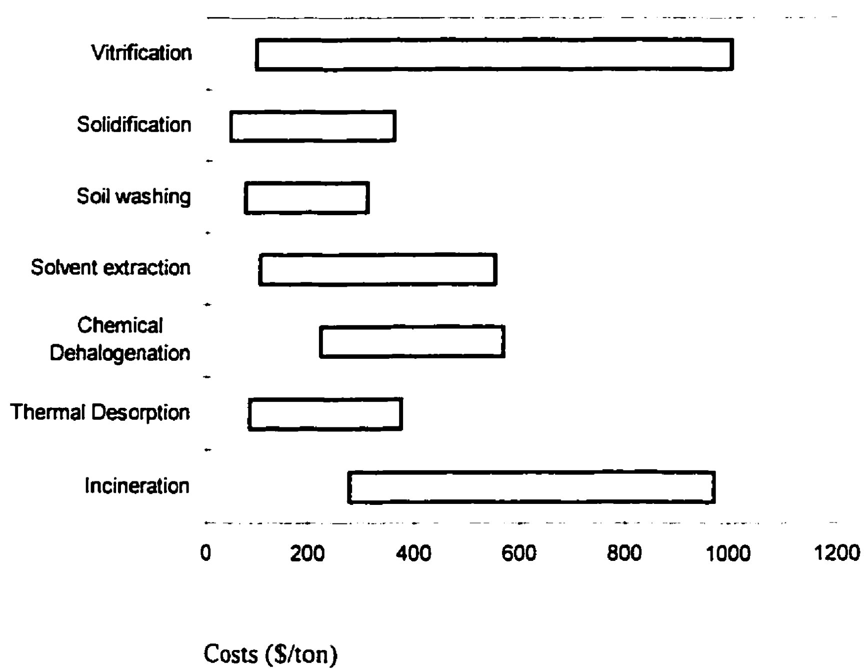


Figure 1.3. Estimated cost for different approaches of PCB dechlorination (Source: from US EPA, 1997).

Chemical dechlorination of PCBs uses chemical reactions to remove chlorine atoms from organic molecules (Oku *et al.*, 1978). One route to chemical dehalogenation is via base-catalyzed decomposition (BCD), which is an efficient and relatively inexpensive alternative for treating both PCB-contaminated equipment and PCB-contaminated soils and sediments (Amend and Lederman, 1992; Taniguchi *et al.*. 1998). Oku *et al.* (1978) reported that PCBs were dechlorinated completely by treatment with 1.1 equivalents of sodium naphthalenate (I) for 10 min at 0 °C, or with 0.5 equivalents of I for 5 h at 0 °C. Potassio- and lithionaphthalenates were also effective. These reactions proceeded via formation of aryl anions, followed by an SN_2-type arylation.

Takada *et al.* (1996) reported that the base catalyzed decomposition process for PCBs was based on the formation of hydrogen radicals through a liquid phase dehydrogenation reaction. Hydrogen radicals, generated from a suitable hydrogen donor, substitute H for Cl atoms and transforms the PCBs into non-toxic biphenyl. The dechlorination reaction by the BCD process was assumed to be a first-order reaction. They confirmed that the addition of sodium hydroxide had a beneficial influence on the reaction rate. Kawahara *et al.* (1997) investigated hydrogen transfer agents and catalysts to improve the base-catalyzed decomposition of PCBs. In the presence of base, the reaction increased with increased concentration of hydrogen transfer reagents and catalysts. Optimal reaction conditions proved to be 340-350 °C. According to a study (Takada *et al.*, 1997), optimal reaction temperature for PCB decomposition was >320°C for the base-catalyzed decomposition. The optimum concentration of KOH was determined to be 6 times the stoichiometric ratio. The most efficient combination for treatment was transformer oil and KOH. PCBs were dechlorinated completely and PCDD/F were also decomposed.

Another approach to the chemical dechlorination of PCBs is hydrogenative dechlorination in the presence of a metal catalyst(s). In saturated hydrocarbon solvents, Cl can be removed continuously and the catalysts and the solvents can be reused. Ono *et al.* (1996) reported that if a mixture of PCB, hexadecane, and Pd/C was bubbled with H_2 at 210 °C for 180 min, PCBs decomposition reached as much as 99.99%, the reaction products included biphenyl, phenylcyclohexane, and dicyclohexane. Ukisu *et al.* (1996) reported that in the presence of C-supported noble metal catalyst (Pd/C, Rh/C), PCBs could be dechlorinated efficiently to biphenyl and phenylcyclohexane using a propan-2-ol solution of NaOH at <82 °C. They postulated that the dechlorination reaction include H^+ transfer from propan-2-ol to the PCB substrate.

Polychlorinated biphenyls can also be degraded chemically by contacting a Lewis acid catalyst (a combination of $AlCl_3$ and $FeCl_3$), in a non aqueous medium in the presence of a cation (Wilwerding and Hoch, 1990). When present in oil, PCBs can be removed and dehalogenated by extraction of the oil with a cyclic ketone- or ester-based solvent containing an electrolyte. The PCBs can be dechlorinated by applying an electrical potential to the solvent in an electrolytic cell containing an anode (C or RuO_2-coated Ti) and (Hg) cathode. The solvent can be recycled during processing (Byker, 1984).

In short, most of chemical methods can achieve a very efficient dechlorination of PCBs. However, some chemical dehalogenation/dechlorination processes that use polyethylene glycol can cause the formation of dioxins and furans as byproducts (U.S. Agency for toxic substance and disease registry, 1993; US EPA, 1996).

1.6.3 Bioremediation

Bioremediation uses microorganisms to decompose or detoxify organic compounds, a process for destroying PCBs in both aerobic and anaerobic environments. The degradation of PCBs in soil or aquatic systems entails different mechanisms of chemical, biochemical or thermal destruction (Rantanen *et al.*, 1975). Substrates with a high degree of chlorination including 1248, 1254 and 1260 are resistant to biodegradation and are degraded only slowly in the environment.

Aerobic oxidative dehalogenation involves the oxidation of PCBs by aerobic microbes, especially by bacteria of the genus *Pseudomonas*. This involves the addition of oxygen to the biphenyl ring(s) (Boyle *et al.*, 1992). Although different bacterial species seem to produce benzoate through PCB metabolism, further breakdown of benzoate seems to differ among the different microbes. Nevertheless, the by-products are less toxic to animals and the environment (Bevinakatti and Ninnebar, 1992).

The reductive dechlorination of PCBs by anaerobic bacteria removes chlorines directly from the biphenyl ring (with replacement by hydrogen), resulting in a product mixture in which the average number of chlorines per biphenyl is reduced (Mousa *et al.*, 1998). Specifically, monochlorobiphenyl and ortho-substituted dichlorobipenyls are degraded in this way. Byproducts of this process are less toxic and can be degraded further by the aerobic microbes (Kawahara *et al.*, 1997).

Although several different dechlorination processes were observed for PCBs in sediment (Ye *et al.*,1992), there exists a similarity between degradation patterns (Alder *et al.*, 1993). Highly chlorinated congeners were degraded less readily than the less chlorinated congeners. The molecular shape and the position of chlorine atom substituents in the PCB also affected the rate of biodegradation. Unlike chemical dechlorination, PCBs with fewer chlorine atoms are more readily degraded in bioremediation than PCBs with a higher chlorine content.

The anaerobic biotransformation of PCBs is a relatively slow process. Rhee *et al.* (1993) investigated microorganisms in Hudson River sediment using the commercial mixture Aroclor 1242. They found that there was no change in congener composition at the given concentration of PCBs during 7 months of incubation. However, appreciable shifts in the degree of chlorination were observed in sediments.

Sokol *et al.* (1993) investigated the microbially meditated dechlorination kinetics of polychlorinated biphenyls (Aroclor 1248) spiked into sediments at 16 concentrations. The results demonstrated that a threshold concentration was observed at 35-45 ppm. No dechlorination was observed below the threshold level and the dechlorination rate increased with an increased PCB concentration in the sediment above the threshold concentration.

Many environmental factors can affect the degradation of PCBs. Natarajan *et al.* (1997) reported that the dechlorination rate at 30 °C was increased relative to the rate at either 12 or 37 °C by anaerobic microbial granules in a phosphate buffered medium under sediment-free conditions. The dechlorination rate was more rapid under strictly anaerobic conditions than under anoxic conditions. The dechlorination was enhanced appreciably by the addition of a carbon source. To date, however, no bioremediation system has been identified as being capable of biodegrading PCBs on a scale large enough to be used for site remediation (U.S. Agency for toxic substance and disease registry, 1993; US EPA, 1996).

1.7 Innovative techniques for remediation and dechlorination of PCBs

Over the last few years, increasing interest in the reactions of reducing metal systems has been sparked by concerns about environmental protection. An increasing number of research groups are working to assess the utility of these reactions in the treatment of contaminated materials. The most extensively studied reducing metal powders have been zero-valent copper, iron, magnesium, nickel and zinc (Seymour *et al.*, 1986; Ross *et al.*, 1987; Chuang *et al.*, 1995; Appleton, 1996; Roberts *et al.*, 1996; Shannon, 1996; Johnson *et al.*, 1998). Recent research has shown that dramatic improvements in rate and selectivity of dehalogenation can be obtained by employing bimetallic systems such as Ag^o/Fe^o, Pd^o/Fe^o, Pt^o/Fe^o and Ni^o/Fe^o (Boronina *et al.*, 1995; Grittini *et al.*, 1995; Bizzigotti *et al.*, 1997; Balko and Tratnyek, 1998; Doyle *et al.*, 1998). These bimetallic materials are considered to have extensive environmental and industrial applications.

1.7.1 Dechlorination of PCBs by zero-valent metal particles

Zero-valent copper (Cu^o), iron (Fe^o), magnesium (Mg^o), nickel (Ni^o), tin (Sn^o) and zinc (Zn^o) have been used to enhance the degradation of chlorinated organic compounds (Boronina *et al.*, 1996; Wafo *et al.*, 1996; Korte *et al.*, 1997; Su *et al.*, 1999). Hartmann *et al.* (1997) reported that halogen compounds were dehalogenated by contact with reducing agents such as hydrazine, hydrazine hydrate, hydroxylamine or their salts or alkali metal dithionites in solution in the presence of solid metal catalysts (e.g., Fe^o, Cu^o, Mo^o, Ni^o, Cr^o, Mn^o, Co^o, Ti^o or V^o) at 0-100 °C.

Tatyana *et al.* (1995) investigated the dechlorination of organohalogen compounds in water systems by magnesium, tin and zinc. In the CCl_4/H_2O system, only a small amount of CCl_4 was destroyed yielding $CHCl_3$ with magnesium. However, CCl_4 destruction was increased to approximately 40% with tin in the tin/CCl_4/H_2O system. CCl_4 and $CHCl_3$ could be destroyed completely but CH_2Cl_2 and CH_4 remained when using Zn powder.

Reaction conditions have a pronounced effect on the rate of reductive dechlorination. Gotpagar *et al.* (1997) examined the effect of feed concentration, initial pH, zero-valent Fe loading and its particle size on the degradation of trichloroethylene (TCE). The degradation rate was first-order with respect to the organic molecule. The amount of trichloroethylene degraded at any given time was directly proportional to the quantity of dissolved Fe. The metal surface area apparently plays a crucial role in the process.

Cheng *et al.* (1998) studied the influence of an external electrical potential on the degradation rates of CCl_4 and CH_2Cl_2 by Fe° and Zn°, respectively. The results indicated that the application of an external electrical potential enhanced the degradation rate of CCl_4. CCl_4 was entirely depleted in 4 min and the half life for $CHCl_3$ was estimated to be about 30 h. Three hour was required to degrade CCl_4 completely and the half life for $CHCl_3$ was 100 h without an applied external potential.

Copper powder can enhance the dechlorination of PCBs, chlorinated dibenzofurans, dibezo-*p*-dioxins, and other aromatic compounds (Hagenmaler, 1987). Ross *et al.* (1987) studied the destruction efficiencies of Al alloy and Al_2O_3 surfaces toward PCBs and related systems, including decachlorobiphenyl and hexachlorobenzene. The dechlorination efficiencies that were observed exceeded 99.99%.

Romanova *et al.* (1992) studied the dechlorination of PCBs by treatment with a organosilicon hydride in the presence of a Ni catalyst. Homogeneous nickel and cobalt organophosphorus complexes, coupled with alkoxyborohydride reagents as a hydrogen source, can mediate chlorine displacement from PCB congeners through a reductive process. The efficiency of chlorine displacement is a function of chlorine position and the shape and steric bulk of the organophosphorus-metal complex (King *et al.*, 1997).

Chuang *et al.* (1995) investigated the zero-valent iron promoted dechlorination of PCBs at elevated temperatures. Above 300°C, dechlorination of Aroclor 1221 began to occur; at 400°C, most of the PCBs were dechlorinated to biphenyl within 10 min. Dechlorination and other reactions of PCBs took place at temperature of 500°C or higher. Almost all PCBs were destroyed by reactions other than hydrogenolytic dechlorination at 600°C. Yak *et al.* (1999) evaluated the method that using zero-valent Fe as the dechlorination agent and subcritical water extraction (SWE) as the transporting medium for remediation of PCB-contaminated soil and sediments. Results demonstrated that using 100-mesh Fe powder and SWE conditions of 250°C and 10 MPa on Aroclor 1260 for 1-8 h, the higher Cl^- substituted homologues were completely reduced to their lower-substituted counterparts. The lower-substituted congeners were subsequently dechlorinated nearly quantitatively.

In other advances, the metals used in dechlorinating organochlorine compounds (OCs) have been developed from micro-scale and electrolytic powders to nanoscale dusts. The nanoscale metal particles have specific surface area 1-2 orders of magnitude greater than commercially available micro-scale metal particles (Zhang *et al.*, 1998). Wang *et al.* (1997) demonstrated that nanoscale particles can rapidly and completely dechlorinate several chlorinated aliphatic compounds and a mixture of PCBs at relatively low metal to solution ratio (2-5 g/100 ml). Surface-area-normalized rate constant (K_{SA}) of nanoscale dusts were calculated to be 10-100 times greater than those of commercially available iron particles.

The success in dechlorinating OCs by zero-valent metallic powders has encouraged several related areas of research. Researchers (Zhao, 1994; Powell *et al.*, 1995; Agrawal and Tratnyek, 1996; Johnson *et al.*, 1996; Pratt *et al.*, 1997; Scherer *et al.*, 1997; Devlin *et al.*, 1998; Gillham *et al.*, 1998; Hung and Hoffmann, 1998) have found that doping of iron, zinc, and nickel with silver, palladium and gold can appreciably increase the rate of dechlorination of chlorinated compounds. Some researchers have even studied Pd/C/Fe ternary systems to remediate the haloorganics, and have reported promising results. The dechlorination technologies are considered to be based on metal corrosion (Fe, Zn and Ni). Palladium (Ag and Au) acts as a facilitor in the hydrodechlorination reaction.

Boronina *et al.* (1998) reported that using zinc dust doped with palladium, gold or silver resulted in 4-10 fold increase in the CCl_4 degradation rate and conversion into methane. The results indicated that bimetallic systems with Pd, Ag, Au as well as the cryo or mechanically activation of zinc, enhanced the metal surface reactivity and changed the priority of reaction pathways.

Zhang and co-workers (1998) demonstrated that using Pd alone and palladium doped Fe to dechlorinate tetrachloroethene (TCE), little degradation of TCE was observed in the presence of Pd particles alone. However, the dechlorination activity was enhanced appreciably with bimetallic particles of Pd/Fe. The dechlorination rate of TCE was faster using Pt/Fe than that when using Pd/Fe particles alone. Nickelized iron (Ni/Fe) exhibited higher activity than the nanoscale iron for dechlorination of trans-dichloroethene (DCE) but with lower activity than with Pd/Fe particles.

Grittini *et al.* (1995) reported that using Pd/Fe bimetallic mixture can completely and rapid dechlorinate a PCB solution at ambient temperature. Biphenyl was the reaction product during the dechlorination of Aroclor 1260 and 1254. PCB dechlorination achieved high efficiency with the acidic palladium-zinc catalytic system (Zhao, 1994). PCBs could also be dechlorinated in the presence of 10% Pd/C using ammonium formate as H^+ donor. Efficiencies of 94-100% dechlorination were achieved in neutral media at 60°C and ambient pressure (Metheson and Tratnyek, 1994).

1.7.2 Mechanism of dechlorination of PCBs by zero-valent metallic particles

The fundamental mechanisms of the degradation process have been of broad interest since the initial studies of zero-valent metal promoted dehalogenation were reported (Metheson and Tratnyek, 1994; Allen-King *et al.*, 1997; Zdemir and Tfekci, 1997; Arnold and Roberts, 1998; Eykholt and Davenport, 1998; Gotpagar *et al.*, 1998; Yoshihiro *et al.*, 1998). Recent studies have demonstrated that the dechlorination of both unsaturated and saturated chlorocarbons in water systems appear to take place by complex parallel sequential processes.

Metheson *et al.* (1994) postulated three possible pathways that might be contributing to the dechlorination of alkyl halides. The first pathway starts with an electron transfer from the Fe^o surface to the adsorbed target materials. In the presence of a proton donor like water, the metal/halogenated system undergoes reductive dehalogenation:

$$M^o + RX + H^+ \rightarrow M^{2+} + RH + X^-$$

where M^o represents the zero-valent metal, R is the alphatic molecule, and X is chlorine atom.

With certain metal powders, this dehalogenation process can undergo the second step:

$$2M^{2+} + RX + H^+ \rightarrow 2M^{3+} + RH + X^-$$

The third pathway involves hydrogen molecules produced as a product of corrosion with water.

$$M^o + RX + H_2O \rightarrow M^{2+} + RH + X^- + OH^-$$

Each metal possesses a characteristic standard reduction potential, which determines its ability to spontaneously dechlorinate an organochlorine compound. The less positive the reduction potential, the faster and more complete the chemical reduction (Metheson *et al.*, 1994). The standard reduction potentials of common zero-valent metals have been reported to be as follows (Kaplan *et al.*, 1996; Weber, 1996; Allen-King *et al.*, 1997; Zdemir and Tfekci, 1997; Arnold and Roberts, 1998; Gotpagar *et al.*, 1998; Yoshihiro *et al.*, 1998):

$$Cu^o \rightarrow Cu^{2+} + 2e^- \quad E^o = 0.337V$$

$$Cu^o \rightarrow Cu^+ + e^- \quad E^o = 0.521V$$

$$Fe^{o} \rightarrow Fe^{2+} + 2e^{-} \quad E^{o} = -0.440V$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \quad E^{o} = 0.770V$$

$$Ni^{0} \rightarrow Ni^{2+} + 2e^{-} \quad E^{o} = -0.250V$$

$$Zn^{0} \rightarrow Zn^{2+} + 2e^{-} \quad E^{o} = -0.763V$$

Matheson *et al.* (1994) also concluded that the carbon tetrachloride degradation in water by iron was the result of direct electron transfer from the iron surface. The metal served both as an electron donor and as an adsorbent and catalyst (Cheng *et al.*, 1997). However, chlorocarbon degradation by metal particles in water has also been considered to be a heterogeneous, surface-mediated process (Wafo *et al.*, 1996).

The mechanisms discussed above are based on the metal corrosion process. However, catalytically promoted dechlorination might represent another important mechanism of dechlorination. Yumin *et al.* (1995) studied the mechanism of catalytically promoted PCB dechlorination. When titanocene dichloride ($CpTiCl_2$) reacted with sodium borohydride ($NaBH_4$), it produced titanocene borohydride ($CpTiBH_4$). In the presence of amine, $CpTiBH_4$ produced the unsaturated compounds, CpTiH, that was capable of promoting the dechlorination of PCBs. With the addition of pyridine, the catalytic rate was enhanced appreciably. Kawahara *et al.* (1997) proposed a three-step base-catalyzed mechanism of decomposition for PCBs. Initially, hydrogen species were generated from the paraffin oil then the hydrogenation of aromatic catalysts (phenanthrene, anthracene and alkyl naphthalenes) to form dihydroaromatics occurred. Alternatively, the absorption of hydrogen by hexagonal forms of carbon or transition metals occurred, and finally the hydrogen species was transfered to the activated PCB. The product biphenyl can be degraded further or possibly can form adducts or polymers (Tratnyek *et al.*, 1997). Yao (1997) reported that dechlorination occurred mostly on the more substituted ring. Antisymmetric congeners are more readily dechlorinated than relatively more stable symmetric isomers. Dechlorination occurred preferentially at the position to produce symmetric products. The *pi*-electronic densities of 4-Cl and 3-Cl affect their relative reactivities. Correlation analyses using K_{SA} revealed that dechlorination generally was more rapid at saturated carbon centers than unsaturated carbons and that high degrees of halogenation favoured rapid reduction (Johnson and Tratnyek, 1995; Johnson *et al.*, 1996).

A newly proposed dechlorination mechanism has involved the transient organometallic concept (Romanova *et al.*, 1992). During the dechlorination process, an initial electron transfer from the metal surface was followed immediately by direct attack of the chlorocarbon on the metal surface yielding a transient organometallic specie or radical-like specie, the C-Cl bond was then weakened and the chlorine was released.

In the bimetallic systems, dechlorination pathways are altered relative to mono-metal systems. Boronina *et al.* (1998) studied the dechlorination by zinc doped with Pd, Ag and Au. Ag and Au enhanced the dechlorination as well as Pd. Because Pd is a relative catalyst metal capable of facilitating bond cleavage of H-H, C-H and C-Cl bonds, it was concluded that the catalytic processes were of lesser importance, and that the doped metals serve only to facilitate the electron transfer. It was confirmed by Muftikian *et al.* (1996), who investigated the nature of the Pd/Fe surface by X-ray photoelectron spectroscopy, that the reactive Pd/Fe surface was formed by the stepwise reduction of Pd(IV) in solution to Pd(II) that replaced protons on the hydroxylated Fe-oxide surface and forms Pd(II)-O-Fe bonds. These bonds were unstable and collapsed spontaneously to yield reactive palladized iron. Enhanced reactivity of palladized iron was believed to be due to hydrogenation because Pd has the ability to intercalate hydrogen into its lattice (Grittini *et al.*, 1995). During dechlorination, the chlorinated organic compound is adsorbed to the Fe surface and reacts with the hydrogen intercalated by the Pd.

1.8 Application of supercritical fluid on the remediation of PCBs

1.8.1 Supercritical fluid extraction

The supercritical phase was first described by Baron Cagniard de La Tour in 1822. He found that the gas-liquid boundary disappeared when the temperature of certain materials was increased by heating each of them in a closed glass container. Although Hannay and Hogarth (1879) demonstrated that a supercritical fluid has a strong solvating power for solids, it is only in the last two decades that numerous industrial and academic research and development laboratories have investigated the underlying fundamentals and process applications of supercritical fluid solvents. Supercritical fluid extraction (SFE) was introduced by Zosel in 1963. Since then, SFE technique has been developed rapidly (US EPA, 40 CFR 279) During the last ten years, the applications of supercritical fluids have seen emphasis in the following areas:

1. Environmental control and hazardous waste treatment
2. Chemistry and biochemistry
3. Removal of nicotine from tobacco
4. Cleaning of electronic parts
5. Extraction in the food and pharmaceutical industries

The most widely used SF solvent is carbon dioxide (CO_2) because it is not toxic, not flammable, not expensive and does not threaten the ozone layer. It can efficiently and economically improve recovery, increase reproducibility, decrease the use of halogenated solvents and provide solvent free extracts to the measurement instrument (Papilloud *et al.*, 1996; Bonshtain *et al.*, 1998). Its advantages include:

1) Supercritical CO_2 possesses a high thermal diffusivity and low kinematic viscosity

   that permits rapid mass transfer in tightly packed matrices. Compared to convential liquid extraction techniques, it can reduce the time required for the quantitative extraction and recovery of analytes from a wide variety of samples.

2) Its liquid-like density and high compressibility increase the solvating power. The solvent strength can readily be controlled/modified since the solubility depends on the pressure and temperature used for the extraction.

3) Its critical temperature and critical pressure are readily achieved with common laboratory equipment.

4) Supercritical CO_2 is the least expensive solvent with the exception of water.

1.8.2 Extraction and mobilization of PCBs with supercritical CO_2 fluid

Supercritical fluid technologies, as alternatives to conventional procedures, have been used to extract various herbicides from environmental matrices because of its desirable properties that include efficiency, selectivity and speed (Bunte *et al.*, 1996; Luque and Tena, 1996; Papilloud *et al.*, 1996; Reighard and Olesik, 1996; King *et al.*, 1997). These properties are being exploited for the direct extraction of acidic and polar contaminants from soils, sediments and contaminated aqueous matrices (Meredith and Burk, 1998). Studies with SFE have demonstrated that the dithiocarbamates, β-diketones and hydroxamic acids are effective chelating agents for a broad range of transition metal ions. Glennon *et al.* (1997) applied fluorinated mono hydroxamic acids and their N-substituted derivatives in the SFE of metal ions, in particular Fe(III), using unmodified supercritical CO_2. The extraction efficiency of Fe(III) from spiked filter paper can reach 97% with new ligands such as perfluorooctanohydroxamic acid under optimized conditions. The extraction efficiencies were determined to be a function of pressure and temperature.

Ashraf-Khorassani *et al.* (1997; 1999) demonstrated that nickel(II), copper(II) and chromium(III) could be extracted efficiently from aqueous media into SFE using fluorinated acetylacetonate chelates. The solubility of fluorinated acetylacetone chelates in SFE was at least an order of magnitude higher than that of non-fluorinated analogs.

Similarly, 2-methyl-5-hexyloxymethyl-8-quinolinol (HMO6Q) and 5-hexyloxymethyl-8-quinolinol (HO6Q) in supercritical CO_2 could extract gallium(III) from weakly acidic solution. The extractability of gallium(III) was dependent on the temperature and pressure of the supercritical CO_2 (Ohashi *et al.*, 1997).

Using both pure and methanol-modified supercritical CO_2, it was possible to extract both spiked mercury complexes and mercury ions from a variety of matrices including sludge, fly ash, soil, filter paper, and sand. The recovery of Hg(II) from soil, fly ash and sludge using sodium diethyldithiocarbamate (as the *in-situ* chelating agent) was <40% with pure CO_2 (400 atm) at 80°C, while recovery of

Hg(II) from the same matrices using lithium trifluoroethyldithiocarbamate was >90% under the same conditions (Boronina *et al.*, 1996). Wang *et al.* (1995) achieved quantitive extraction of Hg^{2+} from sand and cellulose-based filter papers using proton-ionizable crown ether (as an extract) in methanol (5%) modified supercritical CO_2 at 60 °C and 200 atm. Methanol-modified supercritical CO_2 containing the macrocyclic ligand also was capable of extracting Hg^{2+} from aqueous samples. Formation of extractable metal chelates with the ligand at the pH defined by the CO_2-H_2O system appeared to be an important factor in determining the extraction efficiencies of the metal ions.

Fiddler *et al.* (1999) extracted 16 common organochlorine pesticides (OCPs) from liquid whole eggs using supercritical CO_2. The OCPs included aldrin; α-, β-, δ- and γ-BHCs; DDD, DDE, and DDT; dieldrin; endosulfans I, II and sulfate; endrin; endrin aldehyde; heptachlor and heptachlor epoxide. Under condition of 10000 psi, 40 °C and $scCO_2$ flow rate of 3.0 l/min, the recoveries ranged from 81.8 to 108.3% at 0.05 ppm for an extraction time of 40 min.

Creutznacher (1997) used supercritical CO_2 as a solvent for extracting PCBs from contaminated soil samples. The results were compared with the Soxhlet-extraction in terms of extraction reliability and environmental exposure. Higher recoveries were found for more highly chlorinated PCBs with SFE. The consumption of organic solvents for 16 soil samples was 1600 ml for the Soxhlet-extraction and only 80 ml for the SFE. Researches have demonstrated that 11 phenolic and nitroaromatic compounds from a spiked river sediment can be extracted efficiently by methanol-CO_2 mixtures under supercritical conditions (Creutznacher *et al.*, 1994; Creutznacher, 1997)

1.9 Summary

In this study all effort would be made to try to develop a method that can determine PCB concentration rapidly, conveniently and quantitatively in contaminated soils/sediments; to develop a novel approach that can dechlorinate PCBs quantitatively and efficiently using supercritical carbon dioxide coupled with zero-valent metal/bimetallic metal mixture technologies; to establish a process that combine PCB extraction from polluted soils/sediments using surfactant suspensions with PCB mobilization by back-extraction; to develop a technique that combine PCB extraction from surfactant suspension with *on-line* dechlorination; and finally to optimize the PCB mobilization, dechlorination process to be operated efficiently, continuously and environmental friendly.

Chapter 2
Preface

In Chapter one, PCB properties, historical usage patterns, techniques for their mobilization from soil/sediment as well as possible treatments for PCB destruction were reviewed. The current problems of PCB contamination were discussed. Novel approaches/techniques that combined $scCO_2$ with zero-valent metal/bimetallic particles for PCB extraction/ mobilization and dechlorination were proposed.

As a prelude of PCB detoxification, Chapter two reports a novel method for the determination of total PCB content in contaminated soil/sediment. It is suggested that the contaminated sample be mixed with magnesium flakes, potassium hexachloropalladiate (K_2PdCl_6), propan-2-ol and water then permitted to react for a certain period of time. Under optimized conditions, all PCB congeners are anticipated to be converted to biphenyl and then recovered by extraction into hexane. Finally quantification by gas chromatography with flame ionization detection is used to estimate the total burden of PCB compounds that were present in the sample.

Approaches to the determination of polychlorinated biphenyl (PCB) concentrations in soils/sediments by dechlorination to biphenyl

2.1 Introduction

As a prelude to optimizing remediation techniques/procedures for soils and sediments burdened with polychlorinated biphenyl compounds (PCBs), a rapid technique to determine the levels of the target analytes in these matrices was required. Conventional methods have employed a variety of approaches for extraction/mobilisation followed by quantification of the analytes by high resolution gas chromatography (GC) frequently with electron capture or quadrupole mass spectrometric detection (Buethe and Denker, 1995; Frame, 1997; Smedes and Boer, 1997). Successful approaches to the mobilisation stage of the analysis have included extractions with supercritical carbon dioxide (Glazkov, 1999) and sub-critical water (Akgerman and Yeo, 1993) as well as the more conventional Soxhlet, sonication (Harrison and Melnychuk, 1995), solid-phase (Abdul, 1990; Akgerman and Yeo, 1993) or microwave-assisted extraction (Auerbach, 1997). Alternative approaches to the quantitation stage of the analysis have included immunoassay techniques (Huang *et al.*, 1997; Weerasooriya *et al.*, 2000) and conversion of the various PCB congeners to a common derivative prior to or during chromatography. Two approaches, complete chlorination (Beck *et al.*, 1997; Deshpande *et al.*, 1999; Kim and Lee, 2000) to decachloriobiphenyl or complete hydrodechlorination (Ang and Abdul, 1995; Sabatini *et al.*, 1998; Dierkes *et al.*, 2000; Haegel *et al.*, 2000; Kitiyanan *et al.*, 2000; Scamehorn and Harwell, 2000; Zhou and Rhue, 2000) to biphenyl have been pursued. Earlier dechlorination methods were directed to the potentiometric determination of chloride ion liberated by sodium dispersion (Ware *et al.*, 1988), the action of $LiAlH_4$ in an inert atmosphere (Sabatini *et al.*, 1998; Haegel *et al.*, 2000) or the action of Pt/Pd catalysts at elevated temperature (Kitiyanan *et al.*, 2000; Zhou, 2000). More recent procedures have employed facilely prepared iron/palladium (Fe^0/Pd^0) (Doyle *et al.*, 1998) or magnesium/palladium (Mg^o/Pd^o) bimetallic mixtures (Vane *et al.*, 2000) that function efficiently at room temperature in mixed aqueous organic medium. Alternate procedures have involved the use of ammonium format and Pd/C again in mixed medium (Anwer and Spatola, 1985; Barren *et al.*, 1993).

The generation of a single derivative to estimate the total PCB burden in natural matrices circumvents the influence of field weathering and variations in volatility that collectively cause appreciably alternations to the populations of specific PCB congeners with time. Subsequent quantification of aged field residues based on the "standard" commercial PCB mixtures can become increasingly uncertain. These difficulties can be confounded by the presence of chlorinated pesticides or other chlorinated organics in the extracts that must be removed prior to quantification.

Additionally, conversion to a single derivative provides increased detectability so that flame ionisation can suffice and the requirement for detection by electron capture and the attendant variations in congener-specific responses can be avoided. This Chapter extends the dechlorination procedure to soils and sediments. The principle disadvantage of the derivatisation approach remains the loss of all congener-specific information.

2.2 Material and methods

2.2.1 chemicals, solvents and standard reference materials

Magnesium granules (12~50 mesh, 99.8% purity) and potassium hexachloropalladate (K_2PdCl_6) were purchased from Alfa Aesar, Ward Hill, MA. Triton DF 16 and biphenyl were purchased from Sigma-Aldrich, Oakville, ON. Hexane, propan-2-ol (HPLC grade) and acid washed sea sand were purchased from Fisher Scientific, Ottawa, ON. Aroclor 1242 mixtures were kindly donated by Monsanto Company, Sauget, IL. Aroclor 1260 was purchased from Supelco, Bellefont, PA. Standard reference material, SRM 1939a, was purchased from National Institute of Standard and Technology, USA. CRM 481 and CRM 536 were purchased from European Commission LGC Lt. Teddington, UK. All chemicals, solvents and materials were used as received.

2.2.2 Soil samples and pretreatment

One agricultural soil and two field contaminated soil samples were collected from appropriate sites. The agricultural soil has been cultivated continuously for more than 70 years. The PCB-contaminated soil samples were collected from (i) a manufacturing facility where intermittent contamination had occurred from broken hydraulic lines during 1960s and 70s and (ii) a railway facility where PCB contamination had accumulated for more than 17 years. The soil samples varied in pH, texture, and organic matter (Table 2.1). After sample collection, all soils were air dried and were passed through a 2 mm sieve (10 mesh) and mixed thoroughly. One third of all the samples were further ground and passed through 50 mesh sieve, and then stored in refrigerator (-4 ^{0}C) for use.

2.2.3 Aroclor standard solution

Aroclor 1242 stock solution (1%, v/v) was prepared by diluting 1.0 ml pure Aroclor 1242 to 100 ml with hexane. Diluted working solutions of Aroclor 1242 (10 μg/ml) were prepared by further diluting 0.1 ml of 1% Aroclor 1242 solution with hexane or propan-2-ol. The 1% Aroclor aqueous emulsions were prepared by diluting 1 ml of Aroclor 1242 or 1248 or 1254 or 1260 stock solution plus 4.0 ml of Triton DF16 to 100 ml with distilled water. Biphenyl standard solution was prepared by diluting biphenyl standard (50.0 mg) to 100 ml with hexane.

2.2.4 Soxhlet extraction

EPA method 3540 was followed. Briefly, an accurately weighted aliquot of soil, 10 g, was mixed with 10 g anhydrous sodium sulfate, then added to an extraction thimble and extracted with 50 ml refluxing acetone-hexane (1+3, v/v) during 20 h. The extracts were subsequently concentrated to 40 ml under a gentle stream of nitrogen.

2.2.5 Sonication extraction

EPA method 3550 was followed. Briefly, a Polytron homogenizing unit (N.Y. 11590, Brinkmann Instruments, Mississauga, ON) was used with the output control knob set at

Table 2.1. Description of principle properties of soil/sediment samples

Samples	Certified PCB conc. (mg/kg)	pH 1:1 water/soil	Organic matter(%)	Particle size(mesh)	Note
Soil 1	N/A	7.1	2.1	10~50	Agricultural soil that had been under active cultivation during the last 70 years
Soil 2	N/A	7.38	4.8	~50	Soil from a railway facility contaminated with Aroclor 1242, 1248,1254 and 1260
Soil 3	N/A	7.75	3.6	~50	Soil from a manufacturing facility contaminated with Aroclor 1242,1254, oil, grease and heavy metals
SRM1939a	27.2 ± 3.0		N/A	~325	Contaminated freshwaterriver sediment
CRM 481	472.5 ± 29		12	~170	Industrial soil
CRM 536	0.34 ± 0.04		N/A	~120	Freshwater harbour sediment

11 and the mode switch was on pulse. A aliquot of soil (20.0 g) was mixed with 33.3 ml of acetone-hexane (1+3, v/v) and sonicated for 3 min. The procedure was repeated three times and a total volume of 100 ml was filtered and combined. The extracts were concentrated to 40 ml with a gentle nitrogen stream.

2.2.6 Extract clean-up

During Soxhlet or sonication extractions an appreciable quantity of the organic matter was co-extracted. The concern was that these organic materials might interfere the derivatization of PCBs. In an attempt to eliminate the effect of organic co-extractives, concentrated sulfuric acid was used to break down the compounds by dehydration or oxidation without affecting PCB compound. Sulfuric acid (4 ml, 17 M) was combined with 40 ml extract. After 30 min reaction, the decomposition products and excess acid were removed by washing the extract with distilled water.

2.2.7 Biphenyl conversion and determination

Magnesium flakes (2 g, 10-50 mesh), potassium hexachloropalladate (K_2PdCl_6), 10 mg, propan-2-ol, 2 ml, and test substrate were combined in a 50 ml flask. Distilled water, 2 ml, was added to initiate the reaction and the mixture was stirred for 1 min. The stirring procedure was repeated every 30 min. After 0.5-6 h of reaction, the mixture was extracted with 2 ml hexane (by vortex stirring for 1 min). After separation of the layers, one ml of the organic phase was withdrawn for biphenyl quantification. For sand or soil/sediment matrices, 1 g of sample was added to the reaction vial after the Mg particles (2 g) and 10 mg of K_2PdCl_6. The reaction procedure, as described above, was followed.

Quantification of biphenyl product was carried out using a Hewlett-Packard model 5890 (II) gas chromatography (GC) equipped with flame ionization detection (FID) and a model 5791 autoinjector. The 30 m (0.53 mm i.d.) DB-5 column was held at 50 °C for 1 min then ramped to 270 °C at 10 °C/min and held for 5 min. Analyte identity/purity was corroborated with a Hewlett-Packard model 5890(II) GC equipped with split/splitless injection and with a model 5971 mass-selective detector (MSD). An HP-1 column (30 m X 0.25 mm i.d.) was used and the MSD was operated in an electron impact (EI) mode.

Samples were resolved with a temperature program that started at 50 °C for 2 min followed by ramping to 280 °C at 10 °C /min then held for 5 min.

2.3 Results and discussion

2.3.1 Conversion of PCB compounds to biphenyl

Biphenyl formation from PCB mixtures has been reported to be efficient (greater than 98%, Engelmann and Cheng, 2000) under mild conditions in the presence of excess Mg^0 particles and potassium hexachloropalladate. As summarized in Table 2.2, conversion factors can be calculated based on the mean molecular weight for each commercial formulation.

Observed conversions to biphenyl of Aroclors 1242, 1248, 1254 and 1260 in propan-2-ol/water solution are summarized by the linear regressions of Figure 2.1 and for comparison, the FID response to biphenyl standard is also presented. As indicated in Figure 2.1, there was good agreement between the measured amount of biphenyl generated from the Aroclor standard mixtures and the amount predicted for quantitative conversion when the dechlorination was conducted in propan-2-ol/water solution. Within experimental error, the ratio of the slope of the regression equation for each Aroclor formulation relative to the regression line for biphenyl standard (Table 2.2) was similar to the corresponding ratio of their molecular weights (and accounted for approximately 95% conversion). Thus, over the limited range of concentrations (0.5-20 μg/ml) each formulation was converted efficiently but not quantitatively to biphenyl. To identify the parameters that influenced the efficiency of conversion of Aroclor mixtures, various matrices were also studied. Figure 2.2 summarizes the biphenyl conversion within (i.) a four percent (v/v) nonionic surfactant (Triton DF 16) emulsion; (ii.) a sand mixture; and (iii.) the propan-2-ol/water solution. Reaction products were extracted with 2 ml hexane after 2 h reaction.

There were no substantial differences in the contents of biphenyl generated from Aroclor 1242 that had been added, at 0.3-27 μg/g, to the different matrices. From the results of biphenyl formation from 1242, 1248, 1254 and 1260 in different media, several conversion models were established. As summarized in Table 2.3, all models were significant and could be used to estimate the concentration of PCBs in the different

Table 2.2 Conversion coefficients [a] for Aroclor formulations

Aroclor Mixture	Slope linear regression	Average M.W. for mixtures		Conversion coefficient (mass 12xx to mass $C_{12}H_{10}$)		Slope12xx/ $Slope_{biphenyl}$
1242	1289.3	258.2[b],	257.5[c]	0.5972,	0.5988	0.566
1248	1142.1	289.4[b],	291.9[c]	0.5328,	0.5283	0.501
1254	984.8	329.7[b],	326.4[c]	0.4677.	0.4724	0.432
1260	914.7	368.0[b],	366.0[c]	0.4190,	0.4213	0.401
biphenyl	2279.6	154.2		1.0	1.0	

[a]: Ratio was calculated by dividing the MW for biphenyl by the mean MW for the Aroclor formulation.

[b]: Data were adapted from Alford-Stevens *et al.* (1986).

[c]: Data were taken from Erickson (1997).

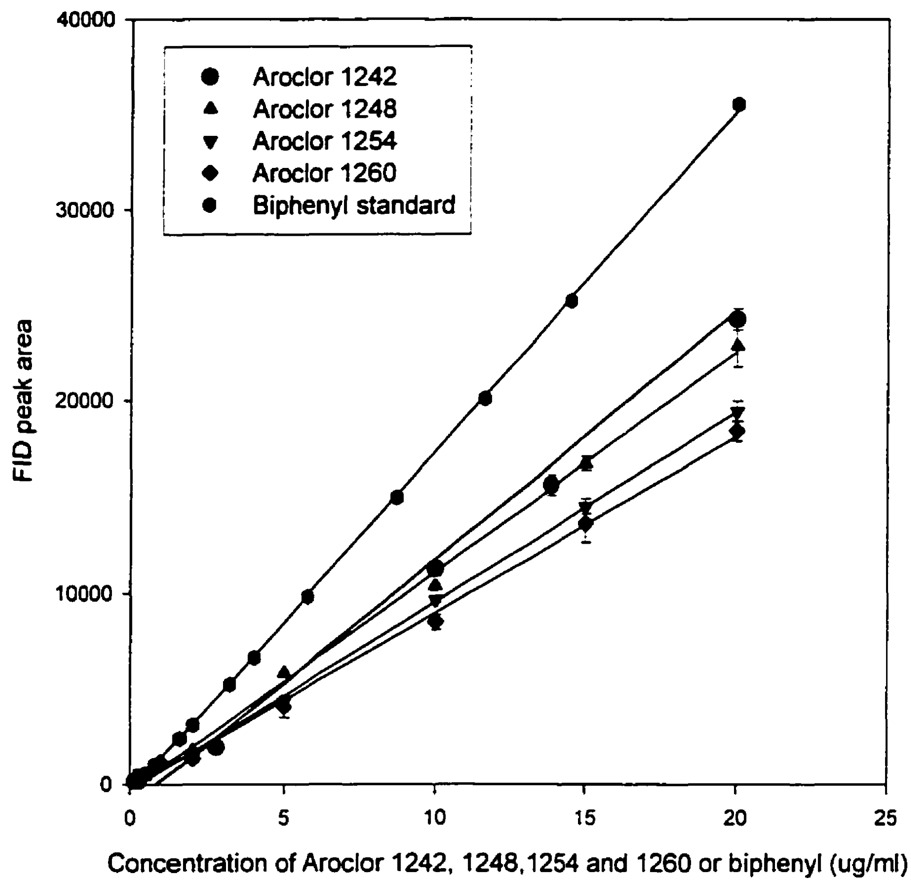


Figure 2.1 Linear regression of flame ionization peak area as a function of concentration (0.3-22 μg/g) of biphenyl, Aroclor 1242, Aroclor 1248, Aroclor 1254 and Aroclor 1260.

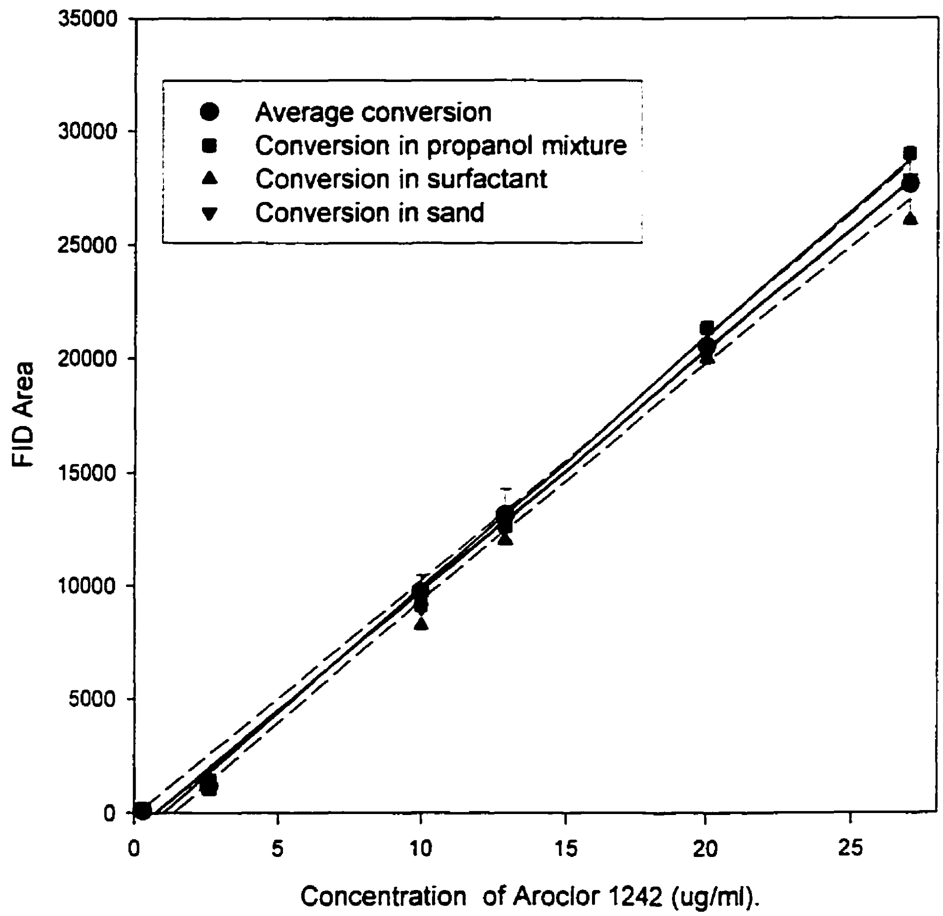


Figure 2.2 Means (plus 95% confidence interval) for biphenyl recovered from sand, surfactant emulsion or propan-2-ol/water solution for Aroclor 1242 formulation added to each matrix at 0.3-27 μg/g.

Table 2.3 Linear regression models for the conversion of Aroclor formulations to biphenyl in different matrices.

Aroclor	Matrices	Regression models[a]	Range (ppm)	Coefficient of determination $(R^2)^b$
1242	Propanol mixture (3h reaction)	Y=1141*PCB-778.3	0.1-45	0.993
	Surfactant solution	Y=1106.1*PCB-1136	0.1-45	0.997
	Sand matrices	Y=1059.4*PCB-878.6	0.1-45	0.997
	Soil matrices (6h reaction)	Y=1230*PCB+563.7	0.1-140	0.993
	Average	Y=059.9*PCB-816.4	0.1-45	0.993
1248	Propanol mixture	Y=1142.1*PCB-336.9	0.1-20	0.996
	Soil matrices (6h reaction)	Y=1060*PCB+38.4	0.1-20	0.996
1254	Propanol mixture	Y=984.8*PCB-298.4	0.1-20	0.998
	Soil matrices (6h reaction)	Y=873.7*PCB+210.3	0.1-20	0.995
1260	Propanol mixture	Y=823.7*PCB-9.5	0.1-40	0.997
	Soil matrices (2h reaction)	Y=183.8*PCB+419.5	0.1-40	0.984
	Soil matrices (6 h reaction)	Y=770.1*PCB-845	0.1-40	0.996

[a] Y= flame ionization response.

[b] Significant at the 99% level of confidence (p<0.0001).

matrices. The Student T-test did not identify any statistically significant differences among models for different media. To monitor the conversion efficiency at higher concentrations, Aroclor 1242 and a 25 ml volume of hexane extractant were used. The reactions were performed with the same conditions of reagents as before [2g Mg^o, 10 mg K_2PdCl_6, 4 ml of 1+1 (v/v) propan-2-ol, water]. The results are summarized in Figure 2.2. Again, the efficiencies of conversion for Aroclor 1242 added at 69-6900 μg/ml to each of the three matrices were within the 95% confidence interval of the mean. Again, there were no significant differences among models for different media (Table 2.3). Neither the presence of the surfactant nor sand had any discernable effect on the conversion of PCB compounds to biphenyl at either higher or moderate concentrations.

2.3.2 Biphenyl conversion within soil matrices

To test the efficiency of the dechlorination of PCBs compounds within soil matrices, a spike of a cultivated soil (soil No.1) was used. Figure 2.3 summarizes the recoveries of biphenyl from Aroclor 1242 and 1260 standard spiked into the soil. For comparison, data obtained in propan-2-ol/water mixture are also presented. Surprisingly, the biphenyl concentrations generated within the soil were modestly greater (2.4-6.7%) than if the same quantity was added to the propan-2-ol/water mixture. However this increase, although consistent, remained within the 95% confidence interval associated with the linear regression model.

As indicated in Table 2.3, soils that had been spiked with Aroclor 1242 or 1248 or 1254 or 1260 standard, resulted in recoveries of biphenyl that were in good agreement with predicted values. It was observed that the Aroclor 1260 conversion model provided the closest agreement for the estimation of PCBs concentration for contaminated soil samples, especially close for certified reference materials. In consequence, all estimations of PCB concentration with soil samples were calculated based on the Aroclor 1260 model.

The method limit of detection in terms of direct PCB conversion to biphenyl within the soil was approximately 150 μg/kg using the model of three times baseline noise divided by the slope. The capacity to convert PCB mixtures to biphenyl within the soil was

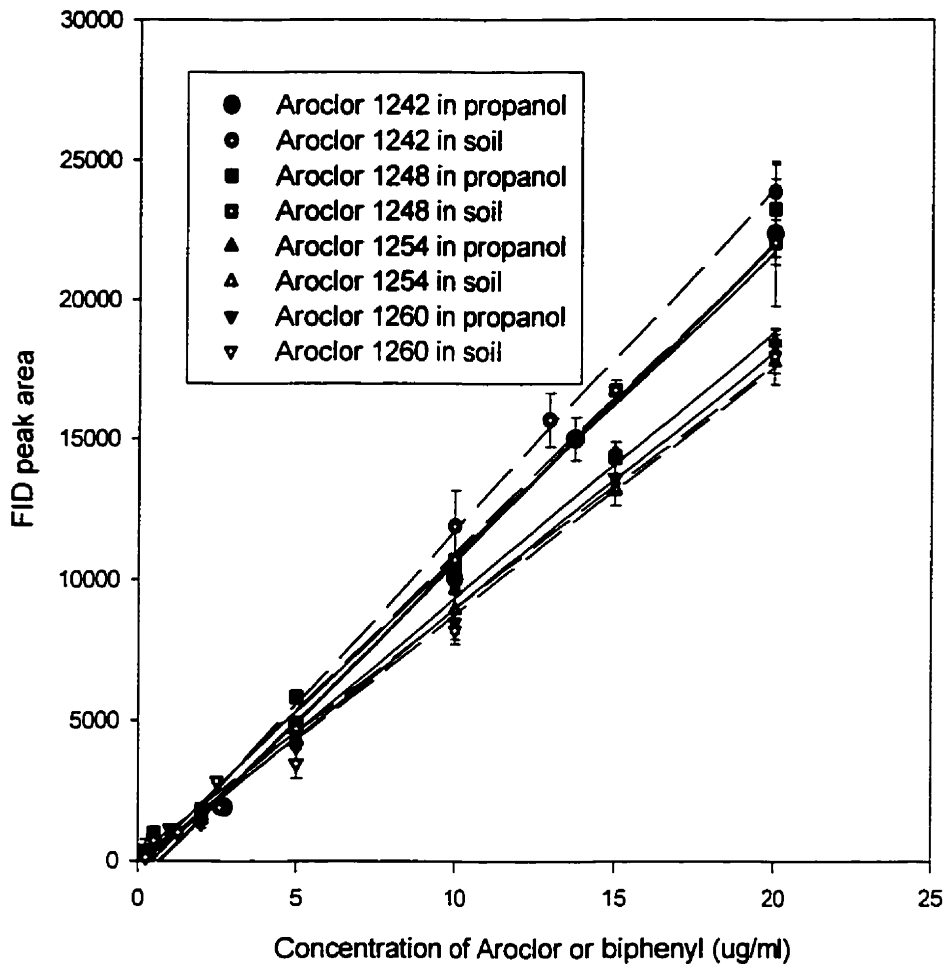


Figure 2.3. Variations in recoveries of biphenyl from Aroclor 1242, Aroclor 1248, Aroclor 1254 or Aroclor 1260 added to soil or propan-2-ol/water at 0.3-22 μg/g.

increased when the quantity of added magnesium was increased. One gram of Mg was insufficient for quantitative conversion within the soil if the PCB concentration was in excess of 5 mg/kg. This was true especially for more highly chlorinated substrates such as Aroclor 1260. All subsequent experiments were conducted with 2 g Mg added to the sample matrix. The quantity of K_2PdCl_6 used for the reaction mixture has less of an effect on the conversion efficiency of the PCBs. In preliminary studies, the yield of biphenyl from Aroclor 1242 was similar for increasing amounts of K_2PdCl_6 (10-40 mg) added to 2 g Mg in the presence of various quantities of 1242 substrate. Subsequent experiments were carried out with 10 mg K_2PdCl_6. The conversion of PCBs to biphenyl within soil, was also time dependent. There were substantial differences between the recoveries after 2 h and 6 h of reaction in the soil matrix. Although the calibration plots generated with 1260 substrate for both reaction times provided good fits with linear models (coefficients of determination, R^2=0.996, 0.983), 2 h of reaction was insufficient to quantitatively dechlorinate the substrates within the soil. By contrast, there was a good agreement with the theoretical biphenyl content of Aroclor 1260 for the longer reaction time. As measured by GC-FID (and peak purity corroborated by GC-MS), the conversion of PCBs to biphenyl within soil matrices was greater than 98% over the substrate concentration range of 1-52 μg/g.

The soil particle size influenced the dechlorination rate for PCBs. For samples of soil No.1 that had been spiked with Aroclor 1242 at 5 mg/kg, no differences in recoveries were observed from substrate that had been sieved to pass a 50-mesh screen vs. material that had been sieved to pass a 10-mesh screen. Analogous results were obtained for soils 2 and 3, the samples with a smaller particle size required a longer reaction time. In this study, 2 h of reaction were suitable for soils sieved to 10-mesh, 4 h for the samples of 50-mesh and 6 h for the samples of greater than 125-mesh.

2.3.3 Certified Reference Materials

The contaminated soils in this study were characterized by a relatively low content of organic matter that might have affected the recovery of biphenyl from PCBs. Other soil obtained between the PCBs concentration determined by dechlorination to biphenyl and

Table 2.4 Total soil PCB concentrations as determined using different procedures

Methods	Soil 1	Soil 2	Soil 3	RSM1939a	CRM 481	CRM 536
Direct conversion within the soil matrices	N.D.[a]	20.8 ± 1.2[b]	19.3 ± 0.9	32.7±1.5	437.4 ± 14.2	1.8 ± 0.2
Method of standard additions to the soil	N.D.	22.5 ± 1.4	21.3 ± 1.8	---	---	---
Conversion on the Soxhlet extract	N.D.	30.3 ± 6.6	36.2 ± 2	35.4 ± 1.8	478 ± 46.5	2.2 ± 0.2
Conversion on the sonication extract	N.D.	24.9 ± 1.1	28.1 ± 1	---	---	---

[a]: N.D. none detected- lessd than 0.1 mg/kg

[b]:one relative standard devation based on 3 replicate determination

properties were anticipated to have less of an effect on the conversion. Table 2.4 summarizes the results obtained for soil/sediment matrices. Acceptable agreements were the certified PCB content for two of the three reference materials. The PCB content of the third reference material (certified 0.34 μg/g) was appreciably overestimated by the biphenyl conversion procedure. Acceptable agreements were also observed between the estimated PCB concentrations for additions of standard back to contaminated soils and estimates based on direct conversion within the soil matrix.

To corroborate the hypothesis that organic matter could provide a source of biphenyl in soil samples, Soxhlet and sonication extractions were conducted with the three soils and the reference materials. For identical derivatization procedures performed directly on the three soils in the absence or presence of added PCB substrate, no contribution from the organic matter was observed. By contrast, both the sonication and the Soxhlet extracts from the soils 2 and 3 as well as the reference materials did reveal a contribution to the apparent biphenyl recovery from the background. These results indicated that soil samples, even with relatively low content of organic matter, can be converted in part to biphenyl under the mild reaction conditions. The biphenyl that results from soil organic compounds could cause an overestimation of PCB concentration in soil under the conversion conditions (CRM 536 in Table 2.4). Attempts were made to overcome the contribution from this source. Clean-up with concentrated H_2SO_4 was ineffective however. The use of this approach can result in increased variability of recoveries. (European Commission, BCR information, CRM 481 manual).

In summary, the direct derivatization within the sample matrix can be used to estimate the PCB concentration for soil/sediments and contaminated solutions. The concentrations of PCBs in two of the three reference materials (27.2 and 473 mg/kg) were determined successfully. The principle advantages of this procedure include convenience and simplicity but the principle disadvantage is that organic matter can also contribute to the apparent analyte recovery and must be accounted for in accurate estimates. The Aroclor 1260 model can be used to estimate the PCB concentration in contaminated soil/sediments samples.

Chapter 3

Preface

In Chapter two, a novel method for the determination of PCBs in contaminated soils was developed and validated. The reaction was very efficient in propan-2-ol/water, surfactant emulsion or sand mixture and virtually complete in soil provided that excess magnesium and the K_2PdCl_6 were added to the sample prior to the addition of water. High PCB loadings were readily determined in the field contaminated soils either by direct determination within the matrix or by standard additions.

Using this newly developed method, a novel remediation approach for soils contaminated with PCB compounds is designed and evaluated. However, before carrying out the remediation technique, an approach that is capable of dechlorinating commercial PCB mixtures using heated columns of zero-valent metal or bimetallic mixture in a continuous process is described, optimized and then incorporated into the process. In Chapter 3, supercritical carbon dioxide ($scCO_2$) is combined with zero-valent metal(s), tested and then optimized for dechlorinations. An efficient PCB dechlorination scheme results.

Reductive dechlorination of polychlorinated biphenyl compounds in supercritical carbon dioxide

3.1 Introduction

A popular strategy to effect abiotic dehalogenations has been to mediate the reduction in aqueous media in the presence of a sacrificial metal in its elemental form. Zero-valent iron (Gilham and O'Hannesin, 1994; Matheson and Tratyek, 1994; Helland *et al.*, 1995; Warren *et al.*, 1995; Orth and Gillham, 1996; Johnson *et al.*, 1996; Wang and Zhang, 1997; Sayles *et al.*, 1997) and iron-palladium (Muftikian *et al.*, 1995; Grittini *et al.*, 1995; Muftikian *et al.*, 1996) bimetallic mixtures have become especially popular for this purpose. In anoxic aqueous media, free metal ions, chloride ion and hydrogen gas were produced by reaction at the surface of metal particles and protons were consumed. The process kinetics were dependent on solution pH, surface area of the metal particle, substrate concentration, buffer selection and solvent composition (Johnson *et al.*, 1996). Dechlorination approximately followed first-order kinetics and rate coefficients tended to increase with time, an observation that was postulated to have resulted from an increase in reactive metal surface area due to cathodic depolarization and pitting of the iron surface (Helland *et al.*, 1995). Dechlorination occurred under oxic conditions as well, although the rates were appreciably slower. A rapid pH increase was synchronous with dissolved oxygen consumption and the pH remained constant after the oxygen had been depleted. This was attributed to the proton and oxygen consuming aerobic corrosion of the Fe^{o} surface (Helland *et al.*, 1995).

Normalization of the apparent rate constants for the dechlorination of different halogenated substrates to the iron surface area yielded a specific rate constant (k_{SA}) that varied by only one order of magnitude for individual halocarbons (Wang and Zhang, 1997). Surface area normalised rate constants for nanoscale Fe^{o} particles (1-100 nm diameter) were 10-100 times higher than for commercial particles (Wang and Zhang, 1997). Correlation analysis also revealed that dechlorination is generally more rapid at saturated carbon centres than at unsaturated carbons and that high degrees of halogenation favoured rapid reduction (Johnson, 1996).

Based on the low concentration of chlorinated degradation products in the solution phase it was suggested that most of the substrate remained sorbed to the iron surface until complete dechlorination had been achieved (Orth and Gillham, 1996). Prolonged exposure of the Fe^{o} or Pd^{o}/Fe^{o} surface to a saturated solution of aqueous organochlorine compounds resulted in the growth of a hydroxylated iron oxide film that deactivates the Pd^{o}/Fe^{o} surface. The thick hydroxylated iron oxide film could be removed and the original activity of the Fe^{o} (Pd^{o}/Fe^{o}) surface restored by washing the surface with a dilute acid (Matheson and Tratnyek, 1994; Muftikian *et al.*, 1995; Muftikian *et al.*, 1996; Balko and Tratnyek, 1998).

A mechanistic model for the zero-valent metal (Fe^{o}) mediated dechlorination has suggested a surface mediated process (Weber, 1996) and indicated that rates of decomposition were limited by the sparing solubilities of substrates in the aqueous phase (Sayles *et al.*, 1997). When iron was used to mediate anoxic dechlorination, the slow adsorption of the target compounds to the iron surface and the desorption of hydrocarbon products became the rate-limiting steps that retarded the overall process appreciably (Hardy and Gillham, 1996). It is often considered that water is a necessary component component of metal-mediated corrosion reactions with chlorinated alicyclics. However, there are several literature reports (Archer, 1978; Archer, 1982; Smentkowski *et al.*, 1989; Smentkowski *et al.*, 1990) emphasising that zero-valent iron or aluminum can react dfirectly with these substrates to yield chlorocarbon radicals, metal chlorides and/or chloride ion.

Somewhat less is known about reactions of halogenated aromatics with zero-valent metals. Copper metal has been reported to dechlorinate polychlorodibenzo dioxin (PCDD) and furan (PCDF) derivatives (Hagenmater *et al.*, 1987). Similarly, Fe^{o} can mediate the dechlorination of chlorinated benzenes (Morlando, 1997), DDT and derivatives (Sayles *et al.*, 1997) and chlorinated phenols (Grittini *et al.*, 1996). Although polychlorinated biphenyl compounds (PCBs) are generally considered to be unreactive to Fe^{o} at ambient temperature, they have been dechlorinated efficiently with bimetallic iron mixrures. A methanol-water solution of a commercial mixture of PCBs when contacted, for a short time, with palladized iron at ambient temperature, the only reaction products were biphenyl and chloride ions (Grittini *et al.*, 1995). Success has also been achieved using Fe^0 at elevated temperatures. At 400 °C in the presence of solvent, PCB mixtures underwent hydrogenolytic dechlorination in the presence of Fe^0 powder that led to the complete loss of chlorinated congeners (Chuang *et al.*, 1995) and the recovery of a maximum of biphenyl. Nanoscale Fe^0 particles have also been demonstrated to mediate PCB dechlorinations efficiently (Wang and Zhang, 1997). More recently, sub-critical water at 250 °C and 10 MPa pressure has been used to mediate PCB dechlorinations by Fe^0 (Yak *et al.*, 1999).

As a remediation strategy, extractions are limited in that the target toxicant(s) can only be transferred/concentrated from one medium to another but are not detoxified per *se*. A more efficient strategy would be to couple the extraction with an *on-line* modification of the toxiforic groups. The objectives of this Chapter were to develop and optimize the operation of a continuous reactor to dechlorinate PCBs. It was anticipated that supercritical carbon dioxide ($scCO_2$) could be used advantageously to mobilize PCBs from particulate media and to transport them through the reactor. Supercritical fluids including $scCO_2$ possesses several advantages that can be exploited in dechlorinations including appreciable substrate solubility (Anitesscu and Tevlarides, 1999) and enhanced rates of solute partitioning and diffusion relative to the liquid phase. On the other hand, CO_2 has been reported to cause the gradual deactivation of Pd supported catalyst (Munakata *et al.*, 1988). PCBs have been purged efficiently from soils with $scCO_2$ (Bjorklund *et al.*, 1999; Pilorz *et al.*, 1999). It remains among the least expensive of solvents. It is non-polar yet is readily separated from non-polar solutes, non-explosive, virtually non-toxic, non-flammable, relatively non-reactive, and waste emissions do not directly increase the burden to greenhouse gases.

3.2 Materials and Method

3.2.1 Chemicals

Copper (electrolytic grade, 40-100 mesh, nominally 99.5% purity), iron (40 mesh, nominally 99.5% purity), nickel (50-100 mesh, nominally 99.5% purity), zinc particles (100 mesh, nominally 99.9% purity) and sodium dispersion, 40% (w/v) in oil, were purchased from Alfa Aesar, Ward Hill, MA and used as received. Acetic anhydride (AcA), ethylene glycol dimethyl ether (1,2-DME), hexane, acid washed sea sand and silver nitrate were purchased from Fisher Scientific, Ottawa, ON and were used as received. Aroclor 1242 and Aroclor 1248 mixtures were kindly donated by Monsanto Company, Sauget, IL.

3.2.2 Ag^o/Metal^o Bimetallic mixtures

The general preparations described by Zhang *et al.* were followed. Ag^o/Fe^o and Pd^o/Fe^o were prepared from 40-mesh iron that had been washed copiously with 6M HCl and rinsed with distilled water. Sufficient aqueous $AgNO_3$ or K_2PdCl_6 to result in a 2% (w/w) surface coverage of the iron, was added to the aqueous iron suspension that was gently mixed on a rotary evaporator for 12 h. Ag/Ni^o was prepared in similar fashion by reaction of aqueous $AgNO_3$ [sufficient to provide a 2% (w/w) surface coverage] with aqueous suspension of pre-washed 50-100 mesh nickel granules during 12 h.

3.2.3 Mixed particle size Pd^o /Fe^o

Mixed particle size Pd^o /Fe^o was prepared by mixing freshly precipitated micron-scale iron particles with 40-mesh iron granules (Zhang *et al.*, 1998). Aqueous 1.6 M $NaBH_4$ was added dropwise to 1.0 M $FeCl_3 \cdot 6H_2O$ with constant stirring. The precipitated product was mixed with an equal quantity of freshly washed 40-mesh Fe^o particles and the mixture was treated with sufficient aqueous K_2PdCl_6 to result in a 2% surface deposit of Pd^o.

3.2.4 Reactor

The dechlorination assembly (Figure 4.1) consisted of standard HPLC fittings and column assemblies that were rated to 6,000 psi. A diaphragm compressor (Newport Scientific, Jessup, MD) delivered liquid carbon dioxide from the eductor tube of the K-type cylinder of CO_2 [bone dry grade ex MEGS, Montreal QC] to a large heated (1.4L) reservoir (temperature and pressure equilibration vessel, TPEV) that served as both a pressure dampener and as a source of supercritical carbon dioxide (scCO2) for the system. The supercritical solvent (~0.8 or 1.5 l/min of decompressed gas) was

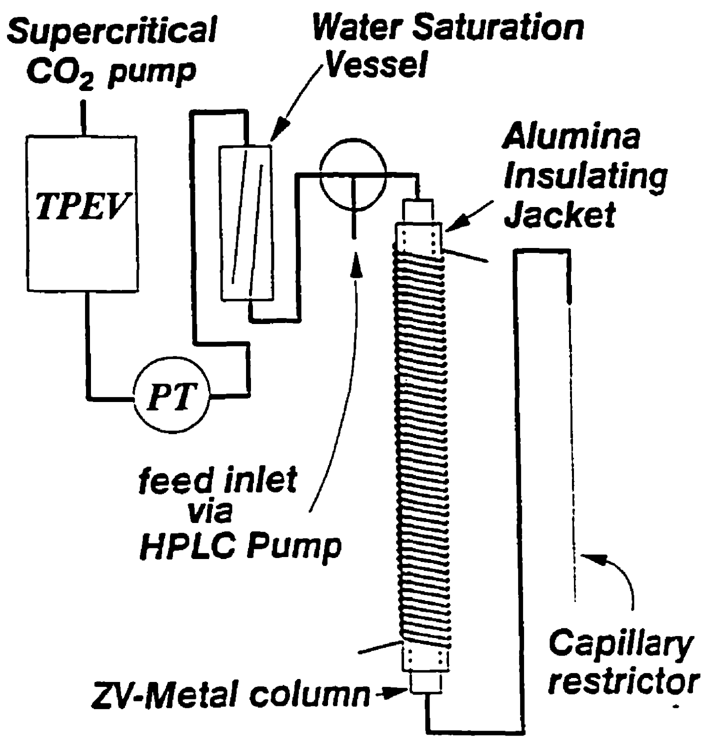


Figure 3.1 Dechlorination reactor assembly consisting of a temperature and pressure equilibration vessel (TPEV), a pressure transducer (PT), a saturation vessel (SV), a mixing tee to merge the supercritical carbon dioxide with feedstock solution, one or more zero valent metal columns and a capillary restrictor all connected in series.

transferred to a five ml saturation vessel (SV, Keystone Scientific. Bellefonte, PA) mounted vertically, a pressure transducer (PT) connected to a digital readout meter, a mixing tee and a reactor unit. Polychlorinated biphenyl (PCB) substrate, dissolved in a suitable solvent, was delivered at 0.1 ml/min to the mixing tee (1/16"i.d.), merged with the $scCO_2$ stream (~4 ml/ min) and fed to one or two stainless steel (ss) HPLC column assemblies [10 mm inner diameter (i.d.) x 25 cm] that were filled with test zero-valent metal (or metal mixture) encased in an insulating alumina jacket (fashioned from thin walled alumina 12 mm o.d. 10 mm i.d. tube, Alfa Aesar, that had been cut lengthways to provide two semi-cylinders) and mounted in series. The ss column-alumina jacketed assemblies were encased separately with 80-turn coils of high resistance heating wire that were energized form variable transformers. Pressure within the assembly was maintained at the desired pressure with a flexible polyamide coated silica capillary restrictor (~25 cm x 0.05 mm, Chromatographic Specialties, Brockville, ON).

3.2.5 Reactor operation

After a short delay to purge residues of air from the system (during which time only $scCO_2$ was fed to the reactor), feedstock 0.1 ml/min of 2-20% (v/v), was added continuously via the HPLC pump to the $scCO_2$ stream and transported to the reactor. Measurements at the exit of the capillary restrictor indicated a flow rate corresponding to 800 - 850 ml/ min of decompressed gas. The exit tip of the capillary restrictor was immersed in hexane (25 ml) to trap products from the reactor eluate. Each experiment was continued until six successive traps had been collected, each corresponding to 10 min of cumulative trapping of reactor eluate. The course of the dechlorination was monitored by gas chromatography (GC) or occasionally by GC-MS to monitor the spectrum and identities of products and by titration to measure levels of residual organically bound chlorine in the eluate.

3.2.6 Organically bound chlorine

The general procedure of Ware *et al.* (1988) was followed. Residual organically bound chlorine in the hexane trapping solution was determined by titration with standardised $AgNO_3$ (~0.01M). Sodium dispersion, 2 ml, was added to a vigorously stirred 10 ml aliquot of hexane trapping solution that had been further diluted 5-fold with fresh hexane. Methanol, 1ml, was added dropwise; the reaction was continued for 5 min then quenched by the addition of propan-2-ol (15 ml) followed by 90 ml water. The aqueous phase, after separation from the organic phase, was diluted to 100 ml in a volumetric flask. A 20 ml aliquot of the reaction mixture was acidified to pH 6-7 with nitric acid (7M), supplemented with 5 drops of potassium chromate indicator solution then titrated with $AgNO_3$. Blank determinations for chloride in reactor eluate consisted of an identical procedure in the absence of added sodium dispersion.

3.2.7 Biphenyl formation from PCB mixtures.

Aroclor mixtures were converted quantitatively to biphenyl by reaction with a solid mixture of Mg^0 and K_2PdCl_6 following the procedure of Doyle *et al.*(1998) (Chapter 2).

3.2.8 Gas Chromatography determination

Gas Chromatography was performed on a Varian Model 3700 GC fitted with a 25 m megabore DB5 column and a flame ionization detector. Helium, delivered at 3.0 ml/min, served as the carrier gas and after an initial temperature hold at 50 °C during 5 min, the column temperature was ramped to 250 °C during 30 min then held at the upper temperature for a further 5 min. GC-MS were performed on a Saturn-3400 system. The DB-5 capillary column (30 m x 0.2 mm), eluted with helium at 1.0 ml/min, was temperature programmed from 40-300 °C during 45 min then held at the final temperature for a further 5 min. Eluting components were identified tentatively by comparison of experimental mass spectra with spectra catalogued in the data base and corroborated by co-chromatography and spectral matching with authentic standards.

3.3 Results and discussion

3.3.1 The efficiency of PCB dechlorination

The dechlorination efficiency (yield) was defined as one minus the ratio of the quantity of organically-bound chlorine in the reactor eluate divided by the chlorine content in an equivalent quantity of feedstock. The extent of dechlorination was influenced appreciably by the identity of the zero-valent (ZV) metal, by the temperature and pressure within the reactor column(s) and especially by the composition of the feedstock. As summarised in Table 3.1, the replacement of water-ethylene glycol dimethyl ether (1,2-dimethoxyethane, DME) mixture with acetic anhydride (AcA) was beneficial to both the dechlorination yield and the repeatability among the six samples collected sequentially during 1 h of operation. Moreover, the dechlorination efficiency seemed to depend on the content of acetic anhydride in the transporting solvent. Whereas 5% and 10% (v/v) of acetic anhydride (AcA) in the DME feedstock provided mean dechlorination efficiencies of 63 ± 10 and 74 ± 9% respectively, an increase in the AcA content to greater than 40% (v/v) resulted in the virtually complete (~99%) dechlorination of feedstock containing 10% PCBs (Figure 3.2). The error bars of this Figure reflect one relative standard deviation (RSD) associated with three replicate determinations, by titration, of residual organically bound chlorine in the eluate trap (mean RSD for the ten separate samples was ±1.3%). Figure 3.2 also summarises the influence of operating pressure on the mean dechlorination efficiency. An increase of 1500 psi in operating pressure increased the mean dechlorination yield by approximately twenty percent. Increased operating pressure result in increased densities of the $scCO_2$ and a greater solvating power of the fluid for the substrate PCBs. Because the components of the reactor were standard HPLC fittings that were rated to 6000 psi at ambient temperature, it was decided arbitrarily to limit the operating pressure of the reactor to 4500 psi or less for reason of safety. The presence of water was not necessary for the dechlorination reaction (Table 3.1). The requirement for at least some water in the reductive dechlorination at metal surfaces had been suggested by the reported lack of any measurable reaction at ambient temperature of neat chlorinated liquid substrate in contact with reducing metal surfaces. It was anticipated that, in the presence of $scCO_2$, the pH of the entrained aqueous phase would be decreased sufficiently (2.8-2.95, Toews *et al.*, 1995) to minimize the build-up of an oxide (hydroxide)/carbonate layer on the ZV metal surfaces. In consequence, we had added the saturator vessel (SV, Figure 3.1) to the $scCO_2$ inlet line. However, when water was removed from the transporting solvent and the SV was removed from the inlet train no diffferences in the dechlorination efficiencies were detected. If AcA alone or diluted with ethylene glycol diethyl ether was fed a single reactor column containing ZV iron (Fe^0) (400 °C, 4500 psi) no starting material was

Table 3.1 variations in the mean[a] percent dechlorination (± 1 SD) for 2 successive columns (i.) containing various zero-valent metals and (ii.) with different solvent compositions to transfer a 20% (v/v) Aroclor 1242 to the reactor.

ZV-Metal	Feed stock composition (v/v) in the presei of 20% (v/v) Aroclor 1242	Mean dechlorination r (%) for two columns
Cu	5%H_2O, 75%DME	36.0 ± 11.3
Cu	10%DME, 70% Acetic anhydride	86.0 ± 7.6
Fe	5%H_2O, 75%DME	36.3 ± 30.4
Fe	10%DME, 70% Acetic anhydride	94.5 ± 4.4
Ni	5%H_2O, 75%DME	67.8 ± 8.1
Ni	10%DME, 70% Acetic anhydride	91.7 ± 6.1
Zn[b]	5%H_2O, 75%DME	67.0 ± 11.4
Zn[b]	10%DME, 70% Acetic anhydride	89.8 ± 7.5

[a]: Determined at 400 °C using 2 columns.

[b]: Determined at 200 °C using 2 columns.

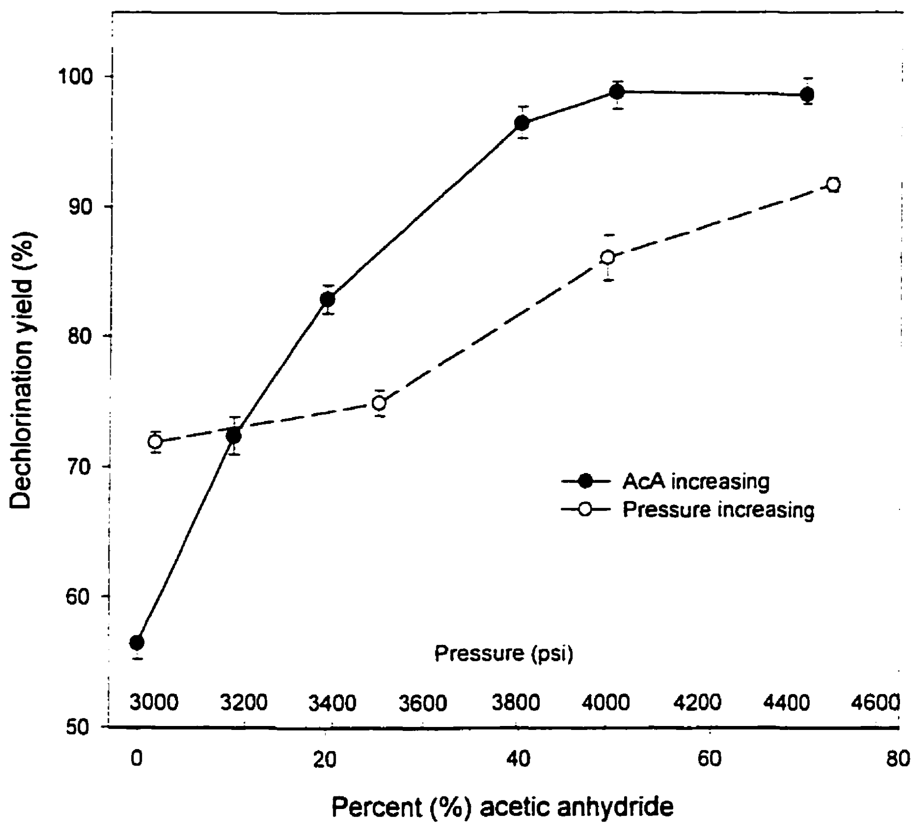


Figure 3.2 Variations in the dechlorination efficiency for 10% (v/v) solutions of Aroclor 1242 in 1,2-dimethoxyethane with (a.) increasing percent of acetic anhydride in the solvent mixture delivered to two Ag^0/Fe^0 columns at 400 °C and 4500 psi or (b.) with increasing pressure for the same feedstock delivered to two Ag^0/Fe^0 columns at 400 °C.

detected in the trapped column eluate. Fourier transform infrared (FTIR) spectroscopy indicated that in addition to residual dissolved carbon dioxide, the product mixture was composed predominantly of methyl ketone(s). A possible source for these compounds would involve the capture of alkyl radicals by a methylated carbon monoxide radical species. $ScCO_2$ is known to form short chain (C_1-C_5) alkyl radicals by catalytic reduction at iron surfaces (Hardy and Gillham, 1996).

3.3.2 The effect of temperature on dechlorination efficiency

The dechlorination process was also temperature dependent. As summarized in Table 3.2, an increase in the operating temperature (as measeured by the outer skin temperature of the reactor columns) improved both the extent of dechlorination and the repeatability between cumulative 10-minute traps that had been collected sequentially during 1 h. For zero-valent zinc, the metal granules were observed to soften appreciably at reactor skin temperatures above 200 °C, so that dechlorination trials were limited to this temperature. Trials were also conducted with Aroclor 1248 (Table 3.2). Yields between the Aroclor 1248 and 1242 are not directly comparable because of differences in density (20 °C) [(1.44 *vs*. 1.38 respectively), (Ware, 1988)] and differences in the spectrum of congener for these mixtures (Doyle, 1998). Additionally, for incomplete dechlorinations, identical rates of reaction would have resulted in lower dechlorination yields for Aroclor 1248 because of the greater chlorine concentrations in the substrate.

The effect of increased operating temperature can be seen more clearly in Figure 3.3 which compares Fe^0 meditated dechlorination efficiencies for sequential traps at different operating temperatures. There was a gradual decrease in dechlorination yield with increasing trap number. The gradual decrease in efficiency was characteristic of all four ZV-metals and the three bimetallic mixtres that were studied. The negative slopes of the spline curves were greater at lower than at higher operating temperatures for different zero-valent (ZV) metal substrates. Other zero-valent metals (Cu^0, Ni^0, and Zn^0, Figures 3.3, 3.4) behaved similarly but the dechlorination was not as extensive.

Table 3.2 Influence of temperature, for two reactor columns connected in series, on the mean percent dechlorination (± 1 RSD) of feedstock containing 20% (v/v) Aroclor 1242 (or Aroclor 1248), 70% (v/v) acetic anhydride and 10% (v/v) dimethoxyethane.

	Temperature					
ZV-Metals	200 °C		300 °C		400 °C	
	1242	1248	1242	1248	1242	1248
Cu	69.1 ± 9		73.1 ±23		86 ± 8	
Fe	86.0 ± 8	69±15	87.6 ±10	71.8 ±1	94.5 ± 4	92 ± 6
Ni	55 ±12	68.9±15	61.9 ± 14	67 ± 2	92.5 ± 6	89 ±2
Zn	68.9 ±15					
Ag/Fe	63.3 ±17		73.3 ± 10		97.5 ± 3	
Pd/Fe	60.2 ±23	56.1 ±26	74.9 ±16		96.4 ± 3	93 ± 5

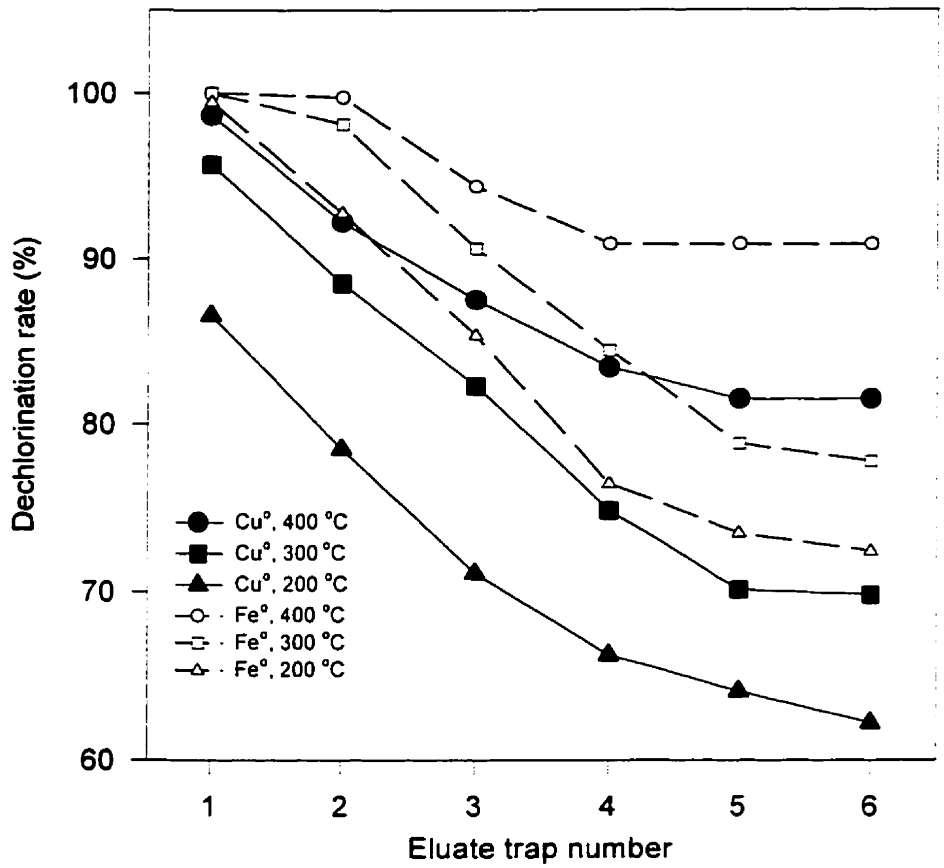


Figure 3.3 Efficiencies for Cu^{o} meditated (filled symbols) or Fe^{o} meditated (hollow symbols) dechlorinations of 20% (v/v) Aroclor 1242 solution delivered at 0.1 ml/min to two reactor columns maintained at 400 °C and 4500 psi (mean dechlorination in six successive traps, 86± 8% and 95± 4% respectively), or at 300 °C (mean dechlorination in the six traps, 73 ± 23% and 88 ± 10% respectively) or at 200 °C (mean dechlorination in the six traps, 69 ± 9% and 84 ± 12% respectively).

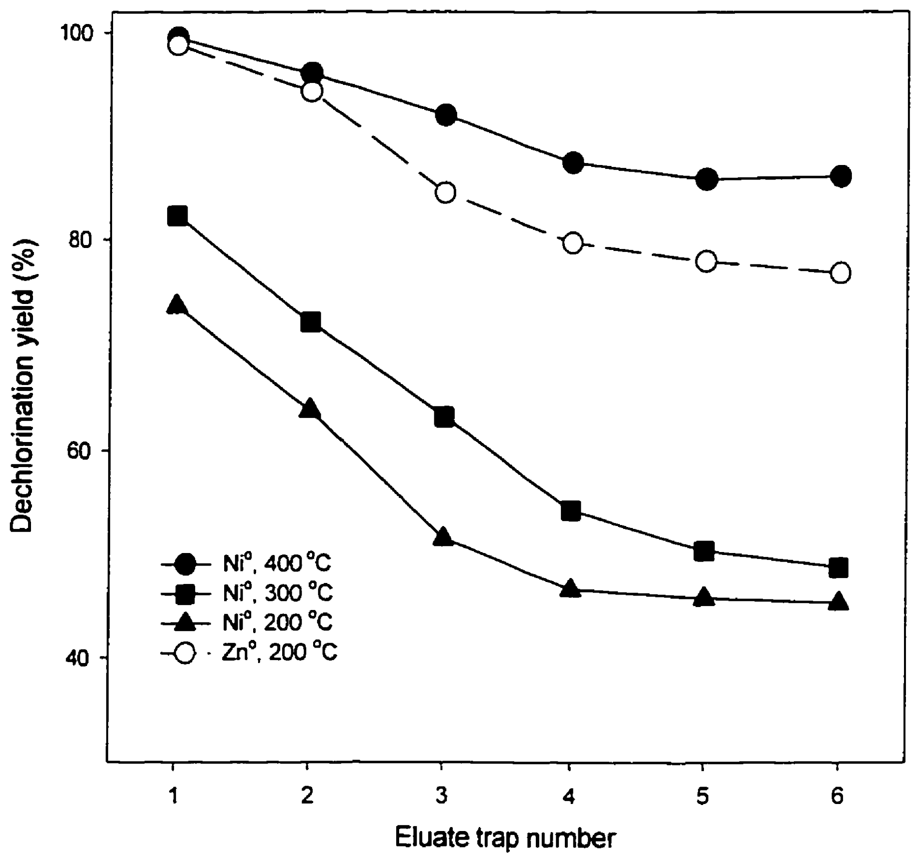


Figure 3.4 Efficiencies for Ni^0 meditated (filled symbols) or Zn^0 meditated (hollow symbols) dechlorinations of 20% (v/v) Aroclor 1242 solution delivered at 0.1 ml/min to two reactor columns maintained at 400 °C and 4500 psi (mean dechlorination in six successive traps, 91± 6%), or at 300 °C (mean dechlorination in the six traps, 67 ± 6%) or at 200 °C (mean dechlorination in the six traps, 54 ± 11% and 85 ± 11% respectively).

3.3.3 The dechlorination efficiency of bimetallic mixtures

In addition, three bimetallic mixtures of ZV-metal [(Ag^o/Fe^o, Figure 3.5), (Ag^o/Ni^o, Figure 3.6), and (Pd^o/Fe^o, Figure 3.7)] were assessed for dechlorinating efficiency in this system. All three mixtures further improved both the dechlorination yield and the repeatability of the reaction over 1 h (Table 3.3). For these trials, the reactor temperature was maintained at 400 °C and the substrate composition was varied using two ZV-metal columns. Although efficient, the reactions were not quantitative. For a single reactor column (Table 3.4), there was no apparent differences between the use of acetic anhydride or methylisobutyl ketone (IBMK) in the transporting solvent although the use of 2-heptanone depressed dechlorination by approximately 10 percent. Surprisingly, the inclusion of 1,2 DME (10%, v/v) in the solvent increased the yield by 9 and 14 percent over neat acetic anhydride for the Ag^o/Fe^o and the Ag^o/Ni^o mixtures respectively. The dechlorinating activities of silver-coated iron and nickel were also more durable as seen in Table 3.3. Although the efficiency of dechlorination appeared to decrease monotonically for the Ag^o/Ni^o bimetallic mixture, it appeared to level off for the Ag^o/Fe^o support-term trials.

Two Ag^o/Fe^o reactor columns in sequence, that resulted in a 9% decrease in organically–bound chlorine, provided a chromatogram that was reduced approximately 94% in total peak areas in the PCB eluting region indicating that the majority of products were eluted more rapidly. When only biphenyl dissolved in DME comprised the feedstock for the Ag^o/Fe^o column (operated under optimized dechlorination conditions), a maximum of only

84% could be recovered in the hexane traps indicating further reaction. There were no products that were more retained than biphenyl on the GC column. With Ag^o/Fe^o bimetallic mixture and 99.5% dechlorination of the 1242 substrate only two chlorinated products (*o*-chlorobiphenyl and 2, 4 dichlorobiphenyl and/or 2, 6 dichlorobiphenyl, (which collectively accounted for appreciably less than 1% of the starting material) were detected by GC-MS (Figure 3.8). Similarly, for substrate that had been 99.8% dechlorinated, only *o*-chlorobiphenyl was detected among the chlorinated products. Other non-chlorinated products that were identified tentatively include methylbiphenyl(s), dimethylbiphenyl(s), toluene and short chain esters of 1,2-benzenedicarboxylic acids. The

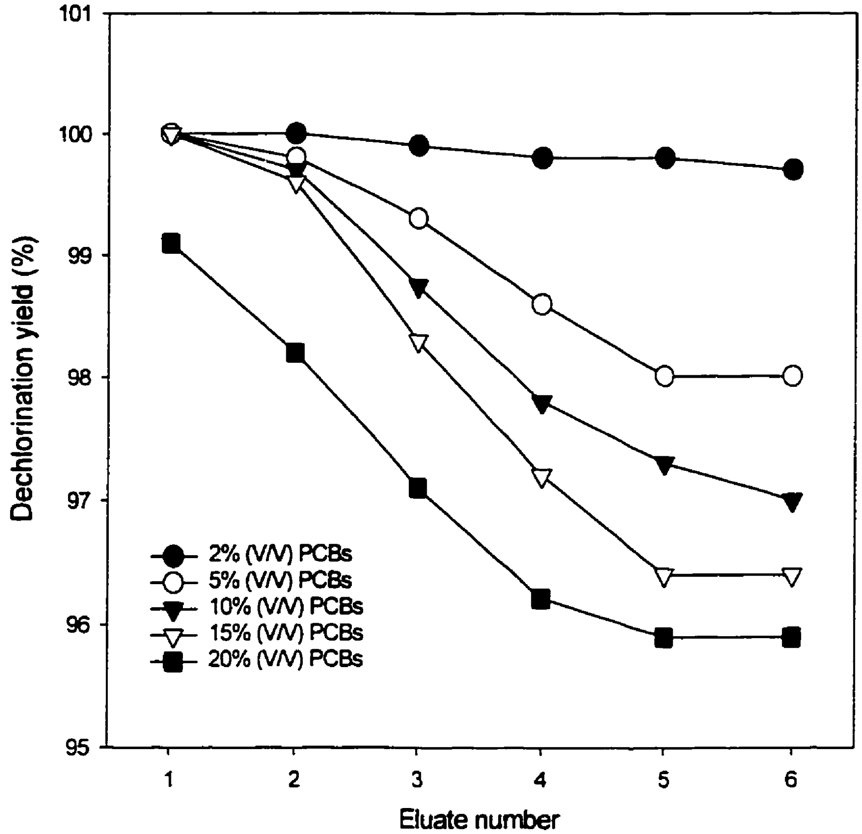


Figure 3.5 Dechlorination efficiencies for 2%, 5%, 10%, 15% or 20% (v/v) Aroclor 1242 feedstock delivered to two columns mounted in series of Ag^{0}/Fe^{0} (mean dechlorination for six successive traps, 99.8 ± 0.1%, 98.7 ± 0.9%, 98.3 ± 1.2%, 98.0 ± 1.6% and 97.0 ± 2.6% respectively) at 400 °C and 4500 psi.

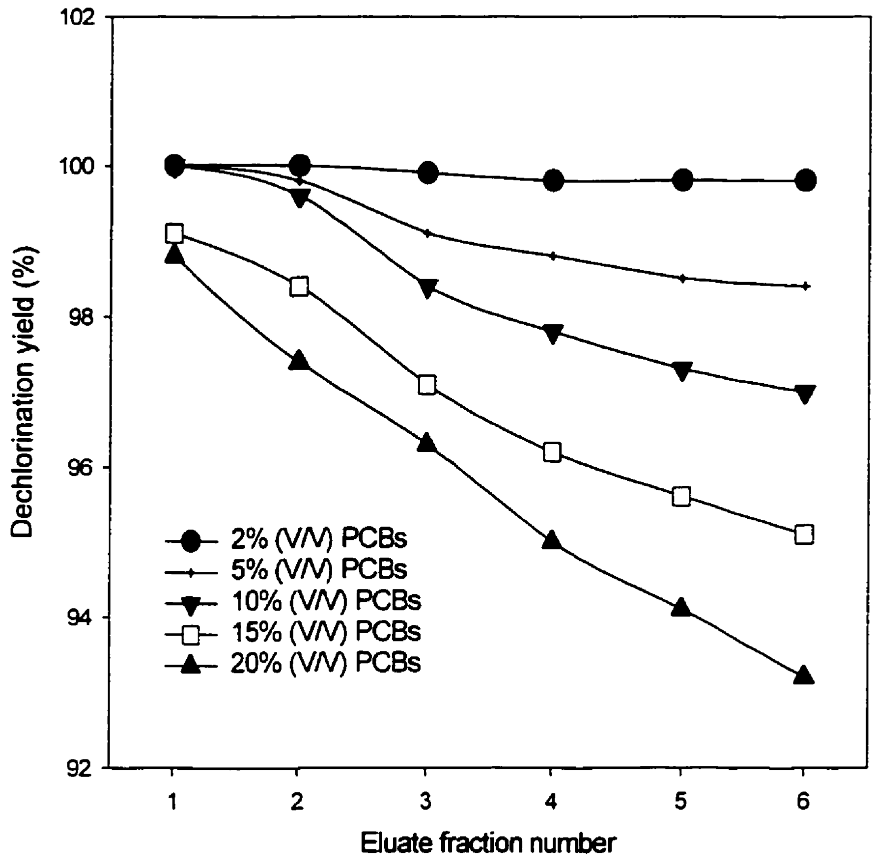


Figure 3.6 Dechlorination efficiencies for 2%, 5%, 10%, 15% or 20% (v/v) Aroclor 1242 feedstock delivered to two columns mounted in series of Ag^0/Ni^0 (mean dechlorination for six successive traps, 99.9 ± 0.1%, 99.0 ± 0.8%, 97.8 ± 1.1%, 83.9 ± 8.9% and 95.8 ± 2.1% respectively) at 400 °C and 4500 psi.

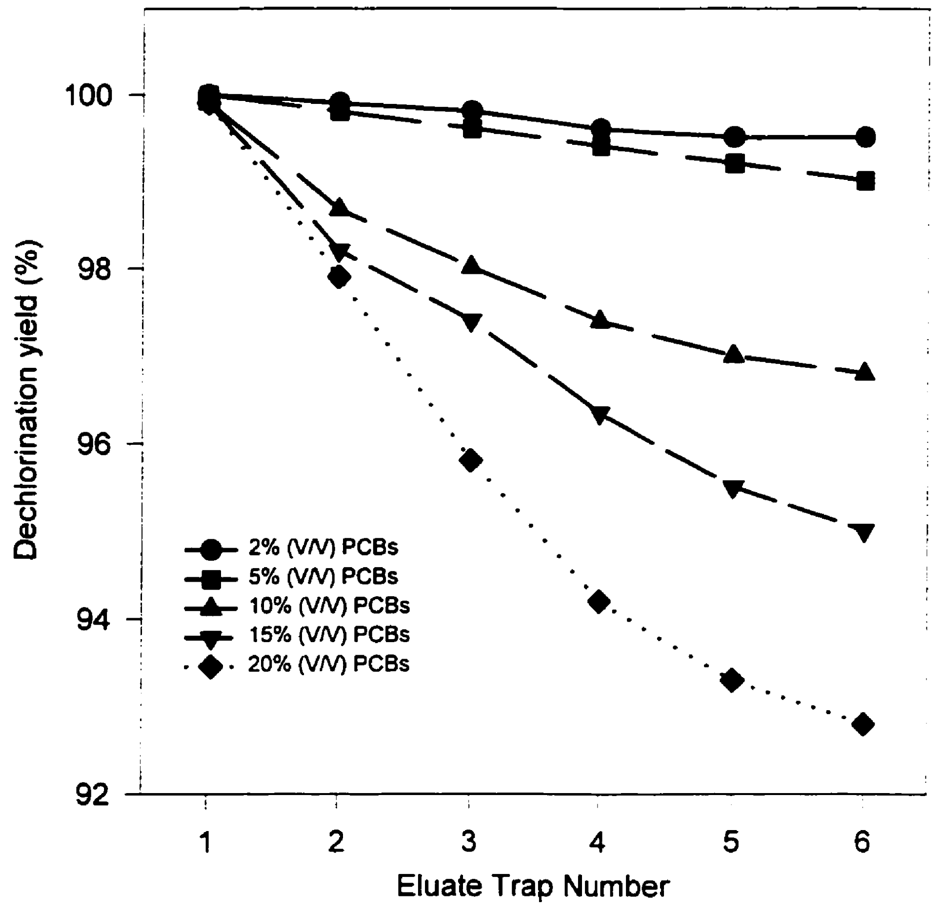


Figure 3.7 Dechlorination efficiencies for 2%, 5%, 10%, 15% or 20% (v/v) Aroclor 1242 feedstock delivered to two columns mounted in series of Pd^0/Fe^0 (mean dechlorination for six successive traps, 99.9 ± 0.2%, 99.0 ± 0.8%, 97.8 ± 2.1%, 97.0 ± 2.4% and 96.1 ± 3.1% respectively) at 400 °C and 4500 psi.

Table 3.3 Variations in the mean[a] percent dechlorination (± 1 RSD) for 2 successive columns maintained at 400 °C and 4500 psi (i.) containing different zero-valent bimetallic mixtures and (ii.) with varying acetic anhydride-dimethoxyethane mixtures to transfer Aroclor 1242 (or Aroclor 1248) to the reactor.

Bimetall mixture	PCB conten % (v/v)	Feedstock composition (v/v) the presence of 20% (v/v) Aroclor 1242 (or 1248)	Mean % Dechlorination
Ag/Fe	2	20% AcA, 78% DME	99.8 ± 0.1
	5	20%AcA, 75% DME	98.7 ± 0.9
	10	50% AcA, 40%DME	98.3 ± 1
	15	50% AcA, 35%DME	98.0 ± 2
	20	70% AcA, 10%DME	97.0 ± 3
	20	80% AcA	88.9 ± 5
Ag/Ni	2	20% AcA, 78% DME	99.9 ± 0.1
	5	20% AcA, 75% DME	99 ± 0.8
	10	50% AcA, 40% DME	97.8 ± 1
	15	50% AcA, 35%DME	83.9 ± 9
	20	70% AcA,10%DME	95.8 ± 2
	20	80% AcA	81.1 ± 4
Pd/Fe	2	20% AcA, 78% DME	99.9 ± 0.2
	5	20% AcA, 75% DME	99 ± 0.8
	10	50% AcA, 40% DME	97.8 ± 2
	15	70% AcA, 15%DME	97.0 ± 2
	20	70% AcA,10%DME	96.1 ± 3
	20	80% AcA	84.3 ± 5
	5 (Aroclor 1248	70% AcA, 25% DME	97.9 ± 1
	10 (Aroclor 1248	70% AcA, 20% DME	95.6 ± 2
	15 (Aroclor 1248	70% AcA, 15%DME	93.8 ± 5
	20 (Aroclor 1248	70% AcA, 10% DME	92.9 ± 5

[a]: Mean ± 1 relative standard deviation (RSD) of six successive traps of reactor eluate.

Table 3.4 Variations in mean dechlorination efficiencies (± 1 RSD) for one column of silver (or palladium, 2% w/w) iron bimetallic mixture maintained at 400 °C and 4500 psi for 15 or 20% (v/v) Aroclor 1242 and different transporting solvent mixtures.

Bimetallic mixtures	Feedstock composition (v/v)[a]	Mean % dechlorination[b]
Ag/Fe	15% PCBs, 70% MIBK, 5% DME	92.1 ± 2
Ag/Fe	20% PCBs, 80% MIBK	83.6 ± 6
Ag/Fe	15% PCBs, 40% AcA.,45% DME	96.7 ± 7
Ag/Fe	20% PCBs, 50%AcA.,30% DME	88.5 ± 5
Ag/Fe	15% PCBs, 60% 2-heptanone, 25% DME	93.3 ± 4
Ag/Fe	20% PCBs, 70% 2-heptanone,10% DME	79.5 ± 6
Ag/Ni	20% PCBs, 50%AcA.,30% DME	83.9 ± 9
Ag/Ni	20% PCBs, 70%AcA.,10% DME	95.8 ± 2
Pd/Fe	20% PCBs, 50% MIBK, 30% DME	85.9 ± 10
Pd/Fe	20% Aroclor 1248, 70% MIBK, 10% DME	82.0 ± 7
Pd/Fe	20% PCBs, 70% 2-heptanone,10% DME	77.8 ± 9
Pd/Fe	20% Aroclor 1248, 70% 2-heptanone,10% DME	77.0 ± 8

[a]: DME= 1,2 dimethoxyethane, IBMK= methyiosbutyl ketone.

[b]: Mean in six 10-min cumulative traps that were collected sequentially during 1 h.

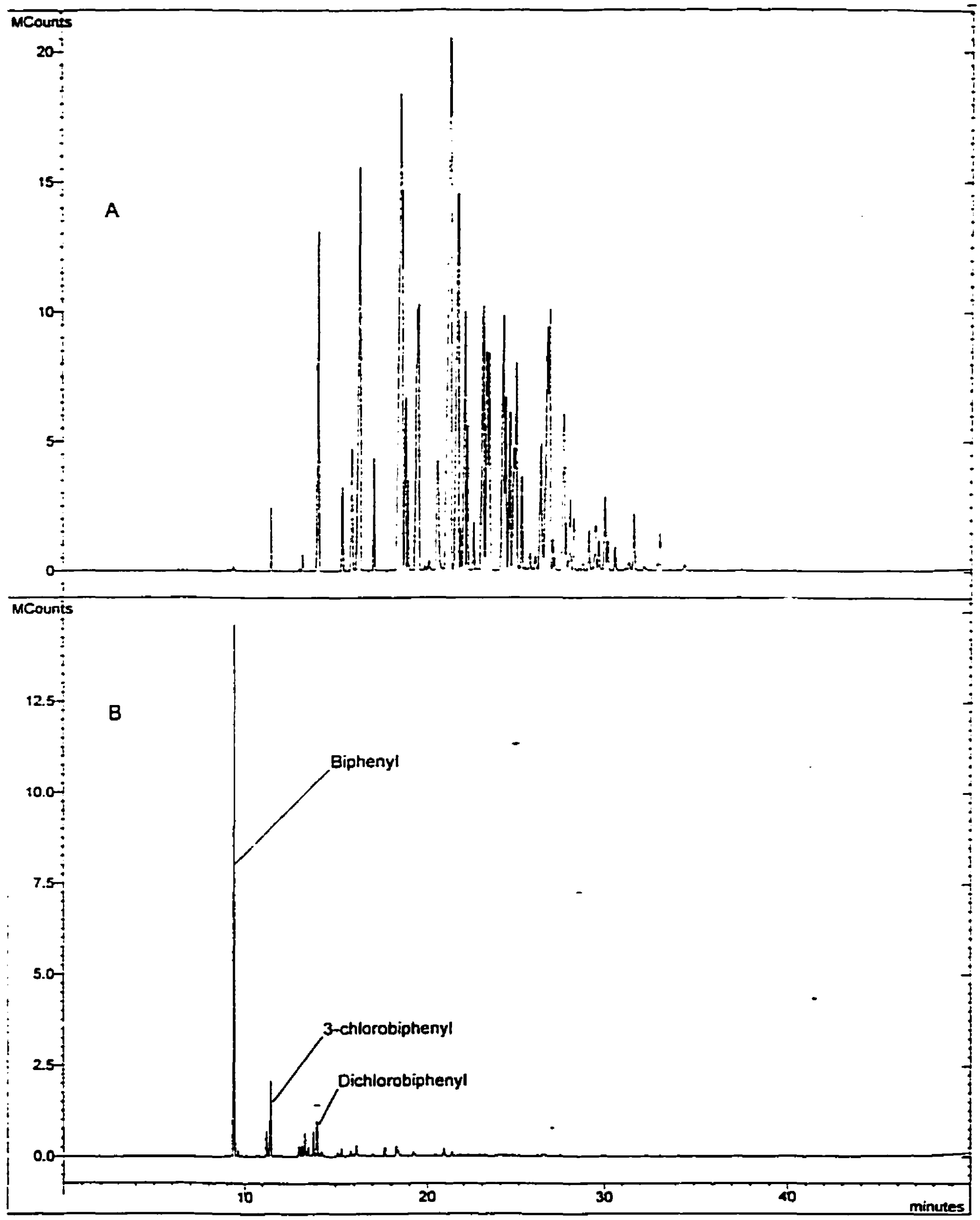


Figure 3.8 GC/MS chromatograms of Aroclor 1242. (A) starting material diluted to 20 mg/L. (B) spectrum of products that resulted from two Ag^{o}/Fe^{o} reactor columns connected in series (conducted at 400 °C and 4500 psi).

latter products (that were observed for 2% loadings of Aroclor 1242 in the mobile phase) are thought to arise via carboxylation and reductive catenation of the CO_2.

Having optimized the reaction conditions for virtually complete PCB dechlorination (based on the loss of organically-bound chlorine) a series of further trials were undertaken to corroborate the efficiency of the process. Initially, the temperature of the single Pd^o/Fe^o column was lowered to 300 °C and 20% (v/v) PCB feedstock in hexane was delivered to the reactor column at 0.1 ml/min. The mean recovery of organically-bound chlorine in successive traps of hexane was virtually quantitative at this temperature (Aroclor 1242, 99.0 ± 4.7%; Aroclor 1248, 103.9 ± 6.6%). Further experiments monitored the eluate for products that could be converted to biphenyl. Aliquots of eluate were reacted with Mg^o and K_2PdCl_6 to produce biphenyl. With 20% (v/v) 1242 in acetic anhydride (70% v/v) dimethoxyethane (10% v/v) as feed stock, the recovery of biphenyl was virtually quantitative, 99.1 ± 8.7% at 300 °C but was reduced to 84.0 ± 12.9% at 400 °C. For these trials, the reactor column was packed freshly prior to each trial. Despite equilibration with mobile phase in the absence of substrate, the contents of the first trap were converted to biphenyl less efficiently. Mean recoveries were based on traps two to six. These results indicated that at the higher operating temperature a portion of the biphenyl derivatives were further degraded on column. To demonstrate an active role for the zero-valent metal(s) in the dechlorinations, companion experiments wre also conducted using silica (sea sand) to fill the reactor column. With the optimized reaction conditions (400 °C, 4500 psi and 800 ml/min of decompressed flow), the mean recovery of substrate(s) in the six trapping solution that could be converted to biphenyl was virtually quantitative (104 ± 11%). Finally the chloride ion accumulated on the Pd^o/Fe^o column during 1 h of continued operation (optimizal operating conditions) as determined by titration of the wash water accounted for 99.6% of the total chlorine in the feedstock.

In further trials, acetone/hexane extract from a spiked sandy soil that had been extracted using a patented SESR (Solvent Extraction Soil Remediation Technology) were dechlorinated with a single Ag^o/Fe^o column maintained at 4500 psi and 400 °C. No chlorine containing materials were detected by GC-MS in the reactor eluate when acetone hexane extract supplemented with 30% (v/v) AcA, that had contained approximately 600 μg/ml PCBs, was fed continuously at 0.1 ml/min to the reactor. Of equal importance, soil co-extractives in the PCB solution did not affect either the course of the efficiency or the reaction perceptibly.

3.3.4 Conclusion

Based on the dechlorination results, it was presumed that the following chemical reactions participated in the dechlorination process:

(1) In the presence of zero-valent metal(s), propan-2-ol (or methanol) is converted to acetone (or formaldehyde) and two hydrogen atoms are released. In a redox reaction, the chlorine atom is reduced to chloride while the sacrificial zero-valent metal is oxidized to ferrous/ferric ion.

$$CH_3CH(OH)CH_3 \rightarrow CH_3C(O)CH_3 + 2H^{\bullet}$$

$$Fe^{0} \rightarrow Fe^{2+} + 2e^{-}$$

$$2C_{12}H_9Cl + 2H^{\bullet} + 2e^{-} \rightarrow 2C_{12}H_{10} + 2Cl^{-}$$

(2) In the presence of zero-valent metal, acetic anhydride reacts with solvent to produce ketone-like products and during this process a hydrogen atom is released. Under the influence of the zero-valent accelerator, the chlorine of PCB is substituted by a hydrogen atom and becomes reduced to chloride:

$$(CH_3CO)_2O + CH_3OCH_3 \rightarrow RC(O)CH_3 + H^{\bullet}$$

$$C_{12}H_9Cl + H^{\bullet} \rightarrow C_{12}H_{10} + Cl^{-}$$

(3) With the solvent reaction produced H^+, the catalyst (Pd or Ag) promoted PCB dechlorination could undergo multiple and/or single substitution process:

$$C_{12}H_{(10-n)}Cl_n + nH^{\bullet} \rightarrow C_{12}H_{(10-n)} + nCl^{-}$$

$$(C_{12}H_9Cl)_n + nH^{+} \rightarrow (C_{12}H_{10})_n + nCl^{-}$$

Successive dechlorinations are considered to be sequential rather than conserted. In summary, it has been demonstrated that zero-valent metal meditated reactions of Aroclor mixtures at elevated temperature in $scCO_2$ provides an efficient technique for PCB detoxification by dechlorination. The quantities of Aroclor 1242 or 1248 substrate that were dechlorinated efficiently (but not quantitatively) are considered to far exceed the burdens in concentrated extracts that could be isolated from polluted environmental matrices.

Chapter 4

Preface

In Chapter 3, an approach that can dechlorinate PCB mixtures (Aroclor 1242 and 1248) efficiently with heated columns of zero-valent metal or bimetallic mixture in a continuous process has been developed. The quantities of Aroclor 1242 or 1248 substrate that were dechlorinated efficiently (but not quantitatively) are considered to far exceed the burdens in the most concentrated extracts that *can* be isolated from polluted environmental matrices.

The following Chapter evaluates an approach/technique for the remediation of PCB contaminated soil. A wide range of surfactants are screened for suitability to extract PCB from contaminated soils *in combination* with $scCO_2$. Soils that had been historically contaminated with Aroclor 1242, 1248, 1254 and 1260 were be evaluated with *ex-situ* soil washing and *in-situ* soil flushing processes. Then the combined PCB-laden aqueous suspensions were to be back-extracted with $scCO_2$ and the eluate was anticipated to be dechlorinated as it traversed a short, heated column of silver-iron bimetallic mixture.

Approaches to the remediation of a polychlorinated biphenyl (PCB) contaminated soil

4.1 Introduction

Proposals for the restoration of soils that have been polluted with polychlorinated biphenyl (PCB) compounds have included incineration, solidification/vitrification (Erickson, 1997), phytoremediation (Dzantor *et al.*, 2000) bioremediation (Alder *et al.*, 1993) and electrokinetic (Kim *et al.*, 1999) approaches. These strategies, however, have been applied as treatments in the field only infrequently because of costs, environmental constraints and efficacy (Kovalick and Kingscott, 1996). Other more efficient methods for treating PCB contaminated soils continue to be proposed, optimized and evaluated (Abdul and Gibson, 1991).

In recent years, the use of surfactants has received increased attention as a means of enhancing the removal of organic contaminants from contaminated soils (Abdul *et al.*, 1990; Burchfield *et al.*, 1994; Huang *et al.*, 1997), especially for those situation when conventional "remove and treat" protocols have proven to be prohibitively costly (Weerasooriya *et al.*, 2000; Kim and Lee, 2000). Surfactants are attractive for the mobilisation/mass transfer of organic contaminants because of their reduced acute toxicity and their favourable rates of environmental degradation to innocuous products. Aqueous surfactant suspensions have been considered as more environmentally friendly than competing organic-solvent based extraction systems (Deshpande *et al.*, 1999; Beck *et al.*, 1997).

Surfactant enhanced soil remediations include both soil washing (*ex-situ*) and soil flushing (*in-situ*) (Scamehorn and Harwell, 2000). These processes become economically feasible only if they are of low cost. A further processing stage that is able to decontaminate the soil extract can help to increase its remediation value (Sabatini *et al.*, 1998) and often combinations of different techniques must be used during the processing

(Haegel *et al.*, 2000). Attractive combinations have involved surfactant recovery and re-use (Zhou and Rhue, 2000).

Other approaches to the removal of hydrophobic contaminants with volatile organic solvents or surfactants have been proposed and tested (Kim and Lee, 2000; Kitiyanan *et al.*, 2000). These separation methods have included: air-stripping or vacuum-stripping within packed columns, hollow fiber membrane contactors (Kitiyanan *et al.*, 2000), liquid-liquid extraction within a hollow fiber membrane contactor (Ang and Abdul, 1995) and pervaporation of surfactant solution (Vane *et al.*, 2000). Although their high removal efficiencies have encouraged researchers to evaluate these processes in the field, often they have not been sufficiently efficient, they have been environmental damaging or they have been viewed as being too expensive. More information of the effects of surfactants on the extraction operation and novel separation techniques remain to be identified/ optimized. Promising in this respect are the reports by Hawthorne and co-workers (1998) who mobilized PCBs from field-contaminated soil with pressurized sub-critical water and the report of Wai and co-workers (1999) who observed the virtually quantitative dechlorination of PCBs during extraction with sub-critical water in the presence of zero-valent iron.

Supercritical carbon dioxide ($scCO_2$) based separations possess several advantages over conventional extractions with organic solvents including cost, a lack of appreciable toxicity of the solvent, increased diffusivities and penetration rates through particulate media, high extraction efficiencies for relative non-polar analytes, and environmental friendliness (Bjorklund, 1999). For particulate matrices, extractions with $scCO_2$ are inherently batch processes in which the extractor is charged with soil, pressurized, extracted with $scCO_2$ then depressurized and the soil is replaced with fresh substrate before the cycle can be repeated. Conventionally, pressure within the extractor is maintained with a capillary restrictor (~50 μm i.d.) that is easily fouled with particles. Two stages of processing were chosen to minimize the fouling. PCBs were to be mobilized from the soil into an aqueous surfactant emulsion and then stripped from the water medium with $scCO_2$. It seemed probable that a surfactant could be identified that would promote the mobilization from soil but would be relatively insoluble in the $scCO_2$ and it was anticipated that the cleaned surfactant suspension could be recycled back to the soil to mobilize more toxicant. It also seemed to be inefficient to simply transfer the toxicants from one medium to another (soil to $scCO_2$) so that an *on-line* detoxification stage was envisaed for the process. The effluent from the $scCO_2$ extractor would be dechlorinated by passage through a short column of zero-valent bimetallic mixture at elevated temperature under conditions that had been demonstrated to dechlorinate a continuous stream of these substrate virtually quantitatively (Chapter 3, Wu and Marshall, 2001). This chapter focuses on the use of surfactants to mobilize PCBs from the PCB-surfactant suspension. Once in $scCO_2$, the dechlorination over Pd^o/Fe^o was also evaluated.

4.2 Materials and methods

4.2.1 Chemicals, solvents and surfactants

Magnesium granules (12~50 mesh, 99.8 % purity), potassium hexachloropalladate (K_2PdCl_6), cobaltous nitrate [$Co(NO_3)_2 \cdot 6H_2O$], and ammonium thiocyanate (NH_4SCN) were purchased from Alfa Aesar, Ward Hill, MA USA. Hexane, ethylene glycol dimethyl ether, isobutylmethyl ketone (IBMK, 99+%), methanol, methylene chloride (CH_2Cl_2), propan-2-ol (all HPLC grade), and glass wool were purchased from Fisher Scientific, Ottawa, ON. Biphenyl, surfactants, antifoam A, and antifoam B were purchased from Sigma-Aldrich, Oakvill, ON. All chemicals (ACS Reagent grade or better), solvents and surfactants were used as received.

The surfactants selected for study included anionic (Aereasol OT, sodium dodecyl sulfate) and nonionic chemicals (Brij 30, Brij 56, Brij 78, Brij 97, Brij 98, Triton X-100, Triton X-405, Triton X-705, Triton CF54, Triton DF16, Tween 20, Tween 40, Tween 60, Tween 80, Tween 85).

4.2.2 Soil samples and pre-treatment

The soil had been contaminated by polychlorinated biphenyl compounds for more than 30 years. The pH of the contaminated soil was 7.4 and organic matter content was 4.8%. The properties of this soil have been described elsewhere (Chapter 2, Wu and Marshall, 2000). The total PCB content was determined to be 30.3 ± 6.6 μg/g and involved Aroclors 1242, 1248, 1254 and 1260. Post sampling, the soil was air dried, mixed thoroughly, passed through a 2 mm sieve (10 mesh), and stored at 4 °C to await further treatment.

4.2.3 PCBs extraction/mobilization

In preliminary trials, 17 surfactants were screened to mobilize PCBs from an aqueous PCB-surfactant mixture into supercritical CO_2 ($scCO_2$). The aqueous suspension (25 ml) consisting of surfactant (3%,v/v), Aroclor 1242 (1%, v/v) and distilled water was supplemented with 5 ml IBMK, and the resulting suspension (30 ml) was well mixed and placed in a cylindrical supercritical fluid (SCF) extraction vessel [320 mm X 15 mm inner diameter (i.d.)]. The vessel was wrapped with a heating tape (Swagelok, Montreal) and heated to the operating temperature (30-80 °C) of the experiment. $ScCO_2$, provided by an $scCO_2$ pump (Newport Scientific Inc., Jessup, MD USA) was then added to the base of the extraction vessel and permitted to percolate up through the surfactant suspension and to accumulate within the headspace above the suspension. The fluid in the headspace was replaced continuously with fresh solvent from below and pressure within the system was maintained with a short section of flexible silica tubing (~25 cm x 50 μm i.d.) that terminated with the stainless steel transfer line and acted as a capillary restrictor. Extractor eluate was trapped in 25 ml hexane contained in a 50 ml test tube. Once suitable surfactants had been identified, $scCO_2$ extractions (second stage) were performed on PCB-surfactant mixtures at various temperatures.

The third stage consisted of evaluations of the optimized surfactant-extraction time-extraction temperature combinations to mobilize PCBs from the contaminated soil. Both sonication (soil washing) and soil flushing within soil packed column were evaluated. The sonication washing treatment was performed by placing the air dried soil sample (10g) into a fritted glass funnel (30 cm X 40 cm, Fisher Scientific), together with surfactant and the suspension was sonicated [Polytron homogenizing unit (N.Y. 11590, Brinkmann Instruments, Mississauga, ON) for 10 min prior to filtration under a gentle vacuum. Separate soil washes were performed with 1, 3, 5% (v/v) aqueous surfactant suspension and each extract was analyzed for PCB and surfactant content. Each sonication-vacuum filtration procedure was repeated 15 times with the same soil sample but with fresh surfactant suspension each time.

An empty HPLC column [30 cm X 1 cm (i.d.) Swagelok, Montreal, QC] was used to perform the soil column flushing experiments. Soil (30g) was packed into the column and terminated with a coarse filter at both column ends. The column was mounted horizontally and flushed for 20 h (1.0 ml/min) with 1, 3 or 5% (v/v) surfactant suspension delivered from an HPLC pump (model 100A, Altex Scientific, Berkley. CA). The effluent was analyzed at hourly intervals for PCB and surfactant content.

Finally, the cumulative soil extracts were back-extracted with $scCO_2$ under the optimized mobilization conditions to recover the PCBs from the surfactant suspension. PCBs that had been extracted into $scCO_2$, were dechlorinated with zero-valent bimetallic mixture (Ag^o/Fe^o) and the cleaned surfactant suspension in the retentate was then re-used for the soil PCB extraction.

4.2.4 PCB analysis

The total content of PCBs in soil was determined by gas chromatography equipped with flame ionization detection (GC-FID) or a Hewlett-Packard model 5890 (series II) gas chromatography equipped with a model 5971 mass selective detector (GC-MS). Both methods were described previously (Wu and Marshall, 2000; 2001). In brief, the PCB concentration in soil extracts was determined by conversion of PCB residues to biphenyl. Magnesium flakes (1 g, 12-50 mesh), potassium hexachloro-palladate (K_2PdCl_6), 2 mg, propan-2-ol (2 ml), and 2 ml soil extract were combined in a 50 ml flask. The mixture was vortex stirred for 1 min, and repeated at approximately 2 h intervals. After 10 h reaction, the biphenyl was extracted into hexane (1 ml) and quantified as described previously (Chapter 2). The estimation of PCB content was based on the calibrations using Aroclor 1260.

4.2.5 Surfactant analysis

The Standard Analysis Method, APHA (Dreebberg *et al.*, 1992), was followed to determine the surfactant concentration in both soil and in the micelle suspension post treatment. Because anionic surfactants proved to be unsuitable, analysis was performed only for nonionic surfactants. A standard calibration curve was generated for each nonionic surfactant. Micellar-suspension (1 ml) was diluted (0-10 fold) to obtain a suitable working concentration. Diluted surfactant suspension (2 ml) contained in a 100 ml flask, was evaporated to dryness on a water bath. The residues were triturated with methylene chloride (10 ml) and the resulting extract was added to a 125-ml separatory funnel containing 5 ml cobaltous thiocyanate solution. After 60s vigorous shaking and phase separation, the lower aqueous layer was transferred, via a funnel containing a plug of glass wool, to a 5 ml spectrophotometer cell. The absorbance, at 620 nm, was determined *vs.* a blank of CH_2Cl_2.

4.3 Results and discussion

4.3.1 Surfactant screening

Seventeen surfactants were screened in this study. Each of the surfactants, along with its relevant properties is listed in Table 4.1. The factors that influenced selection for further study included an ability to increase the mobilization of Aroclor 1242 into $scCO_2$, a lack of appreciable foaming during the extraction process and efficient recovery of surfactant in the aqueous retentate. Surfactant suspension that could be extracted with $scCO_2$ during 30 min, without the addition of antifoaming reagent and/or co-solvent(s) and with only minimal losses to the mobile phase were to be selected. Aqueous mixtures of PCB-surfactant suspension (1% or 3%, v/v) could be extracted with $scCO_2$ if IBMK [17% (v/v)] was added to the suspension coupled, in exceptional cases, with supplementing the $scCO_2$ mobile phase with IBMK (0.4 or 0.2 ml/min added prior to its entry into the extraction vessel).

4.3.2 PCB mobilization from aqueous surfactant suspension

To optimize the extraction conditions, suspensions of 1% (v/v) Aroclor 1242 with each of four selected surfactants [Brij 97, Triton CF54, Triton DF16 or Tween 85, (3%, v/v)] and 5 ml IBMK were extracted with $scCO_2$ (4500 psi and 30–80 °C) for either 30 or 60 min. For suspensions of PCB and Brij 97 that had been extracted for 30 min, mobilization efficiencies increased with increased operating temperature (Figure 4.1). However, the content of Brij 97 in the retentate also decreased substantially with increased operating temperature. As summarized in Table 4.2, the quantity of mobilized PCBs was only 15% for 30 min of extraction at 30 °C, however the content of Brij 97 in the retentate remained

Table 4.1 Chemical and physical characteristics of surfactants selected for the PCB extraction study*.

Trade name	Chemical structure	HLB[a]	Viscosity (cp)	Molecular weight
Anionic				
SDS	Sodium dodecyl sulfate		1.12	288
Aerosol OT	Dioctyl sulfosuccinate		0.95	445
Nonionic				
Brij 35	POE(10) lauryl ether	16.9	1.21	1198
Brij 56	POE(10) cetyl ether	12.9		683
Brij 78	POE(20) stearyl ether	15.3		1152
Brij 97	POE(10) lauryl ether	12.4	1.28	
Brij 98	POE(20) oleyl ether	15.3	1.38	1150
Triton X-100	POE(10) isooctylphenyl ether	13.5		624
Triton X-114	POE(8) isooctylphenyl ether	12.4		
Triton X-405	POE(40)-(aromatic ring)6-(CH)8	17.9		1966
Triton CF54	Alkylaryl Polyether	13.6		
Triton DF16	POE linear alcohol			
Tween 20	POE(20) sorbitan monolaurate	16.9	1.19	1266
Tween 40	POE(20) sorbitan monopalmitate	15.6	1.18	
Tween 60	POE(20) sorbitan monostearate	14.9		1312
Tween 80	POE(20) sorbitan monoleate	15	1.19	1310
Tween 85	POE(20) sorbitan monolaurate	11		1840

*: Source from Kim and Lee (2000); Zhou and Rhue (1985).

[a]: HLB: Hydrophilic-Lipophilic Balance.

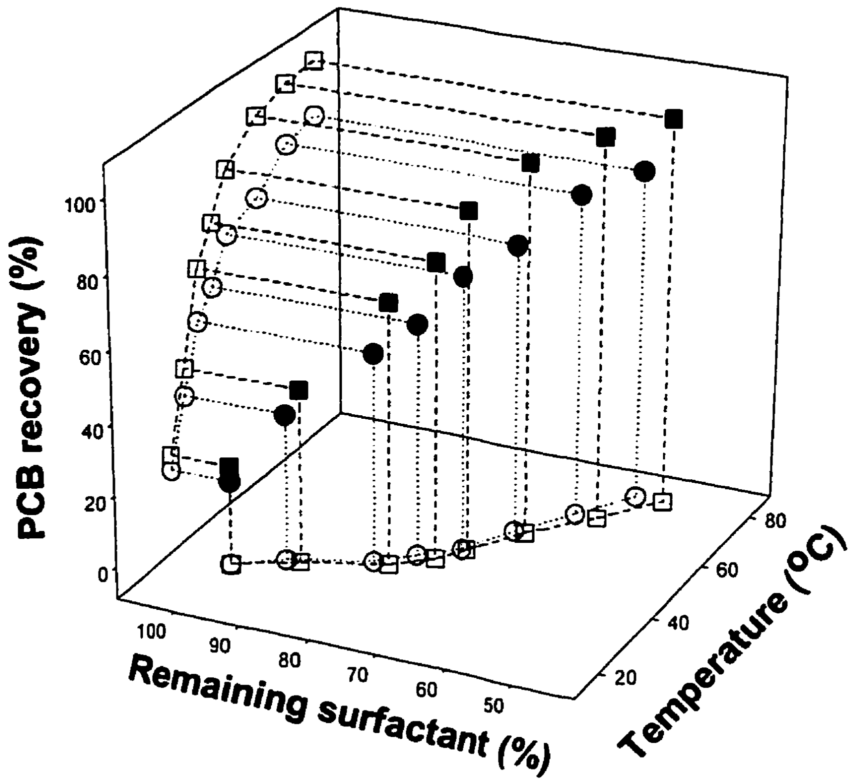


Figure 4.1 PCB mobilization efficiency (%) as a function of operating temperature and surfactant remaining with the aqueous phase (%) for 30 min (●) or 60 min (■) of $scCO_2$ extraction, at 4500 psi, from suspensions containing Brij97 surfactant.

Table 4.2. Remaining surfactant concentrations in the extracts after soil PCB extraction/flushing treatments

Surfactants	Brij 97			Triton CF54			Triton DF16			Tween 85		
Concentration	1%	3%	5%	1%	3%	5%	1%	3%	5%	1%	3%	5%
Sonication treatment No.												
1	68.6± 6.9	76.1± 7.1	79.4± 4.3	62.1± 6.3	74.6± 5.6	80.1± 4.7	63.4± 5.4	70.6± 5.1	78.6± 4.8	60.3± 3.6		
2	80.2± 4.2	89.3± 3.9	92.8± 4.0	83.8± 4.8	87.5± 3.9	94.8± 3.2	78.6± 4.1	86± 3.8	95.2± 3.1	72.5± 4.2		
3	90.1± 2.1	93.5± 2.7	98.5 ± 1.9	91.8± 3.0	98.2± 2.5	99.1± 2.2	89.8± 3.0	98± 2.3	99.5± 2.2	80.9± 2.7		
4	95.6± 1.6	98.0± 1.7	100± 2.0	97.9± 2.3	99± 1.7	100± 1.3	98.9± 2.1	100± 1.5	100± 1.4	89.3± 4.8		
5	99.0± 2.0	100± 1.1	100± 1.8	100± 1.2	100± 1.3	100± 1.0	100± 2.0	100± 1.4	100± 1.2	95.5± 4.6		
Column flushing (min)												
10	32.4± 13.9	38.6± 10.1	43.2± 8.9	37.8± 9.9	42.4± 5.8	45.7± 6.5	39.4± 8.6	40.5± 6.7	47.1± 6.6	43.5± 6.7	47.6± 6.4	48.2± 7.1
20	47.2± 9.8	53.2± 8.9	60.4± 5.5	49.7± 6.5	53.9± 4.5	57.8± 4.1	47.5± 5.8	52.8± 5.4	60.2± 4.5	50.9± 6.8	58.5± 4.5	66.5± 6.1
30	66.3± 7.4	69.7± 5.5	76.8± 3.5	64.9± 4.4	68.9± 2.3	71.9± 3.3	68.1± 4.6	65.7± 3.7	73.2± 4.5	71.4± 4.5	73.6± 3.3	77.7± 4.6
40	75.7± 5.7	80.7± 4.6	89.8± 3.5	79.9± 2.9	83.2± 3.9	87.4± 2.8	78.8± 3.8	85.6± 3.6	88.9± 3.1	83.5± 4.6	88.8± 4.7	90.9± 3.6
50	82.6± 5.4	89.6± 3.6	95.6± 2.7	88.5± 2.4	93.6± 2.9	96.5± 3.7	89.2± 3.5	92.6± 3.2	97.4± 3.4	92.2± 3.8	96.8± 3.9	98.1± 2.4
60	95.8± 4.5	99.8±2.3	99.8± 1.0	98.9± 2.5	98.4± 2.5	99.2± 2.6	97.9± 3.4	99.4± 2.4	98.8± 3.5	100± 2.3	99.6± 2.4	99.2± 1.3
70	98.9± 2.6	99.9± 1.6	99.9± 1.0	100± 1.6	100± 0.5	100± 1.0	100± 1.5	100± 1.7	100± 2.1	100± 1.4	100± 2.0	100± 1.7

virtually unchanged (99.9%) for extraction at this temperature. The PCB mobilization increased to 80% when the extraction was conducted at 80 °C, however the remaining content of Brij 97 was reduced to 58%. Linear regression (Table 4.3) of three factors (PCB recovery, extraction temperature, and surfactant content that remained with the aqueous retentate) indicated that the quantity of PCB and the quantity of Brij 97 surfactant that was mobilized were both related linearly to the operating temperature. Increased operating temperatures enhanced PCB extraction efficiencies but reduced the content of surfactant that remained with the aqueous suspension.

The PCB mobilization efficiency reached 99% if the extraction was continued for 60 min at 60 °C (Table 4.2, Figure 4.1). The quantity of Brij 97 that remained in the treated suspension did not changed substantially when 30 min mobilization (58% retention) was increased to 60 min (54% retention) for extraction at 80 °C. The three-factor linear regression model (Table 4.3) again indicated that the PCB extraction efficiency was related linearly to extraction temperature and increased substantially with increases in this parameter. For the Brij 97 surfactant, the optimized PCB mobilization conditions included supplemental IBMK (0.4 ml/min) that was merged with the $scCO_2$ stream prior to entry into the extraction vessel.

Extraction with 3% (v/v) Triton CF54 were characterized by analogous but not identical results. During the extraction, foaming was readily controlled and 45% of the PCBs were mobilized from the suspension during 30 min of extraction at 30 °C (Table 4.2). Approximately 92% of the surfactant was recovered in the retentate under these conditions. The PCB extraction efficiencies increased with the increased extraction temperature (Figure 4.2), while the remailng content of Triton CF54 in the retentate was decreased appreciably. The PCB mobilization was increased to 92% when the extraction was performed at 80 °C, however, the remaining Triton CF54 in the retentate was decreased to 30% of its initial value. The optimized linear regression model (Table 4.3) indicated that the PCB extraction efficiency was positively related to the operating temperature, but that the content of surfactant in the retentate was negatively related to the temperature.

Table 4.3 Linear regression models for three factors consisting of PCB mobilization efficiency, percent of initial surfactant remaining in the retentate and processing temperature for 30 or 60 min of extraction.

Surfactant	30 min of extraction [a,b]	R^2	60 min of extraction [a,b]	R^2
Brij 97	% PCBs mobilized = 3.5(S)+0.7(T) -6.4	0.998	% PCBs mobilized = 1.4(S)+2.9(T) -68.8	0.996
Triton CF54	% PCBs mobilized = 0.9(S)+2.1(T) +79.0	0.999	% PCBs mobilized = -1.2(S)+0.9(T) +14.0	0.996
Triton DF16	% PCBs mobilized = 0.4(S)+0.6(T) +67.5	0.996	% PCBs mobilized = 0.3(S)+0.7(T)+82.0	0.994
Tween 85	% PCBs mobilized = -2.9(S)+4.9(T) +143.3	0.982	% PCBs mobilized = 12.4(S)-13(T)+130.8	0.989

[a] : S = percent of initial surfactant content remaining in the treated solutions.

[b] : T = extraction temperature.

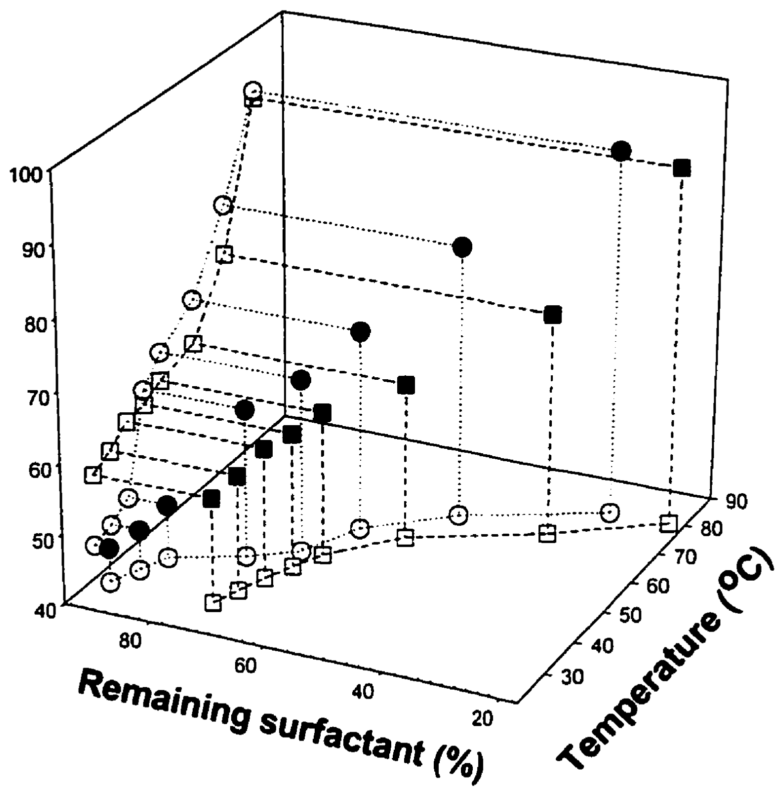


Figure 4.2 PCB mobilization efficiency (%) as a function of operating temperature and surfactant remaining with the aqueous phase (%) for 30 min (●) or 60 min (■) of $scCO_2$ extraction, at 4500 psi, from suspensions containing Triton CF54 surfactant.

The mobilization of Aroclor 1242 was 91% at 80 °C after 60 min, but the content of Triton CF54 that remained with the retentate was only 20% (Table 4.3). When the mobilization was performed at 30 °C, the PCB recovery was 55% and the remaining surfactant content was 74% of its initial value. Unlike the PCB-Brij 97 suspension, approximately 55% of the PCBs was extracted from the PCB-Triton CF54 mixture and 65% of this surfactant was retained by the aqueous suspension post treatment at 50 °C. The linear regression model (Table 4.3) again indicated that operating temperature was positively related to PCB mobilization efficiency but negatively related to the content of remaining surfactant. For mobilizations from Triton CF54 suspensions, it was necessary to supplement the $scCO_2$ mobile phase with 0.2 ml/min IBMK.

PCB mobilization from an aqueous suspensions of Aroclor 1242 and Triton DF16 (3%, v/v) were more efficient, however the quantity of surfactant remaining was relatively lower (Figure 4.3, Table 4.3). The PCB extraction efficiency reached 100% for extraction at 60 °C (or higher) during 30 min, however, the content of remaining surfactant was only 20% (or less). Most of PCB (80%) was mobilized during 30 min at 30 °C and 52% the DF16 surfactant remained in the extraction vessel.

It was possible to mobilize the 1242 mixture very efficiently at various temperatures if the extraction was continued for 60 min. The quantity of mobilized PCB was 91.6% for extraction at 30 °C and 100% at 50 °C (Figure 4.3). However, most of surfactant was co-extracted at the same time. Post processing, the remaining content of Triton DF16 was 40% at 30 °C and only 20% at 50 °C. The linear regression model (Table 4.3) again indicated that extraction temperature was positively related to the PCB mobilization efficiency but negatively related to the remaining content of DF16 surfactant. Increased extraction temperatures did not reduce the remaining quantity of surfactant substantially. It was not necessary to supplement the $scCO_2$ mobile phase with IBMK during extractions of PCB-DF16 suspensions. The addition of IBMK (5 ml) directly to 25 ml of the aqueous suspension was sufficient.

Extraction efficiencies of the aqueous suspensions containing Tween 85 (3%, v/v) depended on the temperature of the extractions. For lower extraction temperatures, PCB recoveries from Tween 85 mixture were relatively higher than from PCB-Brij 97 mixture but lower than from PCB-Triton suspension. The amount of PCB mobilized during 30

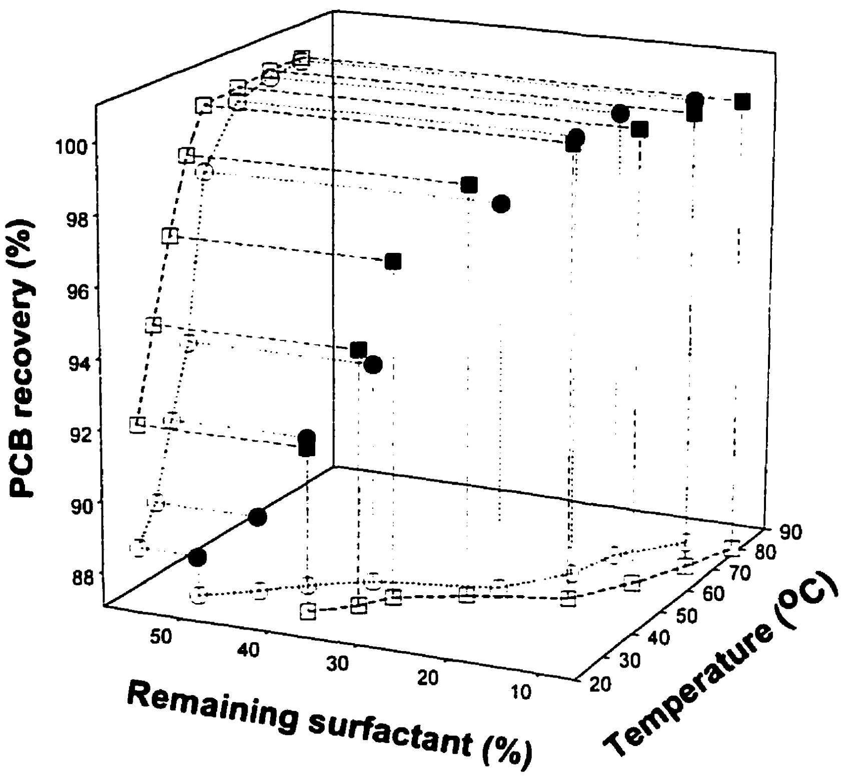


Figure 4.3 PCB mobilization efficiency (%) as a function of operating temperature and surfactant remaining with the aqueous phase (%) for 30 min (●) or 60 min (■) of $scCO_2$ extraction, at 4500 psi, from suspensions containing Triton DF16 surfactant.

min from Tween 85 mixture was 34% at 30 °C and the remaining content of surfactant was 80%. The PCB extracted at 80 °C was 96% and the remaining surfactant content was 34%. Extraction efficiencies again increased with increased operating temperature (Figure 4.4, Table 4.3).

PCB extraction efficiencies were increased substantially for 60 min mobilizations and reached 60% at 30 °C whereas the remaining surfactant content was 72%. If the extraction was performed at 50 °C or above, PCB extractions became quantitative but the content of remaining surfactant was decreased, 50% at 50 °C but only 30% at 80 °C. The experimental results demonstrated that extractions could be effected smoothly if 5 ml IBMK was added to the PCB-Tween 85 mixture (25 ml) prior to extraction.

In summary, optimal surfactant performance was in the order: Tween 85>Triton DF16> Triton CF54> Brij 97.

4.3.3 PCB extraction/mobilization from soil

Since surfactant, at concentrations less than their critical micelle concentrations (CMC), have been reported to promote the sorption of PCBs to soil particles during extraction (Kim and Lee, 2000), the same surfactant at 1, 3 or 5% (v/v) were evaluated for PCB mobilization from the contaminated soil. Both *ex-situ* sonication-washing and *in-situ* flushing of a packed soil column were evaluated. To optimize the sonication treatment with the soil-surfactant suspensions, Brij 97 was selected to define a suitable sonication time. PCB mobilization efficiencies from 10g soil, increased moderately with increased sonication times (Figure 4.5). Although 15-min of sonication mobilized more PCB than the 10-min treatment that, in turn, was more efficient than the 5-min treatment, appreciable foam formation was observed with the later washes. Therefore, 10 min of sonication was employed in subsequent trials. A single "exponential rise to a maximum" term provided an expression that modelled the experimental data accurately. The cumulative percent PCBs mobilized was modelled as the sum of a constant plus an exponential term that took the form $A(1-e^{\lambda x})$ where A is a coefficient, λ is a "time" constant and x represents the number of successive sonication-washings. The optimised models indicated that "t_{50}", the number of sonication-washings required to mobilise one-half of the extractable fraction of total PCB soil burden, was 4.08 and 2.20 for 5-min and

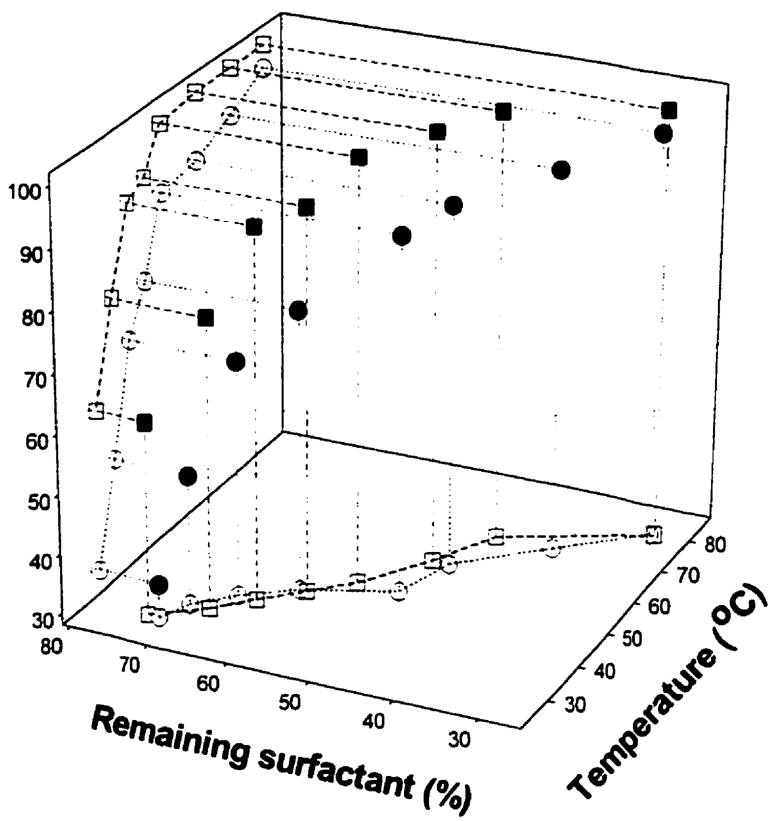


Figure 4.4 PCB mobilization efficiency (%) as a function of operating temperature and surfactant remaining with the aqueous phase (%) for 30 min (●) or 60 min (■) of $scCO_2$ extraction, at 4500 psi, from suspensions containing Tween 85 surfactant.

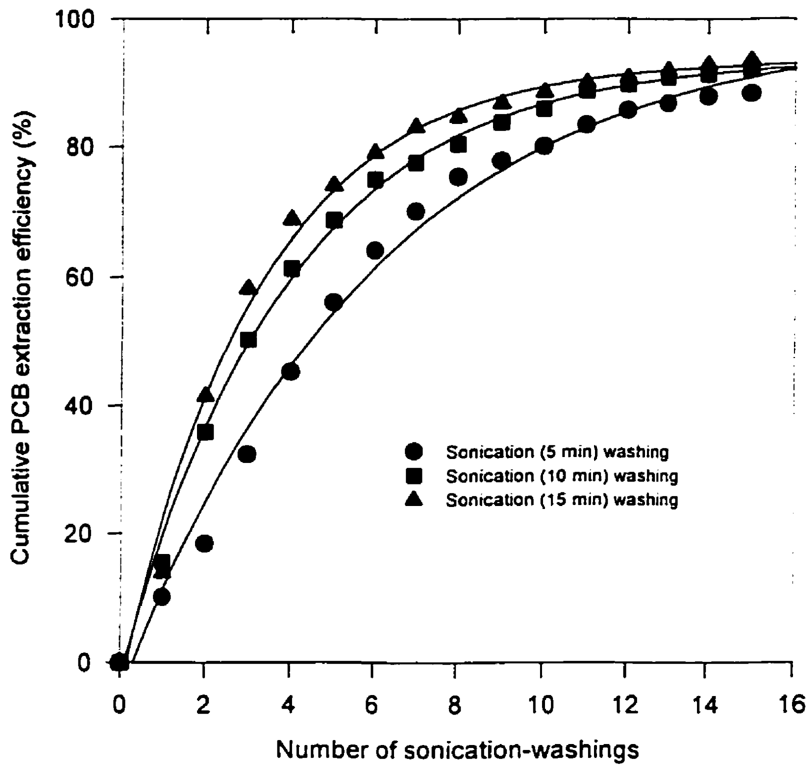


Figure 4.5 Cumulative extraction efficiency from soil (10g) in consecutive 10 ml washes with Brij 97 aqueous suspension (3% v/v) following sonication for 5 min, 10 min or 15 min. The best fit curves were generated with a model consisting of a single exponential increase to a maximum.

10-min treatments respectively. The inclusion of additional exponential terms in the model did not increase the goodness of fit to the experimental data. Thus, there was no evidence for the existence of separate fractions of soil-PCBs that could be differentiated based on their rates of mobilization. This contrasts an earlier report (Bjorklund *et al.*, 1999) that described the $scCO_2$ fractionation of soil-PCBs from "rapidly desorbing, moderately, slowly and very slowly desorbing" sites. If present, the differences in the fractions were masked by including the IBMK within the aqueous slurry.

As illustrated in Figure 4.6, 87%, 92%, or 95% of the PCBs were extracted from the soil (10g) with 15 consecutive sonication-washing treatments using 1%, 3% or 5% (v/v) Brij 97 suspension respectively. An increased concentration of surfactant in the aqueous suspension enhanced PCB extraction (Bjorklund *et al.*, 1999), however, recoveries from 3 or 5% suspension were not significantly different from each other. A single exponential increase to a maximum modelled the experimental data accurately for all three concentrations and indicated "t_{50}" values of 6.93, 2.98 and 2.89 sonication-washes for the 1%, 3% and 5% surfactant solutions respectively. The standard error of estimate (a parameter of goodness of fit) were satisfyingly low (1.94, 1.59 and 3.57 respectively). The mean PCB content remaining in the soil post sonication–washing (± 1 relative standard deviation, RSD) was 2.4 ± 0.6, 1.6 ± 0.3 and 1.5 ± 0.4 μg/g (dry weight basis) for the 1, 3 and 5% (v/v) surfactant suspensions respectively (Table 4.4). The loss of Brij 97 surfactant from the soil suspension was appreciable for the early washes (Table 4.5) but losses became negligible in the later fractions indicating that sorption to soil particles was the principle route of loss. Once the soil had become saturated with surfactant, further losses were negligible. The net percent loss (by difference) to the soil (Table 4.6) was 3.6 ± 3.3, 8.4 ± 4.5 or 10.4 ± 5.6 for the 5%, 3% or 1% Brij 97 treatments respectively. The results of packed column soil flushing trials (Figure 4.6), hollow symbols) were rather similar to the observations in the soil washing experiments. Most of PCBs (>95%) had been extracted/mobilized after 20 h (1200 ml) of continued flushing with 5% (v/v) Brij 97 suspension. Decreasing the concentration of surfactant in the carrier reduced the extraction efficiency. For 1% Brij 97 suspension, 85% of the PCB soil burden had been mobilized after 20h of flushing (Figure 4.6) and differences in extraction

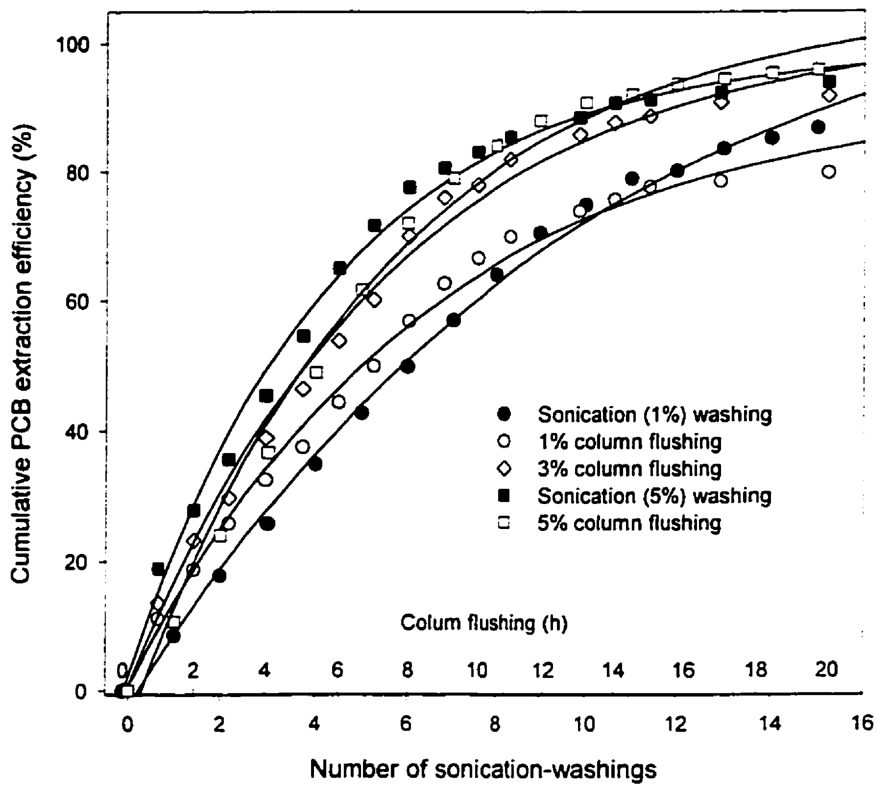


Figure 4.6 Cumulative PCB extraction efficiencies for mobilizations from 10g soil by sonication (10 min)-washing with 1% or 5% or by continuous flushing from 30g soil with 1%, 3% or 5% aqueous suspension of Brij 97 surfactant.

Table 4.4 Residual PCB concentrations (ug/g, dry weight ± 1 RSD based on 3 separate determinations) in soil post 15 consective sonication-washing or continuous flushing during 20h.

	Brij 97			Triton CF54			Triton DF16			Tween 85		
	1%	3%	5%	1%	3%	5%	1%	3%	5%	1%	3%	5%
Sonication-washing	2.4 ± 0.6	1.6 ± 0.3	1.5 ± 0.4	1.0 ± 0.2	0.3 ± 0.1	0.2 ± 0.1	1.5 ± 0.2	0.2 ± 0.1	0.2 ± 0.1	4.8 ± 05	-----	-----
Column flushings	2.7 ± 0.4	2.1 ± 0.5	1.5 ± 0.3	1.2 ± 0.3	0.8 ± 0.2	0.4 ± 0.2	2.8 ± 0.1	0.9 ± 0.2	2.1 ± 0.2	2.0 ± 0.3	1.8 ± 0.3	2.9 ± 0.4

Table 4.5 Surfactant content (%) remaining in the extract post soil sonication-washing (10g) or continuous column flushing (30g)

Surfactants	Brij 97			Triton CF54			Triton DF16			Tween 85		
Concen.	1%	3%	5%	1%	3%	5%	1%	3%	5%	1%	3%	5%
Sonication treatment No.												
1	68.6± 6.9	76.1± 7.1	79.4± 4.3	62.1± 6.3	74.6± 5.6	80.1± 4.7	63.4± 5.4	70.6± 5.1	78.6±4.8	60.3± 3.6		
2	80.2± 4.2	89.3± 3.9	92.8± 4.0	83.8± 4.8	87.5± 3.9	94.8± 3.2	78.6± 4.1	86± 3.8	95.2± 3.1	72.5± 4.2		
3	90.1± 2.1	93.5± 2.7	98.5± 1.9	91.8± 3.0	98.2± 2.5	99.1± 2.2	89.8± 3.0	98± 2.3	99.5± 2.2	80.9± 2.7		
4	95.6± 1.6	98.0± 1.7	100± 2.0	97.9± 2.3	99± 1.7	100± 1.3	98.9± 2.1	100± 1.5	100± 1.4	89.3± 4.8		
5	99.0± 2.0	100± 1.1	100± 1.0	100± 1.2	100± 1.3	100± 1.0	100± 2.0	100± 1.4	100± 1.2	95.5± 4.6		
Column flushing (min)												
10	32.4± 13.9	38.6± 10.1	43.2± 8.9	37.8± 9.9	42.4± 5.8	45.7± 6.5	39.4± 8.6	40.5± 6.7	47.1± 6.6	43.5± 6.7	47.6± 6.4	48.2± 7.1
20	47.2± 9.8	53.2± 8.9	60.4± 5.5	49.7± 6.5	53.9± 4.5	57.8± 4.1	47.5± 5.8	52.8± 5.4	60.2± 4.5	50.9± 6.8	58.5± 4.5	66.5± 6.1
30	66.3± 7.4	69.7± 5.5	76.8± 3.5	64.9± 4.4	68.9± 2.3	71.9±3.3	68.1± 4.6	65.7± 3.7	73.2± 4.5	71.4± 4.5	73.6± 3.3	77.7± 4.6
40	75.7± 5.7	80.7± 4.6	89.8± 3.5	79.9± 2.9	83.2± 3.9	87.4± 2.8	78.8± 3.8	85.6± 3.6	88.9± 3.1	83.5± 4.6	88.8± 4.7	90.9± 3.6
50	82.6± 5.4	89.6± 3.6	95.6± 2.7	88.5± 2.4	93.6 ± 2.9	96.5± 3.7	89.2± 3.5	92.6± 3.2	97.4± 3.4	92.2± 3.8	96.8± 3.9	98.1± 2.4
60	95.8± 4.5	99.8± 2.3	99.8± 1.0	98.9± 2.5	98.4± 2.5	99.2± 2.6	97.9± 3.4	99.4± 2.4	98.8± 3.5	100± 2.3	99.6± 2.4	99.2± 1.3
70	98.9± 2.6	99.9± 1.6	99.9± 1.0	100± 1.6	100± 0.5	100± 1.0	100± 1.5	100± 1.7	100± 2.1	100± 1.4	100± 2.0	100± 1.7

Table 4.6 Surfactant content remaining with the aqueous phase post soil flushng soilsonication washing or remediation of the eluate by back-extraction with $scCO_2$

Surfactants	Brij 97			Triton CF54			Triton DF16			Tween 85		
Concentrations	1%	3%	5%	1%	3%	5%	1%	3%	5%	1%	3%	5%
Surfactant content (%) in eluate post soil sonication-washing	89.6 ± 6	91.6 ± 5	96.4 ± 3	90.1 ± 4	95.6 ±4	98.1 ± 3	91.4 ± 5	96.6 ± 3	98.6 ±4	80.1 ± 7	-----	-----
Surfactant content (%) in eluate post soil colum flushing	90.6 ± 4	93.4 ± 4	97.6 ± 4	89.3 ± 4	94.9 ± 4	98.8 ± 3	92.3 ± 3	95.7 ± 3	97.7± 3	85.6 ± 7	90.8 ± 6	92.3 ± 5
Surfactant content (%) in aqueous retentate post $scCO_2$ extraction	70.2 ± 4	76.3 ± 6	78.8 ± 5	60.9 ± 5	66.6 ± 5	75.3 ± 5	20.3 ± 6	23.6 ± 5	31.6 ± 5	45.3 ± 6	48.6 ± 5	58.8 ± 3

efficiencies between the 3% and 5% Brij 97 suspensions were not significant. The mean PCB contents in the soil post flushing (± 1 RSD) were 2.7 ± 0.4, 2.1 ± 0.5 and 1.5 ± 0.3 μg/g for the 1, 3 and 5% aqueous suspension respectively (Table 4.4). The residual quantities of surfactant sorbed to the soil post flushing were similar to the quantities observed for the sonication-washing experiments. Quantities of surfactant in the extract post processing did not differ greatly (Table 4.6) from the quantities present in the suspension prior to processing.

The PCB extractions from soil by sonication-washing with Triton CF54 were reasonably efficient. As illustrated in Figure 4.7, the quantities of mobilized PCB were 80.1%, 91.1% and 93.5% for aqueous suspensions of 1%, 3% and 5% respectively. The single exponential rise to a maximum also accurately modelled the experimental observations with the CF54 surfactant. Values for t_{50} of 5.74, 5.73 and 2.94 sonication-washing and 3.95, 2.85 and 2.92 h of flushing were predicted for the 1, 3 and 5% suspensions. The quantities of PCBs in the soil post treatment with 1%, 3% or 5% Triton CF54 were 1.0 ± 0.2, 0.3 ± 0.1 and 0.2 ± 0.1 μg/g respectively (Table 4.4). Results for soil column flushing with this surfactant were comparable to extractions by sonication-washing (Figure 4.7, hollow symbols). The PCB extraction was enhanced when the concentration of CF54 was increased from 1% to 3% (v/v) but a further increase from 3% to 5% did not significantly increase the mobilization further. The amount of PCB that remained in the treated soil was 1.2 ± 0.3, 0.2 ± 0.2 or 0.4 ± 0.2 μg/g for flushing with 1%, 3% or 5% Triton CF54 suspension (Table 4.4).

PCB sonication-washing treatments with Triton DF16 proved to be the most efficient among the four surfactants (Figure 4.8). The efficiency of PCB purging from the soil was 89%, 95% and 97% for 1%, 3% and 5% suspension respectively. Analyses of variance (ANOVA) indicated that differences in efficiency among the treatments were not significant. The PCB contents remaining with the soil post washing were 1.5 ± 0.2, 0.2 ± 0.1 and 0.2 ± 0.1μg/g for the 1%, 3% or 5% DF16 suspensions. Soil flushing treatments with Triton DF16 provided analogous results (Figure 4.8, hollow symbols). The quantities of mobilized PCBs were 89%, 95% or 97% with suspensions of 1%, 3% or 5% respectively. The residual PCB contents in the treated soil were 2.8 ± 0.4, 0.9 ± 0.2 and 2.1 ± 0.3 μg/g after flushing with 1%, 3% and 5% DF16 suspension respectively.

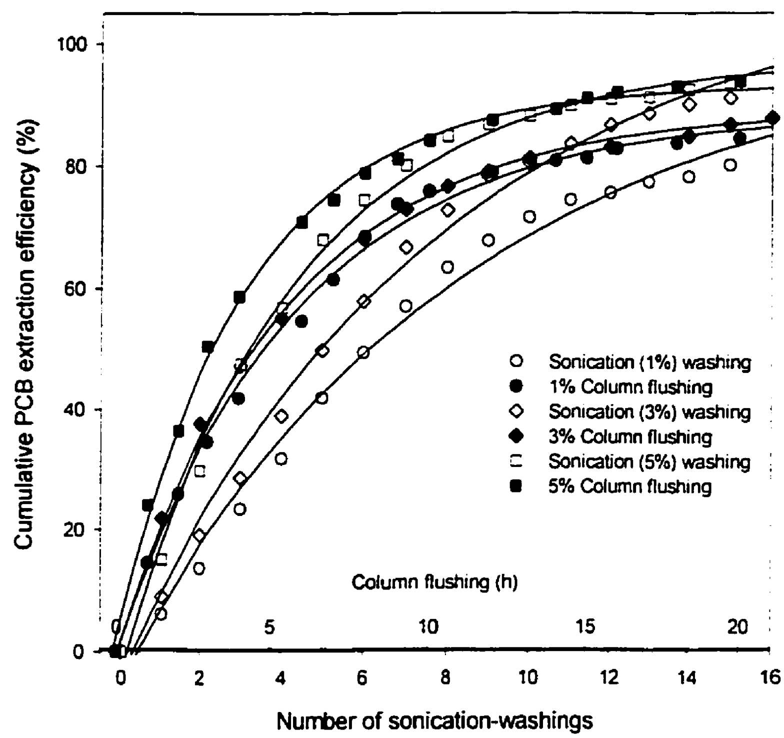


Figure 4.7 Cumulative PCB extraction efficiencies for mobilizations from 10g soil by sonication (10 min)-washing with 1%, 3% or 5% or by continuous flushing from 30g soil with 1%, 3% or 5% aqueous suspension of Triton CF54 surfactant.

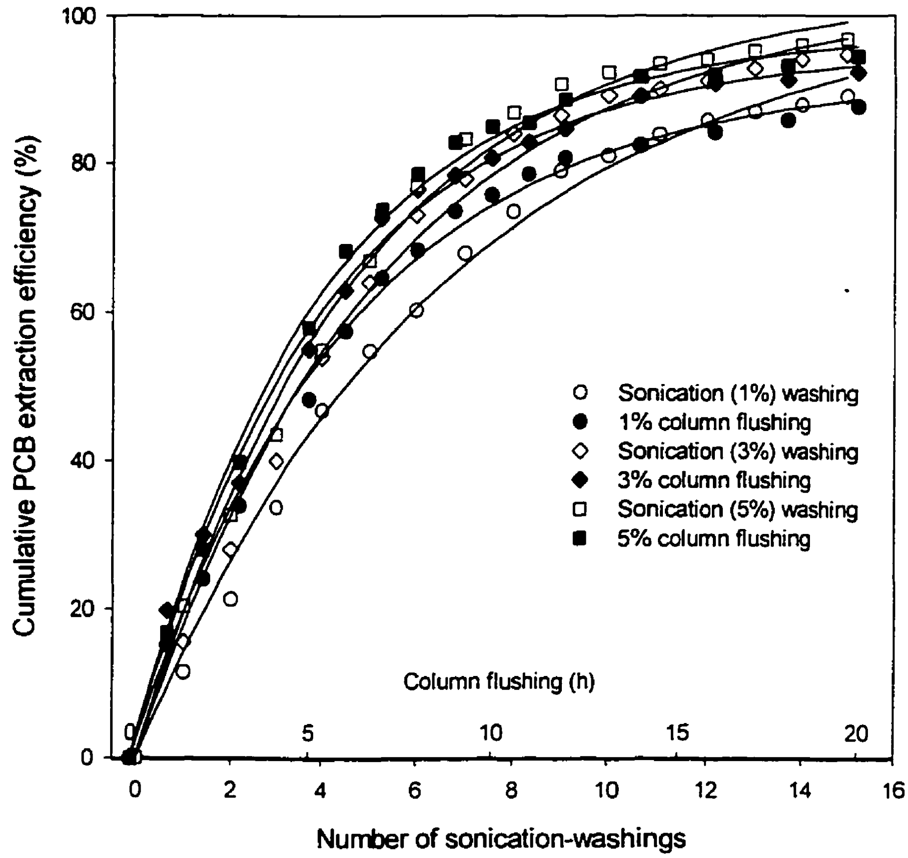


Figure 4.8 Cumulative PCB extraction efficiencies for mobilizations from 10g soil by sonication (10 min)-washing with 1%. 3% or 5% or by continuous flushing from 30g soil with 1%, 3% or 5% aqueous suspension of Triton DF16 surfactant.

Unlike the other surfactants, Tween 85 proved to be less suitable for soil sonication-washings (Figure 4.9). The Tween 85 suspension dispersed soil particles very strongly so that, once sonicated, it became difficult to filter materials from the treated slurry. This behavior was evident even after the initial treatment with the 1% (v/v) suspension. The more treatments that were performed, the more difficult it became to filter the suspension and increased concentration of this surfactant only exacerbated the problem. In consequence, sonication-washing with the 3% and the 5% Tween 85 suspension were not completed. Extracted PCBs amounted to 81% for 1% suspension (Table 4.6) and the residual PCB content was 4.8 ± 0.5 μg/g (Table 4.4). This residual PCB content was higher than for similar treatments with the other surfactants.

The concentration of aqueous Tween 85 solutions had less of an effect on the packed soil flushing treatments (Figure 4.9), although the appreciable soil particle dispersion required higher pressure to force mobile phase through the column. The quantity of PCB extracted from the soil was 85%, 89% and 90% for the flushing trials with 1%, 3% or 5% suspension. The residual PCB contents were 2.8 ± 0.4, 1.8 ± 0.3 and 2.9 ± 0.4 μg/g for suspensions containing 1%, 3% or 5% surfactant. The fraction of surfactant that remained with the soil was also relatively greater than with similar concentrations of other surfactants for both the flushing and washing treatments (Table 4.6).

For the soil cleaning trials, the mean standard error of estimate (a measure of the goodness of fit of the mathematical model to the data) for the 22-trials (2.0 range 1.19-3.57) did not vary appreciably as the quantity of surfactant in the suspension (2.53 for 1% *vs.* 2.55 for 3% *vs.* 2.39 for the 5% sonication and 1.91 for 1% *vs.* 1.8 for 3% *vs.* 1.80 for 5% flushing). The corresponding t_{50} estimates ranged from 6.96-1.92 sonication-washings and from 6.45-2.85 h for the flushing trials. They decreased with increasing surfactant concnetration in the suspension. Despite differences in the quantity of soil treated (10 g for sonication-washing *vs.* 30 g for soil flushing) comparable mobilization efficiencies were achieved with the sonication-washing and column flushing.

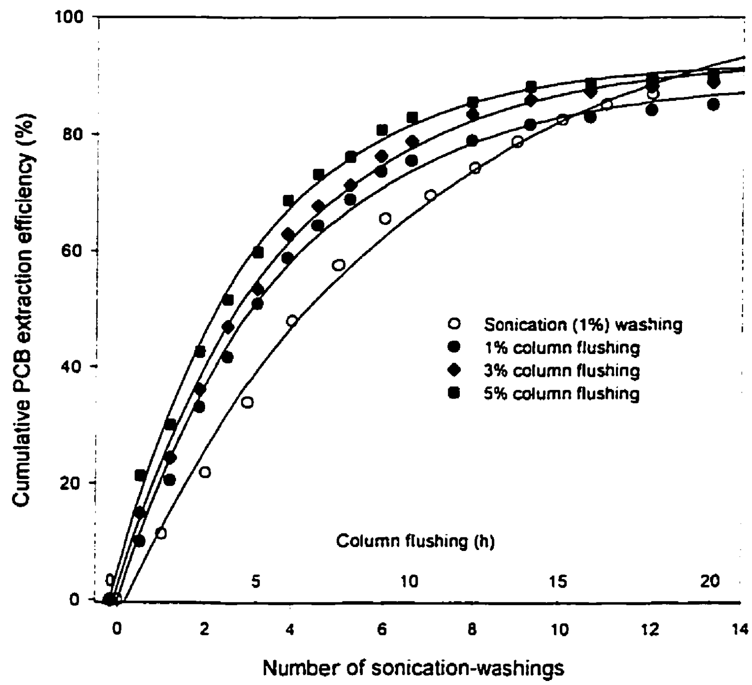


Figure 4.9 Cumulative PCB extraction efficiencies for mobilizations from 10g soil by sonication (10 min)-washing with 1% or by continuous flushing from 30g soil with 1%. 3% or 5% aqueous suspension of Tween 85 surfactant.

4.3.4 PCB separation from soil extract and surfactant regeneration

PCBs were mobilized from the contaminated soil suspensions by back-extraction with $scCO_2$ during 30 min at 50 °C. The results indicated that >99% of PCBs (data not shown) were mobilized from the soil extracts and 23-78% of surfactant (Table 4.6) remained in the aqueous suspension post treatment. The cleaned surfactant suspension could then have been reused to mobilize more PCB from the contaminated soil. Based on the PCB extraction efficiencies, the suitability of surfactants for either soil sonication-washing or column flushing treatments were in the order: Triton DF16 >Triton CF54 >Brij 97 > Tween 85 whereas increased surfactant losses were observed in the order: Tween 85 < Brij 97 < Triton CF54 < Triton DF16.

4.3.5 PCB dechlorination

Once PCBs had been mobilized into $scCO_2$, they were dechlorinated *(on-line)* to biphenyl by passing the effluent through a reactor column of zero-valent silver iron (Ag^0/Fe^0) bimetallic mixture under anoxic condition (Wu and Marshall, 2000). Analysis by GC-MS did not detect any chlorinated products that were eluted from the analytical capillary column within the chromatographic window for PCB compounds. There was no evidence that organic matter or surfactant that had been mobilized from the aqueous surfactant-soil suspension affected the dechlorination efficiency. Dechlorination proved to be both rapid and apparently quantitative.

In total, the results have demonstrated that PCBs can be removed from the soil by extraction with dilute suspensions (1-5% v/v) of aqueous surfactant. The four commercial non-ionic formulations were approximately equally efficient when used with procedures designed to minic either *ex-situ* washing or *in-situ* soil flushing. The removal efficiency from the soil was predicted accurately with a simple exponential expression that included the number of successive treatments and a "time constant" (λ) that was characteristic of the washing process. The number of successive washings required to extract 50% of the PCBs (t_{50}) varied as the concentration of surfactant in the emulsion for both washing and flushing experiments. Equilibration with Triton CF 54 was typical; 5.74 and 2.94 washes were predicated to be required for the t_{50} with 1% and 5% surfactant emulsions, respectively. The mathematical model also accurately predicated the course of the flushing process with the soil column. In this case, the PCB concentration was predicated to be reduced two-fold after 3.95 (237 ml) or 2.92 h (~175 ml) of flushing. Comparable values for sonication-washing and for flushing were observed with similar concentrations of the other surfactants. Despite differences in the quantity of soil treated (10 g for sonication-washing vs. 30 g for soil flushing) comparable mobilization efficiencies were achieved with both procedures.

There were no apparent differences in the avidity with which separate fractions of the total PCB burden interacted with the soil. Although three of the surfactant formulations did not change the physical properties of the soil, one formulation was observed to disperse the soil agglomerates appreciably and required increased pressure to force the aqueous phase through the soil. Nonetheless, large volumes of surfactant suspension were required to mobilize the PCBs efficiently. The challenge remains to improve the efficiency of this stage of the overall process. The PCBs in the cumulative aqueous extracts were back-extracted efficiently (>99%) into $scCO_2$-IBMK. Losses of surfactant to the mobile phase during this stage were appreciable but the dechlorination was quantitative.

Chapter 5
Preface

In Chapter 4, PCBs were extracted from contaminated soil with selected surfactants and mobilized from the PCB containing suspension by back-extraction with $scCO_2$. The results indicated that >99% of PCB were mobilized from the soil extracts and 23-78% of surfactant remained in the aqueous suspension post treatment. The cleaned surfactant suspension could then have been reused to mobilize more PCB from the contaminated soil. The challenge remains to improve the efficiency of this stage of the overall process.

In the current Chapter, models for PCB mobilization from surfactant suspensions with $scCO_2$ is evaluated and the feasibility to both clean the surfactant suspension and to regenerate zero-valent metal/bimetallic particles is re-investigated. It was anticipated that PCB mobilization efficiencies with time could be predicted accurately using mathematical models for PCB mobilization at various PCB burdens, and the combination of PCB mobilization with dechlorination on-line could be established and could be applied to the PCB detoxification process.

Mobilizations of polychlorinated biphenyl (PCB) compounds from surfactant suspension/soil extract with dechlorination on line

5.1 Introduction

Previous studies (Chapter 4: Wu and Marshall, 2001) had demonstrated that polychlorinated biphenyl (PCB) compounds could be mobilized efficiently from contaminated soil(s) into a surfactant suspension and then removed from the aqueous phase by back-extraction with supercritical carbon dioxide ($scCO_2$). It was also possible to detoxify the PCB-laden eluate from the $scCO_2$ extractor with an *on-line* dechlorination process that converted the substrates to biphenyl and chloride. The dechlorination reactor consisted of a column zero-valent bimetallic mixture of palladium and iron (Pd^o/Fe^o) that was heated to 450 °C. The mobilization efficiency from either the contaminated soil or the resulting aqueous surfactant suspension was influenced by the solubility of PCBs in the $scCO_2$ (Yu *et al.*, 1995), the concentration of PCB in the aqueous phase (Akgerman *et al.*, 1993; Glazkov *et al.*, 1999), the operating pressure and temperature (Aranda *et al.*, 1997; Miller *et al.*, 1997) and the solvent modifier that was added to the $scCO_2$ (Auerbach *et al.*, 1996; Anitescu *et al.*, 1999). For optimized reaction conditions, the dechlorination proved to be very efficient, however the time required for efficient scrubbing was anticipated to depend on the loading of PCBs within the soil/aqueous surfactant emulsion. An objective of the studies had been to recycle the surfactant suspension back to mobilize more PCBs from contaminated soil. However, a portion of the surfactant was lost during the initial soil washing and a further portion was lost during the back-extraction stage (Chapter 4). Whereas losses during the initial washing seemed to depend on the quantity of soil treated, losses from the aqueous surfactant suspension depended on the duration and operating conditions of the back-extraction stage. To identify the optimized mobilization conditions that could be coupled with *on-line* dechlorination, it was necessary to examine PCB mobilization efficiencies from a range of PCB concentrations in surfactant suspensions that might be encountered in soil washing procedures. The objectives of the this Chapter were: i) to model the mobilization process of PCBs from various PCB-surfactant mixtures; ii) to optimize operating conditions for the combined PCB mobilization-reductive dechlorination and iii) to extend the PCB mobilization *on-line* dechlorination to a continuous process so as to enable the cleaned surfactant suspensions to be returned to fresh substrate soil to mobilize-detoxify more target PCBs.

5.2 Materials and methods

5.2.1 Chemicals, solvents and surfactants

Magnesium granules (12-50 mesh, 99.8 % purity), potassium hexachloropalladate (K_2PdCl_6), cobaltous nitrate [$Co(NO_3)_2 \cdot 6H_2O$], ammonium thiocyanate (NH_4SCN) and sodium dispersion [40% (*w/v*) in oil] were purchased from Alfa Aesar, Ward Hill, MA USA. Hexane, ethylene glycol dimethyl ether, isomethylbutyl ketone (IBMK, 99+%), methanol, methylene chloride (CH_2Cl_2), propan-2-ol (all HPLC grade), and glass wool were purchased from Fisher Scientific, Ottawa, ON. Biphenyl, Brij 97 and Triton CF54 were purchased from Sigma-Aldrich, Oakville, ON. Aroclor 1242 and Aroclor 1248 mixtures were kindly donated by Monsanto Company, Sauget, IL. All chemicals (ACS Reagent grade or better), solvents and surfactants were used as received.

5.2.2 PCBs mobilization from surfactant suspension or soil extract

The aqueous suspension (90 ml), consisting of surfactant [Brij 97 or Triton CF54 (3%, v/v)], Aroclor 1248 (0.1-1.0%, *v/v*) and distilled water, was supplemented with 10 ml IBMK. The resulting suspension was well mixed and placed in a cylindrical supercritical fluid (SCF) extraction vessel [300 mm X 23 mm inner diameter (i.d.)] that had been fitted with 2 inlet and 2 outlet ports that enabled the addition or removal of sample to/from the vessel during pressurised operation. The vessel was wrapped with a heating tape (Swagelok, Montreal, QC) and heated to maintain the operating temperature at 50 °C. $ScCO_2$, provided from a diaphragm compressor (Newport Scientific Inc., Jessup, MD USA) was added to the base of the extraction vessel and permitted to percolate up through the surfactant suspension and to accumulate within the headspace above the suspension. Fluid in the headspace was replaced continuously with fresh solvent from below and pressure within the system was maintained with a short section of flexible silica tubing (~25 cm x 50 μm i.d.) that terminated the stainless steel transfer line and acted as a capillary restrictor. Extractor eluate was trapped in 25 ml hexane or propan-2-ol contained in a 50 ml test tube. Measurements at the exit of the capillary restrictor indicated a flow rate corresponding to 1500 ml/min of decompressed gas. The extraction was continued for up to 15 h. The cumulative PCB mobilization efficiency was measured after 5 min and subsequently at 10 min intervals. All trials were replicated three times.

5.2.3 On-line PCB dechlorination

5.2.3.1 Dechlorination reactor

The dechlorination assembly consisted of standard HPLC fittings and column (25 x 1 cm i.d., containing 45 g Pd^{o}/Fe^{o} bimetallic mixture) assemblies that were rated to 6,000 psi. The outlet stream from the extractor was connected with a stainless steel transfer line (0.625 mm o.d.) to one or two stainless steel HPLC columns [10 mm i.d. X 25 cm] that were jacketed with an alumina tube (12 mm i.d., Alfa Aesar, that had been cut lengthways to provide two semi-cylinders) and mounted in series. The column-alumina jacketed assemblies were heated separately with 80-turn coils of high resistance heating wire that were energized with variable transformers. Pressure within the assembly was maintained at 4500 psi with a flexible polyamide coated silica capillary restrictor (~25 cm x 0.05 mm, Chromatographic Specialties, Brockville, ON). For diluted PCB substrate, a mixture of Aroclor 1248 (10%, v/v) dissolved in acetic anhydride and DME (8+1) was delivered at 0.1 ml/min to the mixing tee (1/16"i.d.), merged with the $scCO_2$ stream (~4 ml/min) and fed to a single ss (Figure 3.1) reactor column.

5.2.3.2 Dechlorination operation

Two approaches were evaluated to interface the extractor effluent with the dechlorination reactor. The outlet stream from the extractor was merged, via a mixing tee (1/16" i.d.), with a solution [acetic anhydride and DME (9+1)] delivered at 0.2 ml/min by an HPLC pump (Beckman, 100A). The alternate approach involved interposing a second extraction vessel (300 mm X 25 mm i.d.) that contained 20 ml acetic anhydride plus DME, (4+ 1).

After mixing with the solvent in the second vessel, the effluent was transferred to the dechlorination reactor. After a short delay to purge residues of air from the system (during which time only $scCO_2$ was fed to the reactor) Aroclor 1248 [10% (v/v)] feedstock, delivered from the HPLC pump, was merged, at 0.1 ml/min, with the $scCO_2$ stream and transported to the reactor. Measurements at the exit of the capillary restrictor indicated a flow rate of 800-1000 ml/min of decompressed gas. The exit tip of the capillary restrictor was immersed in hexane (25 ml) to trap products from the reactor eluate. Each experiment was continued until six successive traps had been collected, each corresponding to 10 min of cumulative trapping of eluate. The course of the dechlorination was monitored by gas chromatography (GC-FID) and by GC-MS to monitor the identities of products and by titration to measure levels of residual organically bound chlorine in the eluate.

5.2.4 PCB analyses

If the initial PCB concentration in the surfactant mixture was less than 1% (v/v), conversion to biphenyl was used. Aroclor 1248 mixture was converted quantitatively to biphenyl by reaction with Mg^0 and K_2PdCl_6 following the procedures reported previously (Wu and Marshall, 2001). For higher initial Aroclor 1248 concentrations in surfactant suspension (>1%, v/v), the titration method was followed (Wu and Marshall, 2001). In brief, residual PCBs in hexane trapping solution was determined by titration with standardised $AgNO_3$ (~0.01M) post conversion of organically bound chlorine to chloride. Sodium dispersion, 2 ml, was added to a 10 ml aliquot of vigorously stirred hexane trapping solution that had been further diluted 5-fold with fresh hexane. Methanol, 1 ml, was added dropwise. The reaction was continued for 5 min then quenched by the addition of propan-2-ol (15 ml) followed by 90 ml water. Post phase separation, a 20 ml aliquot was acidified to pH 6-7 with nitric acid (7M), supplemented with 5 drops of potassium chromate indicator solution then titrated with $AgNO_3$. Blank determinations for chloride in reactor eluate consisted of an identical procedure in the absence of added sodium dispersion.

5.2.5 Surfactant analysis

The Standard Analysis Methods, APHA (Dreebberg *et al.*, 1992), was followed to determine the residual surfactant concentration post $scCO_2$ mobilization. A standard calibration curve was generated for each surfactant. Micellar-suspension (1 ml) was diluted five-fold to obtain a suitable working concentration. Diluted surfactant suspension (2 ml) contained in a 100 ml flask, was evaporated to dryness then triturated with methylene chloride (10 ml) and the resulting extract was added to a 125-ml separatory funnel containing 5 ml cobaltous thiocyanate solution. After 1 min of vigorous shaking and phase separation, the lower aqueous layer was transferred, via a funnel containing a plug of glass wool, to a 5 ml spectrophotometer cell. The absorbance, at 620 nm, was determined *vs.* a blank of CH_2Cl_2.

5.2.6 Gas Chromatography Mass Spectrometry

The total content of PCBs was determined by gas chromatography equipped with flame ionization detection (GC-FID) or a Hewlett-Packard model 5890 (II) gas chromatography equipped with a model 5971 mass selective detector (GC-MS). Both methods were described in previously reports (Wu and Marshall, 2000; 2001).

5.3 Results and discussion

5.3.1 The efficiency of PCB mobilization into supercritical CO_2

To study the rate of PCB mobilization from surfactant suspension into $scCO_2$, of mixtures containing various concentrations of Aroclor 1248 (0.1-1.0%, v/v) in Brij 97 (3%, *v/v*) or Triton CF54 were extracted at 50 °C and 4500 psi. As illustrated in Figure 5.1 (dashed lines), the quantity of PCB mobilized with time from PCB-Brij 97 suspension were dependent on the duration of extraction and on the initial PCB content. To the extent that the rate of PCB mobilization from surfactant suspension can be approximated as a time constant (λ) multiplied by the PCB concentration (Y) in the suspension at time t

$$dY/dt = \lambda Y \qquad (1)$$

This rate expression can be re-written as an exponential decay function:

$$Y = CY_0e^{-\lambda t} \qquad (2)$$

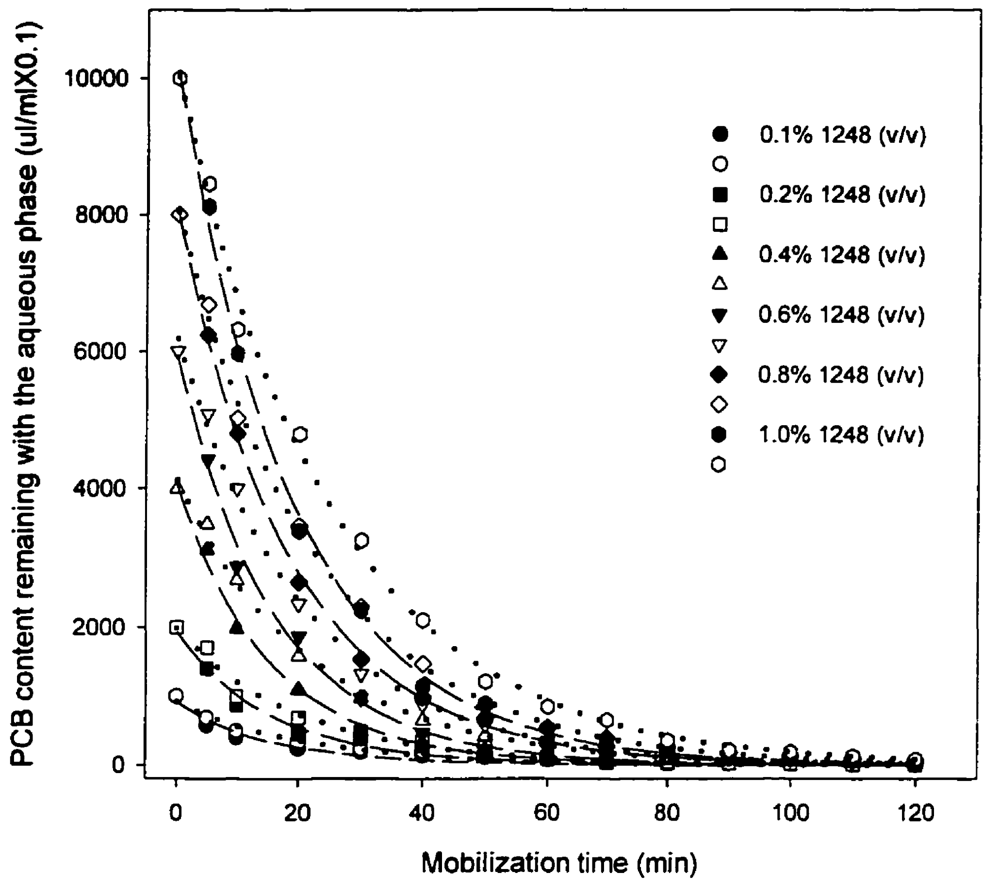


Figure 5.1 Mobilizations, with time, of Aroclor-1248 (0.1-1.0 %, v/v) from (1+9) IBMK-aqueous Brij 97 (3%, v/v) suspension.

where C is a constant of proportionality, Y_0 is the PCB content at time zero and λ is a time constant characteristic of the extraction processes. Expression (2) was observed to provide an accurate estimate (Figure 5.1 and Figure 5.2, dashed curves) of the experimental data for each of the loadings of PCBs in the Brij 97 and Triton CF54 surfactant suspensions respectively. The optimized regression models for mobilizations from Brij 97 are provided in Table 5.1 and from Triton CF54 in Table 5.2. The parameter of the goodness of fit of the model to the data (R^2) for surfactant suspensions (0.989 ± 2%, Table 5.1; 0.983±2%, Table 5.2 respectively) were satisfyingly close to 1. When the extraction process was interfaced with *on-line* dechlorination, the rate of PCB mobilization was decreased (Figure 5.1 and 5.2, dotted lines). The dechlorination reactor (discussed below) contributed appreciably to the back-pressure within the system so that for the same $scCO_2$ head pressure (4500 psi), the flow rate of decompressed gas at the exit of the capillary restrictor, 1500 ml/min, was reduced to 900-1000 ml/min by interposing the heated dechlorination column within the reaction train. When corrected for the differences in flow rates, the curves at each loading in the absence/presence of the dechlorination reactor became virtually identical.

An interesting feature of the exponential decay model is that the time required to mobilize one half of the initial burden ($t_{1/2}$) is predicted to be independent of the initial PCB loading. For the range of loadings studied (0.1-1.0% v/v), the $t_{1/2}$ values were independent (within experimental error) of quantity of PCB formulation that had been added to the suspension. The mean $t_{1/2}$ for the six loadings in Brij 97 was 11.6 min ±11% (Table 5.1) and 10.3 min ±11% (Table 5.2) for the Triton CF54 for mobilizations alone and 15.4 min ± 8% and 16.8 min ±14% for mobilizations combined with dechlorination.

An alternate way to express the course of these mobilizations that is anticipated to be independent of the flow rate of $scCO_2$, is in terms of the number of exchanges of headspace fluid required to reduce the PCB burden in the aqueous suspension to one half of its initial value. For a flow rate of 8.8 ml/min of compressed fluid in the absence of the reactor and 6.0 ml/min when it was connected *on-line*, the mean number of exchange volumes per half life were calculated to be 9.0 ± 8% and 10.0 ± 11% respectively for the Brij surfactant (Table 5.1). Similarly, the number of exchange volumes observed for the

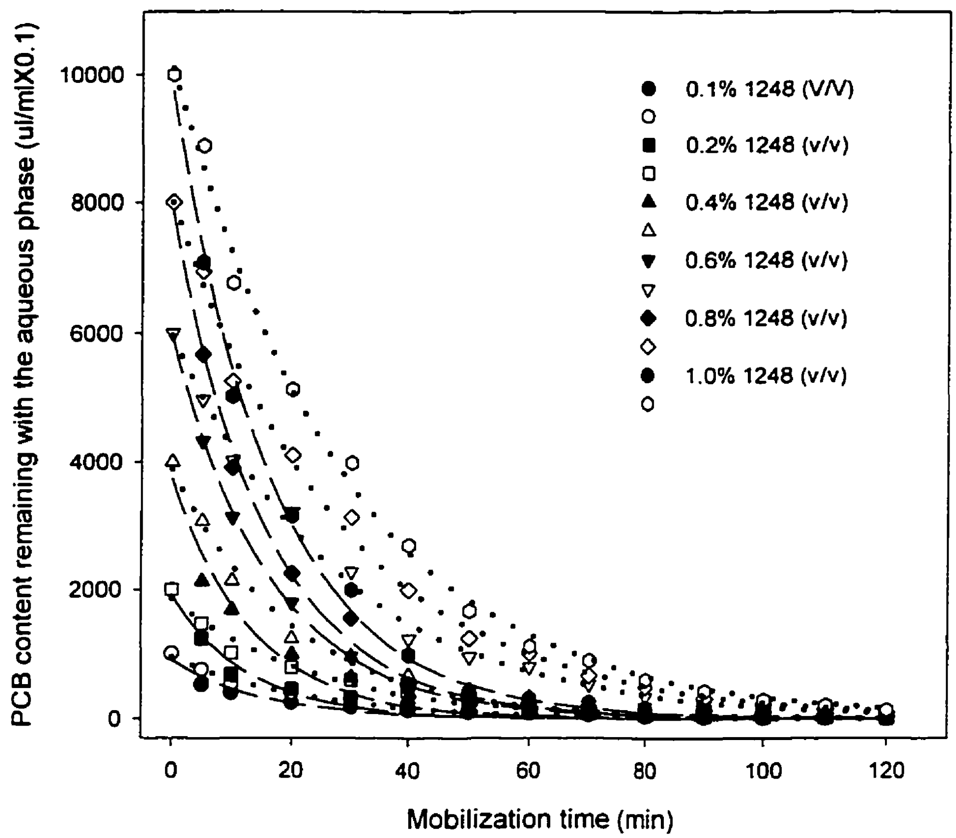


Figure 5.2 Mobilizations, with time, of Aroclor-1248 (0.1-1.0 %, v/v) from (1+9) IBMK-aqueous Triton CF54 (3%, v/v) suspension.

Table 5.1 Best-fit exponential decay models for extractions of Aroclor-1248 from Brij 97 (3% v/v) emulsion into $scCO_2$ (performed at 50 ^{o}C and 4500 psi).

Aroclor-1248 concentration	Optimised decay model for mobilisation	R^2	Fitted Y_0	$t_{1/2}$ min	# headspace exchanges	Optimised model for mobilisation + dechlorination	R^2	Fitted Y_0	$t_{1/2}$ min	# headspace exchanges
0.1	$Y= 832.3e^{-0.0646t}$	0.961	0.0857	10. 6	8.7	$Y=924.7e^{-0.0471t}$	0.979	0.0716	14.8	9.1
0.2	$Y=1938e^{-0.0641t}$	0.983	0.1996	10.8	8.3	$Y=1993e^{-0.0493t}$	0.984	0.1747	14.1	9.3
0.4	$Y=4060e^{-0.0650t}$	0.995	0.4182	10.7	9	$Y=4128e-^{0.0450t}$	0.996	0.3809	15.4	9.2
0.6	$Y=5945e^{-0.0624t}$	0.996	0.6123	11.1	8.6	$Y=6194e^{-0.0476t}$	0.997	0.587	14.6	9.5
0.8	$Y=8045e^{-0.0531t}$	0.999	0.8287	13.1	9.4	$Y=8053e^{-0.0431t}$	0.999	0.7932	16.1	11.3
1	$Y=10120e^{-0.0515t}$	0.998	1.042	13.5	10.3	$Y=10030e^{-0.0395t}$	0.997	0.9993	17.6	11.6
Mean±1RSD		0.989±2%		11.6±11'	9.0±8%		0.992±0.8%		15.4 ± 8%	10.0±11%
Brij 97 content (3% v/v)	$Y= 81.6e^{-0.0516t} + 20.1$	0.988		13.5						

Table 5.2 Best-fit exponential decay models for extractions of Aroclor-1248 from Triton CF54 (3% v/v) emulsion into $scCO_2$ (performed at 50 °C and 4500 psi).

Aroclor-1248 concentration	Optimised decay model for mobilisation	R^2	Fitted Y_0	$t_{1/2}$ min	# headspace exchanges	Optimised model for mobilisation + dechlorination	R^2	Fitted Y_0	$t_{1/2}$ min	# headspace exchanges
0.1	$Y=903.8e^{-0.0681t}$	0.95	0.1009	10. 2	9.3	$Y=897.1e^{-0.0437t}$	0.969	0.0739	15.9	8.8
0.2	$Y=1917e^{-0.0794t}$	0.976	0.202	8.8	8.4	$Y=1887e^{-0.0485t}$	0.983	0. 1752	14.3	7.6
0.4	$Y=3742e^{-0.0760t}$	0.979	0.4041	9.1	8.3	$Y=3270e^{-0.0492t}$	0.986	0.3779	14.1	7.8
0.6	$Y=5942e^{-0.0633t}$	0.998	0.6062	11	11.1	$Y=5931e^{-0.0366t}$	0.997	0.5805	19	9.4
0.8	$Y=7866e^{-0.0633t}$	0.997	0.8083	11	11.5	$Y=8053e^{-0.0355t}$	0.996	0. 7832	19.6	9.4
1	$Y=9756e^{-0.0589t}$	0.997	1.0104	11.8	10.5	$Y=10030e^{-0.0389t}$	0.998	0. 9860	17.9	10.1
Mean ± 1RSD		0.983±2%		10.3±11%	9.9±14%		0.991±1%		16.8±14%	8.8±11%
Triton content (3%,v/v)	$Y=78.9e^{-0.0559t}$ + 16.7	0.976		12.4						

Triton surfactant was 9.9 ± 14% and 8.8±11% respectively (Table 5.2). These results indicate that observed differences in $t_{1/2}$ were the result of changes in the flow rate of mobile phase rather than a change in the efficiency of the process. It is anticipated that the rate of mobilization could be accelerated by further increasing the flow-rate of mobile phase and/or by reducing the volume of headspace above the sample.

5.3.2 Surfactant retention

One of the objectives of the study was to retain as much surfactant as possible within the aqueous retentate (surfactant phase) during the mobilization processes. However, as illustrated in Figure 5.3, the content of Brij 97 or Triton CF54 remaining with the aqueous phase also decreased with increased extraction time. From the decreasing profile with time, it seemed that the decrease of surfactant content in the aqueous suspension was closely related to the mobilization efficiencies of PCBs. Although the Triton CF54 content decreased slightly more rapidly during the early stages of the mobilization process, both surfactants had reached similar concentrations post 40 min of mobilization (Figure 5.3). It was concluded that differences, if present, were within the range of surfactant replicate determinations. The optimized regression models for the content of remaining surfactant provided accurate estimates of the analytical data (R^2, 0.988 and 0.976 (Tables 5.1 and 5.2 respectively) yet they approached a limiting value corresponding to 20.1% for the Brij 97 and 16.7% of the initial content for the Triton CF54 surfactant suspension.

To study the "residual" fraction in more detail, a 15% (v/v) Triton CF54 suspension (90 ml) was extracted for 2 h with $scCO_2$, the mobile phase was interrupted and the sample was amended with IBMK (10 ml) and 1% (v/v) Aroclor-1248. The extraction was then continued for a further 4 h. A total of nineteen 0.5 ml aliquots of aqueous sample were removed at 20-min intervals throughout the 6 h trial. The results are presented in Figure 5.4. Both phases of the trial were adequately modelled as an exponential decay function (R^2, 0.9927, 0.9982) but the rate of CF54 surfactant mobilization was decreased appreciably during the initial 2 h by the absence of IBMK ($t_{1/2}$, 71.1 min). A residual fraction corresponding to 13.2% of the surfactant loading was predicted by the model.

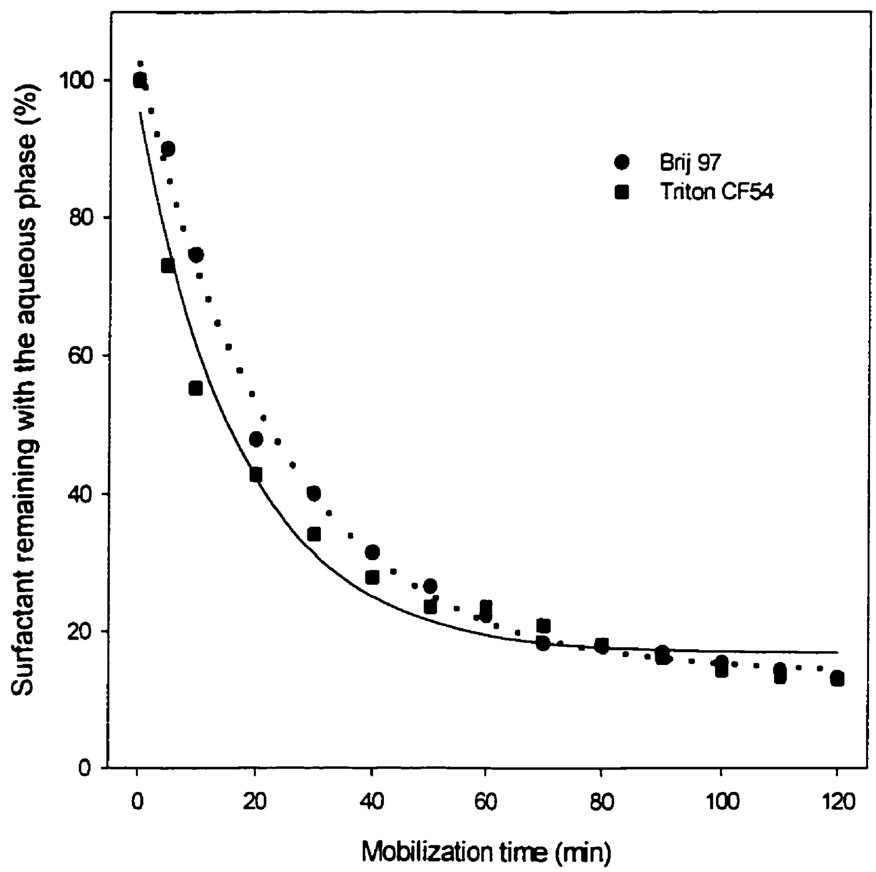


Figure 5.3 Percent surfactant remaining in the aqueous retentate fraction, with time, post extraction with $scCO_2$ at 50 °C and 4500 psi.

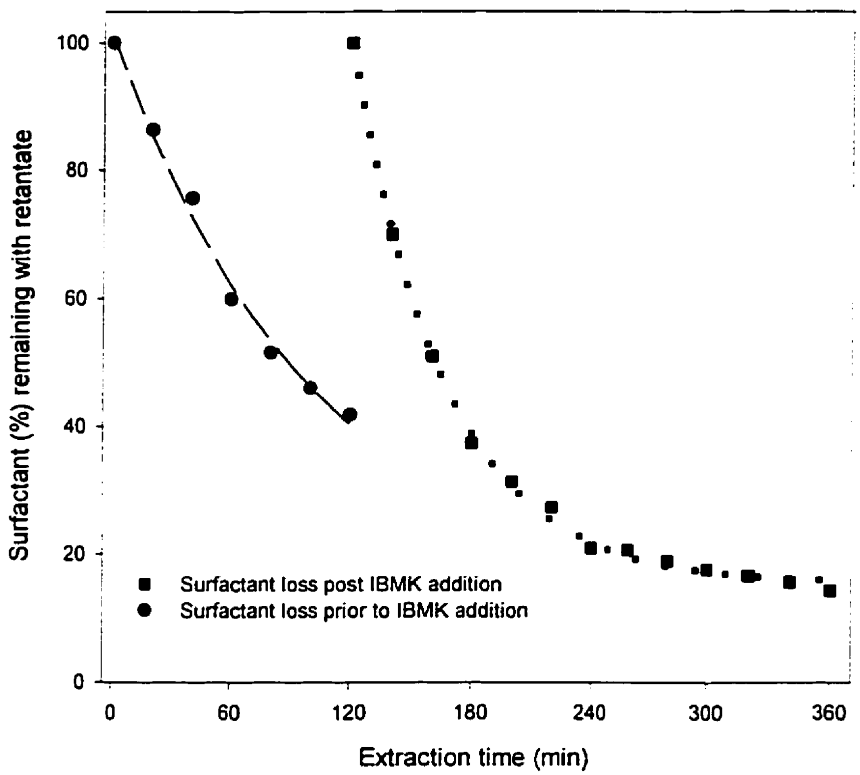


Figure 5.4 Mobilization, with time, of Triton CF54 surfactant in the absence / present of Aroclor 1248 (1%, v/v)-IBMK (10%, v/v).

Post addition of IBMK, the rate of surfactant mobilization was increased ($t_{1/2}$, 27.9 min) but models for both phases of the trial predicted a residual fraction (13.2 and 15.5% pre and post-addition of IBMK respectively). It seems likely that post cleaning of the aqueous retentate with IBMK-scCO_2, this fraction could be fortified with more surfactant and returned to the contaminated soil to mobilize more pollutant(s).

5.3.3 On-line PCB dechlorination

Efforts were turned to interfacing the extractor outlet stream to a heated reactor column(s) of zero-valent bimetallic mixture (Pd^o/Fe^o) so as to effect dechlorination(s) of the effluent *on-line*. Two configurations were evaluated. Because IBMK was a component of the effluent, it was anticipated that a direct coupling might be efficient (Wu and Marshall, 2000; 2001). Effluent from the reactor was trapped in hexane during 3 h of continued mobilization-dechlorination. As recorded in Table 5.3, the dechlorination yields for various PCB concentrations (0.1–1.0%, v/v) ranged from 99.7–72.4% for Brij 97 suspensions and 99.8-73.8% for Triton CF54 suspensions when the outlet stream of mobilized PCBs was interfaced directly to two zero-valent columns (connected in series) that were heated to 400 °C. In an attempt to increase dechlorination efficiency, a second means of coupling was also evaluated. A vessel containing 20 ml mixed solvent (acetic anhydride, DME, IBMK, 8+1+1 v/v/v) was interposed between the extraction vessel and the reactor. With this modification, the dechlorination efficiency was improved appreciably (Table 5.3). The dechlorination yields ranged from 100–90.5% and 100-93.6 % for PCB effluent from suspensions [that had contained 0.1–1.0 % (v/v) Aroclor 1248] in Brij 97 and Triton CF54 suspensions respectively. There were no significant differences between dechlorination efficiencies from Brij 97 and Triton CF54 suspensions.

The exponential model was evaluated for extended mobilization times. Table 5.4 summarizes the predicted and measured PCB and surfactant contents remaining with the aqueous phase post approximately 14 half-lives of extraction. The time predicted to reduce PCB residues in the aqueous retentate fraction to non-hazardous levels (≤0.1 μg ml) ranged between 194-297 min. Post extraction, the measured PCB levels exceeded this level in all cases indicating that for extended extraction times the decay model

Table 5.3 The dechlorination yields of PCB mixtures moilized from suspension of Aroclor 1248 (0.1~1%, v/v), water and Brij 97 (3%, v/v) or Triton CF54 (3%, v/v) using 2 Pd^o/Fe^o reactor columns connected in series. Dechlorinations were performed in $scCO_2$ at 400 °C and 4500 psi.

	Brij 97 suspension		Triton CF54 suspension	
Aroclor 1248 loading (%,v/v)	Dechlorination (%) via direct interface	Dechlorination (%) with solvent reservoir	Dechlorination (%) via direct interface	Dechlorination (%) with solvent reservoir
0.1	99.7 ± 0.2[a]	100	99.8 ± 0.2	100
0.2	92.2 ± 2	99.9 ± 0.1	93.3± 2	99.9 ± 0.1
0.4	89.6 ± 6	98.7 ± 0.3	90.5 ± 4	99.9 ± 0.1
0.6	87.4 ± 5	95.9 ± 3	86.6 ± 5	97.5 ± 2
0.8	76.5 ± 5	92.8 ± 3	74.5 ± 5	95.6 ± 3
1.0	72.4 ± 5	90.5 ± 3	73.8 ± 6	93.6 ± 4

[a] :Mean ± 1 SD for three replicate determination.

Table 5.4 Residues of Aroclor 1248 and surfactant content remaining with the aqueous phase post processing (mobilization with *on line* dechlorination) predicted to be sufficient to reduce PCB burdens to non-hazardous levels (0.1μg/ml).

	Measured PCB residues (μg/ml) in the aqueous phase		Percent of initial surfactant remaining with the aqueous phase	
Aroclor 1248 loading (%, v/v	Brij 97	Triton CF54	Brij 97	Triton CF54
0.1	0.5 ± 0.3 [a]	0.2 ± 0.2	4.4 ± 1	5.5 ± 1
0.2	1.1 ± 0.3	0.5 ± 0.2	14.3 ± 3	15 ± 4
0.4	2.9 ± 0.5	1.2 ± 0.2	13.3 ± 3	15.3 ± 4
0.6	3.6 ± 0.6	2.1 ± 0.3	18 ± 4	16.3 ± 3
0.8	3.9 ± 0.6	2.9 ± 0.4	17.3 ± 4	16 ± 3
1.0	3.8 ± 0.8	3.1 ± 0.4	17 ± 4	16.3 ± 4

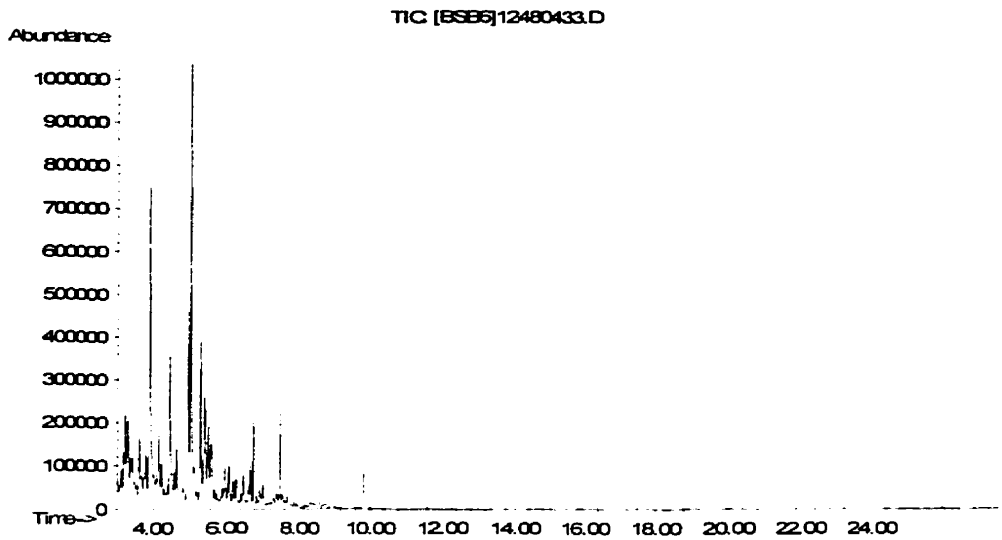
[a] :Mean ± 1 SD for three replicate determination.

appreciably over-estimated the extraction efficiency. If non-hazardous PCB levels are actually required in the aqueous washing suspension, then 3-5 more half lives of extraction are predicted to be required to decrease the content to non-hazardous levels. However, after ~14 half lives of extraction, the surfactant content remaining in the retentate fraction was 16.0 ± 6% and 15.8 ± 0.6% of the quantity added initially and was in reasonable agreement with predicted surfactant levels of 20.1 and 16.7%.

The main products of dechlorination, as identified by GC-MS, were biphenyl and methylated benzenes (xylenes to pentamethylbenzene). In addition, 1,3-dimethyl-5-methylethy-benzene, 1-(2-butenyl)-2,3-dimethyl-benzene, methylated phenols, (xylenols, trimethyl-phenol), trimethyl-cyclohexene, dimethyl-cyclopentane, and trimethyl-cyclopentene were present (Figure 5.5). Presumably the benzene and phenol originated from the biphenyl but the source of the methyl groups remains to be identified. Possible sources include the solvent IBMK or DME but the source might have been the CO_2 as well. Methylated benzenes and methylated phenols had been observed previously for Ag^0/Fe^0 mediated dechlorinations of pentachlorophenol in $scCO_2$ (Kabir and Marshall, 2001).

5.3.4 Extended dechlorination and zero-valent Pd^0/Fe^0 column(s) regeneration

To mimic continuous processing, dechlorinations were also applied to soil extracts (containing 6 μg/ml PCB) that were extracted from a PCB contaminated soil using Brij 97 (3%, v/v) and Triton CF54 (3%, v/v) suspensions (Wu and Marshall, 2001). PCB laden surfactant extract, 90 ml, plus 10 ml IBMK was transferred to the pressurized extraction vessel with an HPLC pump. The process of PCB mobilization-dechlorination was conducted (4500 psi, 400 °C) during 30 min. The $scCO_2$ stream was interrupted, the retentate fraction was drained from the extraction vessel and replaced with fresh soil extract plus IBMK (90 + 10 ml) and the mobilization-dechlorination cycle was repeated. The cycles, operated under optimized mobilization-dechlorination conditions, were continued during 5 h by replacing the cleaned aqueous suspension each 30 min. The dechlorination yield remained virtually quantitative over the course of the extended trial and the PCB content that remained with the aqueous retentate was less than 0.1 μg/ml for 30 min of processing. Thus, neither the organic matter that was mobilized from the soil



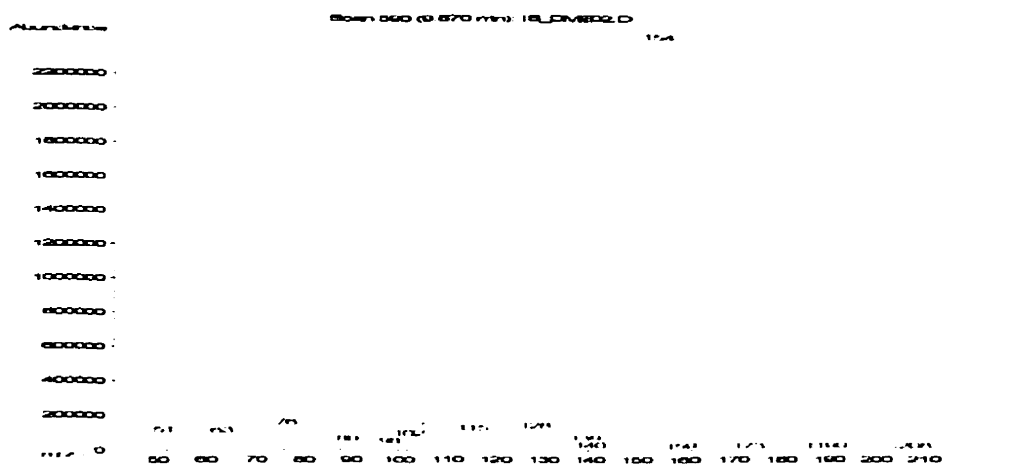


Figure 5.5 GC-MS chromatograms of dechlorination yield of soil extracts. (A) The principle products of dechlorination (1: 4-methyl-2-pentanone; 2: *o*-cresol; 3: 1, 6-dimethylcyclohexene; 4: *m*-xylenol; 5: mesitylene; 6: 4-methylphenol; 7: 2, 6.-dimethylphenol; 8: biphenyl). (B) Mass spectrum of biphenyl, retention time 9.87 min. The dechlorination was performed at 400 °C and 4500 psi with two zero-valent columns of Pd^{o}/Fe^{o} connected in series.

nor the surfactant had any perceptible impact on the dechlorination efficiency. The products that resulted from the dechlorination with soil extract were comparable to those that resulted from the surfactant suspensions.

5.3.5 Regeneration of reactor activity

To accelerate the reduction in dechlorination efficiency with time, that had been observed earlier for PCP dechlorinations (Kabir and Marshall, 2001), the reactor was purposely overloaded by continuously adding excess substrate. PCB substrate [containing Aroclor 1242 or 1248 (10%, *v/v*), acetic anhydride (80%) and DME (10 %)] was merged (at 0.1 ml/min) with $scCO_2$ and delivered continuously to a new column (containing 45 g Pd^o/Fe^o) for 5 h. Repeatabilities for three replicate trials conducted during 5 h were adequate (Table 5.5). The dechlorination efficiency that was observed in successive traps during 15 h of extraction-dechlorination (■ symbol for Aroclor 1242, ▲, ▼,◆ symbols for Aroclor 1248) is illustrated in Figure 5.6. The dechlorination yields decreased with time. The dechlorination efficiency was reduced to 48-59% after 3 h of continued operation and to 34-55% after 5 h of operation. Presumably, catalytic sites on the surface of the Pd^o/Fe^o particles were inactivated by the extended process of dechlorination.

In an attempt to regenerate the Pd^o/Fe^o particle dechlorinating activity three methods were evaluated. The methods included 3 h of *on-line* flushing with $scCO_2$ (■, ▲ Figure 5.6) at elevated temperature (400 °C), flushing *on-line* with 30 ml water-methanol mixture (7+3, ▼, Figure 5.6) at ambient temperature and washing of the column packing *off-line* (◆, Figure 5.6) with 30 ml water. The dechlorination yields indicated that the all three re-activation methods were at least partially effective. The method using 3 h $scCO_2$ flushing *on-line* proved to be the most efficient regeneration method, followed by the *on-line* water-methanol flushing procedure. There was no apparent advantage to removing the packing and re-packing the reactor column with cleaned material.

In summary, the PCBs from surfactant suspension or polluted soil extract were mobilized virtually quantitatively and dechlorinated *on-line*. The combination of PCB mobilization into $scCO_2$ with *on-line* dechlorination was an efficient process for longer processing times, that can be applied to the PCB-containing surfactant slurry. The processing time required to achieve any desired level of cleaning can be predicted accurately. Differences

Table 5.5 Decreases in dechlorination yields with extended processing.

Time	Aroclor 1242 Flushing with $scCO_2$ for 3 h at 5 h interval	Aroclor 1248 Flushing with $scCO_2$ for 3 h at 5 h interval	Aroclor 1248 Flushing with 30 ml water-EOH (7+3) at 5 h interval	Aroclor 1248 Washing with 30 ml water at 5 h interval
30	91.9 ± 2[a]	68.0 ± 5	64.4 ± 2	55.8 ± 6
60	84.8 ± 9	68.0 ± 5	62.3 ± 2	55.4 ± 6
90	84.4 ± 9	62.5 ± 1	61.2 ± 1	54.1 ± 5
120	83.4 ± 9	62.5 ± 1	60.8 ± 2	52 ± 7
150	81.1 ± 10	61.4 ± 1	57.6 ± 2	51.1 ± 5
180	78.5 ± 9	58.8 ± 5	56.8 ± 3	48.2 ± 5
210	75.2 ± 4	57.1 ± 5	53.3 ± 1	39.6 ± 12
240	74.9 ± 4	56 ± 5	51.8 ± 1	39 ± 11
270	72.9 ± 4	56.6 ± 5	48.2 ± 5	35.2 ± 13
300	71.4 ± 4	54.7 ± 5	48.6 ± 3	34.6 ± 12

[a] :Mean ± 1 SD based on three replicate determination.

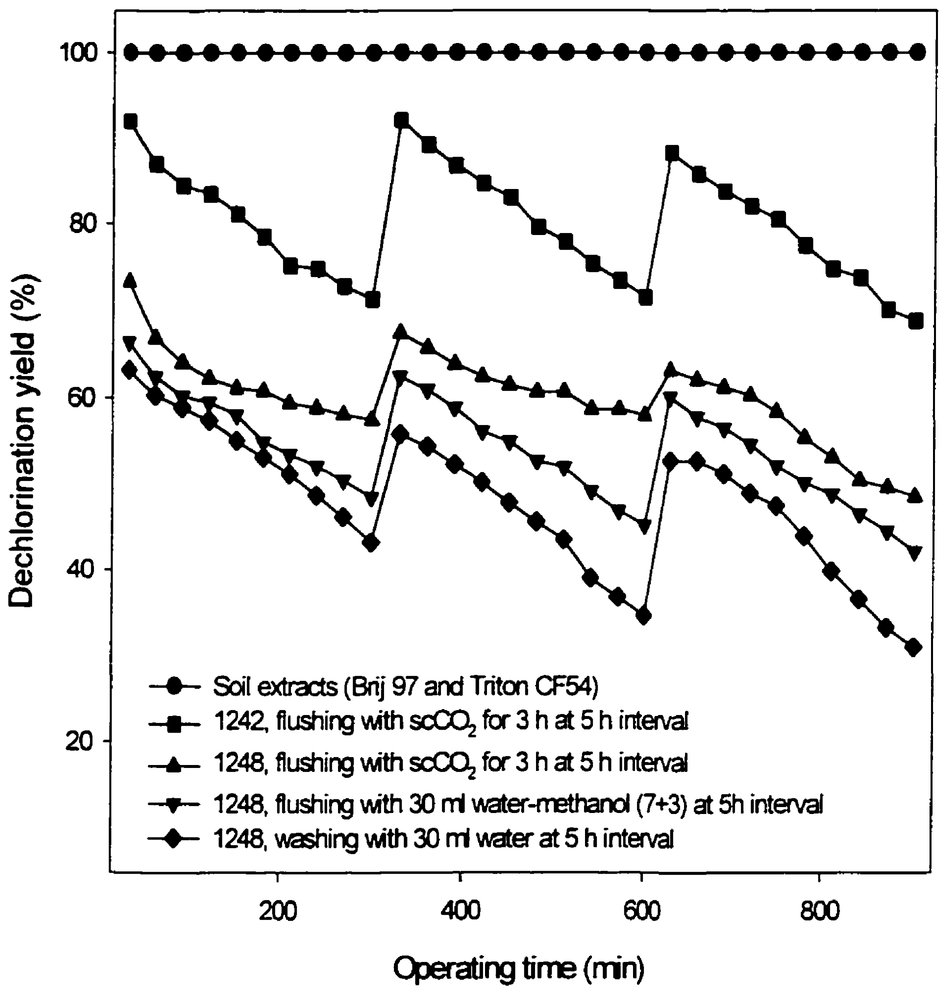


Figure 5.6 Changes, with time, in dechlorination efficiencies of Aroclor 1242 soil extract (●), Aroclor 1242 solution [10% (v/v) ■] or 10% (v/v) Aroclor 1248 (▲,▼,◆) observed in cumulative 30-min traps pre- and post reactivation. At 5 h intervals, the reactor column was washed on line for 3 h at 400 °C with $scCO_2$ (▲),or at ambient temperature with 30 ml water-methanol (7+3) (▼) or the packing was washed with water (30 ml, ◆).

in behaviour between the two surfactants were not evident. The advantage of this approach is that the PCBs can be detoxified rapidly and efficiently and the cleaned surfactant suspension can be returned to the contaminated soil to extract more PCB (contaminants). The disadvantage of the method is that an appreciable portion of the commercial surfactant formulation was mobilized into the $scCO_2$ during processing. The challenge remains to identify $scCO_2$ insoluble surfactant formulations that mobilize the PCBs more rapidly from the aqueous phase.

Chapter 6
Preface

These studies have investigated/optimized a method for PCB determination within contaminated soil/sediments; established novel approaches/techniques for PCB dechlorination with zero-valent metals or bimetallic mixtures; optimized a method for PCB washing/flushing from contaminated soil. Soil washing/flushing was combined with supercritical carbon dioxide ($scCO_2$) mobilization - dechlorination *on-line* using zero-valent metals. The studies have demonstrated that PCB can be dechlorinated efficiently by heated columns of zero-valent metal or bimetallic mixtures. PCBs *can be* flushed efficiently from polluted soils into surfactant suspension and then back-extracted into supercritical CO_2. Finally, the toxicants were dechlorinated virtually quantitatively in a continuous *on-line* process using heated columns of zero-valent bimetallic mixtures. A general conclusion and summary is generated in Chapter six.

Summary and conclusion

6.1 Summary

PCB properties, historical usage patterns, impact on the environment and techniques for their destruction as well as possible treatment for the remediation of contaminated matrices were reviewed in Chapter one. Novel approaches/techniques combining $scCO_2$ with zero-valent metal/bimetallic particles for PCB extraction/mobilization and dechlorination were proposed.

In Chapter two, a new method for the dechlorination of PCB commercial mixtures (Aroclor formulations) to biphenyl was extended to soils. The contaminated sample was mixed with magnesium flakes, potassium hexachloropalladiate (K_2PdCl_6), propan-2-ol and water then permitted to react for up to six hours. Biphenyl, recovered by extraction into hexane, was quantified by gas chromatography with flame ionization detection. The reaction was very efficient in propan-2-ol/water, surfactant emulsion or sand mixture and virtually complete in soil provided that excess magnesium and the K_2PdCl_6 were added to the sample prior to the addition of water. High PCB loadings were readily determined in the field contaminated soils either by direct determination within the matrix or by standard additions. However, analyte concentrations were appreciably over-estimated in Soxhlet or sonication extracts of a certified reference material that contained sub-ppm levels (0.34 mg/kg) of analyte. The over-estimation was considered to result from the conversion, in part, of natural organic matter to biphenyl. The direct derivatization within the sample matrix can be used to estimate the PCB concentration for soil/sediments and contaminated solution suspensions. The concentrations of PCBs in two of the three reference materials (27.2 and 472.5 mg/kg) were determined successfully. The principle advantages of this procedure included convenience and simplicity but the principle disadvantage was that organic matter can also contribute to the apparent analyte recovery and had to be accounted for in accurate determinations. The method of standard additions provided reliable estimate level at sub ppm concentrations. The Aroclor 1260 model can be used to estimate the PCB concentration in contaminated soil/sediments samples.

An approach that can dechlorinate PCB mixtures (Aroclor 1242 and 1248) efficiently with heated columns of zero-valent metal or bimetallic mixture in a continuous process has been developed (Chapter 3). Supercritical carbon dioxide ($scCO_2$) transferred the substrates through the reactor and cumulative ten minute fractions of eluate were trapped in hexane during 1 h of continued operation. The extent of dechlorination were influenced appreciably by the identity of the zero-valent metal (Fe^0>Ni^0 >Zn^0> Cu^0), by the temperature (400>>300 > 200 °C) and pressure (≤ 4,500 psi) within the reactor column(s) and especially by the composition of the feedstock. Although water was both unnecessary and detrimental to the dechlorination yields, the inclusion of methyl ketone(s) in the feedstock solution improved the extent of dechlorination appreciably. Two columns (25 x 1 cm) of Ag^0/Fe^0 or Ag^0/Ni^0 bimetallic mixture resulted in a virtually quantitative dechlorination of substrate Aroclor 1242 (~28 mg/min). Moreover, during 1 h of continued operation, dechlorinations were very repeatable. In preliminary treatments of 30% (v/v) acetone-hexane extract (~600 μg/ml PCBs) of a spiked sandy loam soil, no chlorinated organics could be detected in the PCB eluting region by GC-MS. It has been demonstrated that zero-valent metal meditated reactions of Aroclor, mixtures at elevated temperature in $scCO_2$, provided an efficient technique for PCB detoxification by dechlorination. The quantities of 1242 or 1248 substrate that were dechlorinated efficiently (but not quantitatively) are considered to far exceed the burdens in concentrated extracts that could be isolated from polluted environmental matrices.

An approach/technique for the remediation of PCB contaminated soil was evaluated in Chapter four. A soil that had been historically contaminated with Aroclor 1242, 1248, 1254 and 1260 was decontaminated by two surfactant-meditated cleaning procedures that had been chosen to mimic *ex-situ* soil washing and *in-situ* soil flushing processes. A preliminary screening selected four surfactants (from among 17 commercial formulations) for their ability to mobilize PCBs from the soil while suffering minimal losses to the supercritical carbon dioxide mobile phase. The mobilization was enhanced with minimal foam formation by the presence of 17% (v/v) IBMK in the surfactant suspension. Each of the four surfactants, at 1, 3 or 5% (v/v) concentration, was evaluated by fifteen successive 10-min sonication-filtrations and continuous soil column flushing during 20 h. Filtrates from each sonication-filtration step and samples taken at hourly intervals from column eluate were analyzed for PCB and surfactant content. Both extraction procedures mobilized PCBs efficiently when extended for longer periods and were modelled accurately as the sum of a constant and single-term exponential increase to a maximum. The predicted number of replicate stages required to mobilize 50% of the toxicants varied from 7 to 3 cycles for sonication-washings of the soil or from 6.8 to 2.8 h for column flushing and decreased as the concentration of surfactant in the aqueous phase was increased. The combined PCB-laden aqueous suspensions could then be back-extracted with $scCO_2$ and the eluate could be dechlorinated quantitatively as it traversed a short, heated, column of silver-iron bimetallic mixture.

In Chapter 4, PCBs were mobilized from contaminated soil suspension by back-extraction with $scCO_2$ during 30 min at 50 °C. The results indicated that >99% of PCB were mobilized from the soil extracts and 23-78% of surfactant remained in the aqueous suspension post treatment. The cleaned surfactant suspension could then have been reused to mobilize more PCB from the contaminated soil. Based on the PCB extraction efficiencies, the suitability of surfactants for either soil sonication-washing or column flushing treatments were in the order: Triton DF16 >Triton CF54 >Brij 97 > Tween 85 whereas increased surfactant losses were in the order: Tween 85 < Brij 97< Triton CF54< Triton DF16.

There were no apparent differences in the avidity with which separate fractions of the total PCB burden interacted with the soil. Although three of the surfactant formulations did not change the physical properties of the soil, one formulation was observed to disperse the soil aggregates appreciably and required increased pressure to force the aqueous phase through the soil. Nonetheless, large volumes of surfactant suspension were required to mobilize the PCBs efficiently. The challenge remains to improve the efficiency of this stage of the overall process. The PCBs in the cumulative aqueous extracts were back-extracted efficiently (>99%) into $scCO_2$-IBMK. Losses of surfactant during this stage were appreciable but the dechlorination was quantitative.

A set of models for PCB mobilization from surfactant suspensions with $scCO_2$ has been established and the feasibility to both clean surfactant suspension and to regenerate zero-valent metals/bimetallic particles was re-investigated in Chapter 5. Mobilization efficiencies as a function of time of extraction were predicted accurately using the models for PCB mobilization for a given PCB burden. The mobilization time ranged from 102 to 179 min when mobilizing PCB (1000-10,000 μl/ml) from Brij 97 suspension to "non-hazardous" concentration (≤ 0.1 μg/ml).

The dechlorination yields for various PCB concentrations (0.1–1.0%, v/v) ranged from 99.7–72.4% in Brij 97 suspensions and 99.8-73.8% in Triton CF54 suspensions when the outlet stream of mobilized PCBs was directed to two heated zero-valent columns connected in series. In an alternate interfacing scheme, the outlet stream of mobilized PCB from the extraction vessel was channeled to a second extraction vessel containing 20 ml mixed solvent (acetic anhydride, DME, IBMK, 8+1+1) prior to entry into the reactor columns. The dechlorination efficiency for this interface increased appreciably when compared with the direct coupling. The dechlorination yields ranged from 100 – 90.5% and 100-93.6% respectively for Aroclor 1248 concentrations between 0.1 and 1.0% (v/v) in Brij 97 and Triton CF54 suspensions. The surfactants remaining with the aqueous phase was 14.3 ± 0.2 % for Brij 97 suspension and 15.7 ± 0.2% for Triton CF54 suspension with a 3% (v/v) initial concentration post mobilization/dechlorination processing. Preliminary analyses of HPLC and FTIR of the properties of the residual surfactant in the aqueous retentate did not detect any changes other than the decrease in surfactant concentration. These observations suggested that the treated surfactant suspensions could be recycled to extract more PCBs (pollutants) from the contaminated soil.

During 5 h of continued dechlorination of influent from surfactant suspension that contained 10 % (v/v) Aroclor 1242 or 1248, the dechlorination efficiency decreased gradually with time. Three approaches were evaluated to regenerate the reactivity of Pd^o/Fe^o reactor column including (*i.*) 3 h *on-line* flushing with $scCO_2$ at elevated temperature (400 °C), (*ii.*) *on-line* flushing with 30 ml water-methanol mixture (7+3) at ambient temperature and (*iii.*) washing of the particles with 30 ml water. The recovery of dechlorinating capacity by the three approaches indicated that 3 h $scCO_2$ flushing *on-line* was the most efficient. The average dechlorination yield was 81.7 ± 3% for Aroclor 1242 and 61.4 ± 5% for Aroclor 1248. The *off-line* water wash was characterized by the lowest regeneration capacity. The average dechlorination yield was 56.5 ± 2% for Aroclor 1248 at 5 h continuous operation. The regeneration power produced by *on-line* water-methanol flushing treatment was intermediary between other two treatments and the dechlorination yield was 45 ± 9% for Aroclor 1248 after 5 h of continued operation.

It has been demonstrated that the PCB-surfactant suspension or soil extract can be freed of PCB residues by back-extraction with $scCO_2$. The $scCO_2$ stream can then be dechlorinated quantitatively. The combination of PCB mobilization-*on-line* dechlorination with $scCO_2$ is an efficient process that can be applied to the PCB-containing slurry. The optimal processing time can be predicted accurately. The advantage of this approach is that the PCB in the surfactant suspension can be detoxified in a rapid and efficient manner and the remaining surfactant suspension can be reused to extract more PCB contaminants. The disadvantage is that an appreciable fraction of the surfactant is also lost during the back-extraction stage.

6.2 Conclusions

These studies have identified novel approaches for the detoxification by dechlorination of polychlorinated biphenyl (PCB) compounds and have optimized techniques for the remediation of PCB contaminated soils.

1. A rapid, quantitative analytical method to determine the total PCB concentrations in contaminated soil/sediment by conversion of PCB residues to biphenyl has been developed and validated.
2. A novel technique to efficiently detoxify PCBs and PCB contaminated materials by dechlorination with zero-valent metal/bimetallic particles in $scCO_2$ has been investigated systematically. The results have demonstrated potential applications in industry for PCB detoxification and for environmental remediation.

3. A continuous process that combines PCB mobilization from historically contaminated soil into surfactant suspension followed by back-extraction of the PCBs in supercritical carbon dioxide with *on-line* dechlorination was demonstrated to a be practical approach that enabled the polluted soil to be decontaminated in an economical and environmental friendly way.
4. A set of models for PCB mobilization into surfactant suspensions was established. These models can be used to predict rates of PCB transfer from the soil into surfactant suspension as well as the rates of the subsequent cleaning stages with $scCO_2$.

6.3 Contribution to the original research

1. A novel method for total PCB determination by conversion to biphenyl within contaminated soils was developed and validated. This technique has been demonstrated to be rapid and easily conducted. This technique can be applied in polluted soils and sediments.
2. This study has elaborated a successful process that can be used to remediate/restore soils that has been contaminated with excesses of polychlorinated biphenyl (PCB) compounds. A rapid technique has been developed to detoxify PCB compounds to biphenyl in a continuous process that can dechlorinate some 28 mg of PCB mixture per minute using a short heated column of zero-valent bimetallic mixture of iron doped with either silver or palladium. This loading of chlorinated substrate(s) far exceeds the quantities that might be extracted from a highly polluted matrix such as soil or sediment.
3. Extraction with supercritical carbon dioxide combining PCB back-extraction from aqueous surfactant suspension(s) with optimized on-line dechlorination using zero-valent bimetallic mixture is a novel contribution. The commercial surfactants were screened and promising candidates were selected based on their ability to promote the extraction from surfactant suspension(s). This approach can be used not only on PCB extraction from polluted soils, PCB mobilization and on-line dechlorination, but also can be applied to other matrices that have been contaminated with halogenated compounds.
4. Mathematical modeling of the process of supercritical carbon dioxide extraction combined with PCB back-extraction from aqueous surfactant suspension(s) and with on-line dechlorination using zero-valent bimetallic mixture is a novel contribution. The

models established for PCB mobilization both from contaminated soils/sedimens and from surfactant suspension(s) have a great potential application in the environmental industry.

6.4 Suggestion for further studies

1. The mechanisms of PCB dechlorination using zero-valent metal/bimetallic particles in $scCO_2$ need to be investigate in greater detail. Preliminary studies have indicated that the solvent compositions in the substrate have an appreciable effect on the dechlorination efficiency. Different products of dechlorination were observed during the processes when using various solvent substrate. Although the substrate of [PCB (2-20%, v/v), solvent (10-70%, v/v, acetic anhydride, ethanol, methanol or 2-methyl-propanon), DME (10%, v/v)] demonstrated higher dechlorination efficiency, the solvent function and the source of H^+ still remains to be identified.
2. The by-products of the dechlorination should be monitered carefully under the experimental conditions. Specifically, chlorinated dibenzo-furan and chlorinated dibenzo-*p*-dioxin should be determined post the processing.
3. The technique of interfacing the PCB-laden $scCO_2$ stream with the dechlorination reactor requires further investigation and optimization. The dechlorination efficiency of extractor effluent was increased appreciably when channeled to a vessel containing suitable solvent or co-solvent(s). The technique of dechlorination with zero-valent bimetallic particles might be extend to other organic contaminants in soil using optimized processing conditions.
4. Further investigations need to be carried out to identify other surfactant formulations that are capable of transferring PCBs from soil into suspension more efficiently but that remain insoluble in the $scCO_2$-IBMK mobile phase.

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