Trihalomethane Formation Potentials in Lake Memphremagog

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ABSTRACT

In response to the likely future change in the Canadian Guidelines regulating the maximum allowable concentration of trihalomethanes (THM) in potable water, an investigation into the possible causes and variability of THM precursors was conducted during the summers of 1990 and 1991 at Lake Memphremagog in south eastern Quebec. A number of associated parameters were correlated with THM formation potential (THMFP) with respect to season, depth and position on the lake. The THMFP was quantified indirectly by measuring the THM concentration present after chlorination under standard conditions.

THM concentrations in the samples were found to exceed the US EPA standard of 100 μg/L, sometimes considerably. There did not appear to be any statistically significant contribution to THMFP from human activity. No close agreement was observed between THMFP and any of the associated parameters for the lake as a whole. A few correlations were found between THMFP and nutrient concentrations at individual sites.

ABSTRAIT

En réponse aux changements prévus à la réglementation canadienne concernant la concentration maximale de trihalométhanes (THM) permise dans l'eau potable, une recherche a été réalisé, durant les étés 1990 et 1991 au lac Memphremagog dans les Cantons de l'est, pour déterminer les causes et les variations possibles chez les agents précurseurs de THM. Dans le but d'établir une corrélation entre le potentiel de formation de THM (THMFP) et certains facteurs associé par rapport aux saisons, à la profondeur ou la position dans le lac, le THMFP a été déterminé indirectement en mesurant la concentration en THM après chlorination dans des conditions standards.

La concentration en THM pour la plupart des échantillons dépassait la limite de 100 ug/L établie par l'EPA, par une marge considérable parfois. Il ne semble pas y avoir aucune contribution statistiquement significative au THMFP de la part des activités humaines. Aucun lien n'a pu être établi entre les paramètres associés et le THMFP pour l'ensemble du lac. Enfin certaines corrélations ont pu être établi entre le THMFP et la concentration en éléments nutritifs pour certains sites.

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1 INTRODUCTION

Trihalomethanes (THMs) were first linked to the chlorination of natural waters in 1974 (Rook, 1977). The four most commonly occurring THMs are chloroform ($CHCl_3$), bromoform ($CHBr_3$), bromodichloromethane ($CHBrCl_2$), and dibromochloromethane ($CHBr_2Cl$). THM precursors are known to include humic and fulvic acids, which constitute the major portion of organics in some natural waters, as well as algae and their extracellular products (Scully *et al*, 1988). As it is suspected to be a human carcinogen, chloroform, the most commonly occurring THM, has been banned from use in food or drugs by the U.S. FDA since 1978 (Trussell and Umphres, 1978).

There is a possibility that the present Canadian guideline for the maximum acceptable THM concentration in finished waters (350 μg/L) will be lowered in the near future. The most heavily affected by the proposed new guidelines will be drinking water treatment plants which disinfect with chlorine as the primary treatment and have as a raw water source small lakes which may be eutrophic or even hypertrophic. Ayotte (1987) found that, while only one out of 99 small Québec municipalities surveyed had THM concentrations exceeding 350 μg/L, 27 of them exceeded 100 μg/L. In order to avoid the necessity of expensive treatment processes to remove excess THMs, effective management strategies will have to be developed. The variation of the THM precursor concentrations in the lakes on a seasonal and diel basis will have to be investigated, as

will the use of surrogate parameters for rapid assessment of trihalomethane precursor (THMP) concentrations.

An investigation was conducted during July to September 1990 and May to September 1991 of Lake Memphremagog in south-eastern Quebec. The objectives of the study were to ascertain the level of the total THM formation potential (TTHMFP) present in the lake in comparison with drinking water standards; to examine the variations of THMFP over space and time during the summer season; and to search for surrogate parameters and evidence of algal contributions.

2 LITERATURE REVIEW

2.1 Introduction

In 1974, Rook published an investigation of the Rotterdam water utility which showed the presence of haloforms in significant levels following chlorination. In the U.S that same year, Bellar *et al* (1974) reported significant levels of organo-halides in some drinking waters. Both linked the production of halogenated organics to the chlorination of natural waters which contained organics. The principal compound found was chloroform.

The following year, the U.S. EPA published the results of the National Organics Reconnaissance Survey (NORS) (Symons *et al*, 1975). The survey of 80 cities found THMs to be present in almost every finished water (concentrations ranged from non-detectable to 482 μg/L) but only occasionally, and in small concentrations, in raw water supplies. In 1976 the U.S. National Cancer Institute published a report stating that high doses of chloroform caused cancer in rats. As a result, the U.S. FDA banned its use as an additive in food or drugs (Trussel and Umphres, 1978).

2.2 Regulations

In 1979, the U.S. EPA published drinking water regulations setting the U.S. limits on total THM (TTHM) concentrations in finished drinking waters to 100 μg/L (U.S. EPA, 1979). Presently, the U.S. EPA is developing new disinfection by-product

(DBP) regulations as directed by the 1986 amendments to the Safe Drinking Water Act These regulations may lower the existing standard for total THMs. In addition, the EPA may also regulate individual THMs and promulgate standards for other DBPs (Krasner *et al*, 1991).

In Canada, Foley and Missingham (1976) surveyed 13 water treatment plants in Ontario, of which 3 produced finished water THM concentrations of greater than 100 μg/L. A national survey conducted in 1977 (National Survey. ., 1977) covered 70 municipalities across the country and found the mean value of the concentration of THMs in Canadian drinking waters to be 21 μg/L, apparently well below the U.S average of 68 μg/L found in the NORS (Symons *et al*, 1975). However, the survey had been conducted in mid-winter and failed to take into account possible seasonal and temperature effects. Seasonal effects were subsequently examined by Williams *et al* (1980) The Canadian guideline for the maximum allowable concentration of THMs in drinking water was introduced at 350 μg/L. There is a possibility that this will be lowered in the near future (Guidelines..., 1989).

2.3 Aquatic humic materials

Since the discovery that humic substances appear to be the major THM precursors in most natural waters (Rook, 1977; Babcock and Singer, 1979; Oliver and Lawrence, 1979), many researchers have studied humic substances to better understand the THM formation reaction, and examine the environmental effects on the rate and extent of

reaction. Humics have also been studied as model compounds and surrogate parameters.

2.3.1 Definition of humic substances

Humic substances are a general class of heterogeneous, biogenic, refractory, yellow-black, organic substances that are ubiquitous to all environments. They serve as a major reservoir of organic carbon for the global carbon cycle. Extremely reactive, they are important participants in many geochemical reactions and processes (Aiken *et al*, 1985).

Humic substances do not correspond to any unique chemical entity and cannot be described in unambiguous structural or functional terms. The classic definitions of humin, humic acid, and fulvic acid, isolated from their environments, are from soil science and are based on solubility (Gjessing, 1976):

humic acid - the fraction of humic material that is insoluble in water below pH 2 but soluble in water of higher pH;

fulvic acid - the fraction of humic material that is soluble in water at all values of pH;

humin - the fraction of humic material that is insoluble in water at any pH.

More recently, Thurman and Malcolm (1981) defined aquatic humus as the material which adsorbs on an XAD column from an acid aqueous solution. The portion of the adsorbed material soluble in acid and base is fulvic acid, while the portion insoluble in acid is humic acid.

While it is not possible to write the exact structures for humic substances, it is possible to characterize them on the basis of their physico-chemical behaviour. Molecular weight (MW) is an important defining criterion. soil fulvic acids range from 500 to 5000, while soil humic acids average 3000 to 10^6 (Steelink, 1985). Aquatic humic substances have lower molecular weights than their soil counterparts, perhaps indicative of their various sources, which can be either autochthonous (formed from plankton in the water) or allochthonous (leached into the water from terrestrial plants, leaf litter, soil, or subsurface deposits).

2.3.2 Molecular weight distribution of THM precursors

The molecular weight distribution of THM precursors has been studied so as to obtain a better understanding of the nature and sources of THMPs and develop suitable methods for their removal. Trussell and Umphres (1978) reported that MWs for fulvic acids probably range between 100 and 1000, and humic acids probably have MWs of 100,000 or higher. Humic acids were reported to react more actively with chlorine, producing 117% more $CHCl_3$ per unit TOC than fulvic acids, and to be of greater importance in THM production. However, data gathered indicated that the bulk of aquatic humus present was in the 10,000 to 20,000 MW range; the humic acid fraction being so small as to be insignificant.

In contrast, Schnoor *et al* (1979) found that 90% of the organics in the Iowa River were of MW less than 3000, and that 75% of the THMs were derived from this

lower MW fraction, fulvic acid generally contributing over 90% of the humics in natural waters (Oliver and Thurman, 1983). The highest THM concentration derived from the 1700 to 3000 MW range, while the highest THM yield was from precursors in the 2100 to 5000 MW range (Schnoor *et al*, 1979). The fraction of humics < 1000 MW, including the fulvic acids, was found to be important to THM formation, as was the > 50,000 MW fraction

Similar observations on the MW fraction of THMPs were made by Oliver and Thurman (1983) and a number of other researchers. Bruchet *et al* (1984) and Collins *et al* (1986) also found significant THMP concentrations at < 1000 MW, while Collins *et al* (1986) observed significant contributions from fulvic acids in the 10,000 to 30,000 MW range and El-Rehaili and Weber (1987) noted major contributions from humic acids in the 300 to 40,000 MW range. Likewise, Oliver and Visser (1980) found that 1000 to 10,000 MW was the most important fraction for fulvic acids while 10,000 to 20,000 MW was the most important fraction for humic acids. They also found no difference between the THM potential of humic and fulvic acid. This supports observations made by Oliver and Lawrence (1979) but contradicts findings by Babcock and Singer (1979), who found that humic acid produced twice that of fulvic acid (from peat). The fulvic acid fraction was more important than the humic acid fraction, producing roughly 72% to 80% of the total THMs (Oliver and Visser, 1980).

2.3.3 Model compounds

Model compounds have a similar reaction with chlorine as natural THM precursors and will also have roughly the same yields. They are used to study the kinetics of the THM formation reaction and the effect of environmental conditions on the potential yield. A number of researchers have used humic substances as model compounds. These are either purchased commercially or derived from natural sources (Babcock and Singer, 1979; Oliver and Visser, 1980, Urano *et al*, 1983; Batchelor *et al*, 1987; Reckhow and Singer, 1990, Adin *et al*, 1991). Rook (1980), in a detailed study of humic acids as THMPs, noted that humic acids are benzene and aromatic heterocyclic rings substituted with methoxy-, hydroxy-, and carboxylic functionalities. He found that methylated compounds did not react with chlorine at high pH, that bromine was more reactive with methoxy- compounds, and that phenolic hydroxy- compounds are required for the incorporation of chlorine into aromatic groups.

Humics are complex compounds that require a cleavage step prior to reacting with chlorine. Other work has been done with smaller or more readily available organics. Stevens *et al* (1976) found that methyl ketones will react with chlorine to form THMs, and that ethanol can be oxidized by hypochlorite to be a THM precursor. Morris and Baum (1978), however, pointed out that at pH 7, the time required for the reaction of methyl ketones with chlorine to go to completion, would be almost one year. As more likely compounds, they suggested ß-diketones such as resorcinol, structures with a pyrrole ring, and acetogenins, which are responsible for many natural pigments.

Arguello *et al* (1979) found that acetone was the only methyl ketone that produced THMs. Phenols and anilines were good $CHCl_3$ precursors at high pH, and meta- and para-dihydroxyaromatic compounds such as resorcinol were very efficient precursors. This agreed with Rook (1977), who studied resorcinol, pyrogallol, ethanol, and 1,3-cyclohexanediol under simulated water treatment conditions. Dore *et al* (1982) investigated a number of organic compounds and found that resorcinol gave a maximum yield of $CHCl_3$ at pH 7 to 8, while the maximum yield occurred at pH 11 with acetone.

Cooper and Kaganowicz (1985) studied α-methylbenzylamine (α-MBA) as a THMP and found it to be a good approximation to precursors in natural waters. The THM concentration increased with pH. Trehy *et al* (1986) and Scully *et al* (1988) investigated the chlorination reactions of various proteins and amino acids, although Oliver and Lawrence (1979) had previously noted that amino acids, although present at concentrations up to 200 μg/L, do not contribute much as THM precursors.

2.3.4 Surrogate parameters

Surrogate parameters are commonly defined as those whose concentrations are linearly proportional to the concentration of the target parameter, THMs in this case, and which are easier, cheaper, and/or faster to measure than the THMs. A number of researchers have found relationships with total organic carbon (TOC) (Symons *et al*, 1975; Glaze and Rawley, 1979; Veenstra and Schnoor, 1980; Engerholm and Amy, 1983), while Oliver and Lawrence (1979) found a good correlation ($r^2 = 0.97$) between

TOC and total organohalides (TOX). Oliver (1980) and Hoehn *et al* (1984) found that although THMP levels varied widely over time, TOC concentrations remained fairly constant.

Edzwald *et al* (1985) evaluated UV absorbance (254 nm) as a parameter for non purgeable TOC and THM precursors in two natural waters and in fulvic acid. Although nitrites and bromide were found to absorb UV light, and non aromatic organics would not absorb UV light while still containing TOC, a very good correlation was determined between raw water total THMFP and total UV absorbance.

Batchelor *et al* (1987) proposed using iodoform and bromoform formation potentials (IFP and BFP) to predict THMFP. Both are faster to measure than THMs and the iodine and bromine reactions with the THMPs are similar to that of chlorine. Neutral pH haloform formation potential tests were better predictors than TOC and UV absorbtion, and showed a greater trend to be proportional to THMFP.

Reckhow and Edzwald (1991) used a large number of different waters to test various IFP and BFP tests. The variety of waters was supposed to encompass both types of THMP structures hypothesized to exist in natural humic materials and in raw waters. One is the aromatic, highly reactive, resorcinol type of precursor, and the other the aliphatic, less reactive but longer lived, ketone type of precursor. The 2 hour standard IFP (SIFP) test was judged to be the best. It was as accurate as direct UVA as a surrogate parameter for THMFP, and more accurate than dissolved organic carbon (DOC). The alkaline iodoform test had a slightly better correlation with THMFP than

the 2h SHP test, in spite of the different reaction of iodine at high pH, where its reactivity with methyl ketones becomes quite prominent. This agreed with Arguello *et al* (1979) who found that compounds yielding a positive iodoform test result did not necessarily react to form $CHCl_3$ under conditions of high pH, temperature, or shorter reaction times.

A number of researchers have proposed models for prediction of THM formation using some of the above surrogate parameters as well as pH, chlorine dose, reaction time, temperature, and bromide levels (Urano *et al*, 1983; Engerholm and Amy, 1983; Morrow and Minear, 1987; Amy *et al*, 1987a; Amy *et al*, 1987b; Adin *et al*, 1991).

2.4 Algae and their extracellular products

2.4.1 Algae as THM precursors

Although early work on trihalomethanes and their precursors centred on humic substances as the major source of THMP, algae and their extracellular products are now also considered to be precursors of some importance. Algae would be a significant factor in eutrophic or hypertrophic lakes, and their variations, in precursor concentration and activity, are more likely to be influenced by seasonal and diel patterns than other sources of THMP.

Hoehn *et al* (1978) were amongst the first to suggest algal biomass and algal extracellular products (ECP) as precursors for THMs. They found a correlation between the THM and chlorophyll *a* concentrations during the June to November 1975 period of

study of the Occoquan reservoir in North Virginia

Anabaena cylindrica was investigated by Briley *et al* (1980) for its THM precursor potential. Similar behaviour was observed for THMs resulting from the chlorination of both the algal biomass and ECP; the exponential growth phase exhibited a large increase in the THM concentration followed by a reduction during the stationary growth phase. Although the biomass was found to react more slowly than the ECP, it was nonetheless responsible for the greater portion of the THMs produced. Total organic carbon (TOC) was found to be a poor indicator of THMP as it would continue to increase with increasing culture age.

Hoehn *et al* (1980) reached similar conclusions studying two green algae, *Chlorella pyrenoidosa* and *Scenedesmus quadricauda*, and two blue-green algal species, *Oscillatoria tenuis* and *Anabaena flos-aquae*, despite the fact that insufficient chlorine had been added in some of the experiments so as to leave no residual. The random variation of the $CHCl_3$ to TOC ratio with culture age indicated that organic compounds from the algae at different stages of the life cycle differed considerably in their ability to yield THMs, and that a high ECP THMFP was present in the late exponential growth phase. The algal species studied produced ECPs which yielded, upon chlorination, concentrations of $CHCl_3$ per unit TOC at least as high as those reported for humic and fulvic acids. Another suggestion was the greater significance of ECPs over algal biomass during water treatment due to their faster reaction time. It was also noted that bacteria readily degraded algal ECPs, possibly altering the structure of the ECPs to make them

more amenable to reaction with chlorine.

Nalewajko *et al* (1976) showed that bacterial growth in algal ECP could result in consumption of up to 80% of the ECP within 7 to 8 hours with significant intake occurring within the first 2 hours. In addition, Oliver and Visser (1980) observed that after several months, microbiologically produced humic and fulvic acids had roughly the same THMFP as naturally occurring humic material. The role played by bacteria was confirmed by Hoehn *et al* in 1984. They found that algal ECPs in a lake water were hydrophobic rather than the usual hydrophilic, suggesting that heterotrophic activity could have altered the character of the ECPs, possibly to the point that they become indistinguishable from other organic matter in the lake. Indications were found that algal ECPs do not affect the overall solubility-class distribution of organic matter or the fraction of DOC producing THMs in the lake. They also observed indicators suggesting shifts in THMFP might be attributed to shifts in dominant algal types, as different species probably have different THM yields.

Oliver and Shindler (1980) examined 7 species of cultured algae and a few natural samples for THM precursors. Upon chlorination, the different species yielded THMs in the range of 1.4 to 7.3 μg $CHCl_3$/mg material at pH 7 and 5.3 to 47 μg $CHCl_3$/mg material at pH 11. They found that the mechanisms of chlorine reaction with cellular carbon compounds differ from those with humic materials. Neither the extracellular nor the intracellular materials accounted for more than 20% of the total $CHCl_3$ production. The majority of precursors appeared to be associated with algal cells or cell fragments.

Although Morris and Baum (1978) found $CHCl_3$ from the chlorination of chlorophyll *a*, Oliver and Shindler (1980) indicated that algal pigments were not particularly important THMPs as little correlation was apparent between the algal chlorophyll *a* concentration and the $CHCl_3$ yields from the cultures.

Karimi and Singer (1991), studying Silver Lake Reservoir in California, found THM concentrations ranged from 16 to 71 μg/L. An increase in THM and TOX production of 9.1 μg/L and 63.5 μg/L, respectively, was observed at the reservoir outlet. The lower THM increase may have been due to the volatility of the THMs compared to the non-volatile TOX compounds. The THM and TOX increase was attributed to algal growth in the open reservoir and the addition of chlorine to control these growths. An association between algal population and maximum THMFP was observed, with about 25 μg/L of maximum THMFP produced per 1,000 ASU/mL of algal cells.

Although varying considerably in metabolic activity and in the organic products of metabolism, proteins represent the largest single fraction of organic components of many algae and are an especially important ECP of blue-green algae. Scully *et al* (1988), studying N.E. Tani Lake in Colorado, found that proteins and amino acids appeared to contribute 8 to 11% of the total $CHCl_3$ precursors, and as such, have the potential for producing 115 μg/L $CHCl_3$ regardless of any humic or fulvic acids present in the water. They compared the chlorination reactions of bovine serum albumin (BSA), pepsin, renin, and cytochrome c with that of humic acid. All proteins had similar molar $CHCl_3$ yields of 0.2 to 0.5% compared to 0.78% for humic acid. The rates of reaction

with chlorine were much slower for the proteins than for the humic acid. In fact, Trehy *et al* (1986), in investigating the reaction of amino acids with chlorine, indicated that amino acids would tend to be precursors for the non-volatile compounds while humics would be more efficient precursors for volatiles (such as THMs).

2.4.2 Algae as precursors of other organohalides

Van Steenderen *et al* (1988) studied a pure culture of *Microcystis aeruginosa*: forma *flos-aquae*. Under conditions of phosphorous limitation, the death of this alga resulted in a large release of TOX (6.7 mg/L), otherwise, there was a gradual release of TOX as algal growth continued. Even then, the concentration of TOX excreted after 14 days exceeded 1 mg/L, higher than reported values for other green algae.

Oliver (1983) examined the production of dihalo-acetonitriles (DHAN) from algal precursors. More DHAN was produced from fulvic acid than algae at pH 7, although only 1 to 3% of the organic nitrogen in the fulvic acid was converted. *Anabaena* algae produced more DHAN than *Scenedesmus*, possibly due to having a higher organic nitrogen content.

Wachter and Andelman (1985) studied 2 green algae, *Chlorella vulgaris* and *Chlorella pyrenoidosa*, and one blue-green algae species, *Anabaena flos-aquae*, for the formation of non-volatile organohalides (NPOX). This was in response to studies showing that non-purgeable organic-bound chlorine generally exceeds the volatile fraction produced upon the chlorination of organics in water supplies, and that non-purgeable

organics in finished water are more mutagenic than their precursors. The majority of the organohalides generated from algal ECP were non-purgeable. The filtrate of the *A. flos-aquae* produced more NPOX than the two species of green algae. Differences in the respective amounts of ECP excreted accounted for roughly 50% of the observed differences among algal species in NPOX formation. It was observed that an average of 8.3% of the chlorine demand in the algal filtrates was accounted for by NPOX forming reactions, higher than previously reported.

2.4.3 Seasonal and diel/diurnal effects

THMs and their precursor concentrations vary on a regular basis, as do many other aqueous pollutants. Algal precursors, though, may be more susceptible to seasonal and diel effects. Veenstra and Schnoor (1980) found an extra peak in the MW distribution (AMW 40,000 and greater) of the THMPs in the Iowa River during the summer and autumn. The cause was suggested to be increased algal activity and runoff. Although the heavier MW organics (> 40,000) did not contribute significantly to the total THM concentration, THMP and TOC levels were highest during the summer and autumn. The seasonal variation in the THM levels was due to the nature of the organic precursors and not the environment. Oliver and Visser (1980), however, found that the major $CHCl_3$ precursors in aquatic humic material were the < 30,000 MW fractions and that there was little seasonal effect.

Stevens *et al* (1976) have suggested temperature as the cause of the significant

differences observed between summer and winter THM levels. Arguello *et al* (1979), surveying 14 utilities over one year, found large variations in the THM levels present in the finished supplies, generally less in winter. Williams *et al* (1980) found THM variations ranging from 13 μg/L in January to 120 to 160 μg/L during the summer in the Ottawa/Hull system. McGuire and Meadow (1988), surveying 910 U.S. utilities, found a median maximum THM concentration of 65 μg/L in summer and 50 μg/L in winter. Alarcón-Herrera *et al* (1992) investigating variations in humic substances in a river, found high humic concentrations during the month of April and the summer months which corresponded with high total THM levels in the drinking water.

Hoehn *et al* (1984) examined the diel variations in THMs as a result of characteristics of algal behaviour. They studied THMP variations in a hypertrophic lake. *Microcystis spp* was found to be the dominant algal type during the summer period, giving way to *Chlamydomonas* during the autumn. THMP was highest in early August when algal density was increasing. Maximum diel THMP occurred at 8 am. A significant THMP was also observed during the night with a rise in CO_2, indicating increased heterotrophic activity. THMP decrease after the noon hour was thought to be due to: the intense photo-respiratory state of the algae, a downward migration of the algae away from the midday light, oxygen-induced inhibition of the bacteria, destruction of low MW compounds or hydrolysis of high MW compounds (ECP) by heterotrophic bacteria, or incorporation of precursors into marl ($CaCO_3$) at high pH. DOC showed slight variation during this period. Karimi and Singer (1991) interpreted this as

indicating that ECPs released from photorespiring algae are low MW metabolites that have a low THM formation potential, while compounds released during active photosynthesis are high MW metabolites with high THMFP.

It will be useful to mention the principal conclusions of four Russian studies examining the diel variability of ECPs. Kosenko (1974), investigating *Anabaena variabilis*, observed a noticeable drop in extracellular carbohydrates with a decrease in light; carbohydrates were consumed particularly rapidly in the dark. He suggested that previously released extracellular carbohydrates were being consumed by the algae to meet energy requirements.

Sakevich *et al* (1979,1980), studying the changes in the ECPs of *Microcystis aeruginosa* during different growth phases and light conditions, found that the concentration of ECPs generally increased under adverse environmental conditions. The ECPs were composed of polysaccharides, proteins, amino acids, alcohols, esters, organics acids, carbonyl compounds, and amines. The concentration of ECPs ranged from 17 to 131 mg/L at the start, to 259 to 325 mg/L at the end of the exponential growth period. The ECP to biomass ratio increased at the start of growth, and was lowest in the old cultures. Contrary to van Steenderen *et al* (1988), it was found that under nitrogen or phosphorous limiting conditions, there may be a reduction in organic compounds due to heterotrophic feeding by the algae. If this decrease precedes cell lysis, posthumous release would increase the ECP level.

There was a peak in the soluble organic matter at the start of the log growth

phase, although the concentration was fairly constant by the end of the growth phase. A reduction in ECP content during periods of intensive cell growth was suggested. In a natural water body, the soluble organic matter was observed to decrease at the start of the light period, then increase to a maximum at 3 pm (Sakevich *et al*, 1980). In some cases, significant increases in the dark were observed. Although daily changes in the soluble organic matter are also affected by accompanying bacterioflora, the cause and effect relationship between them was not clear.

Sakevich and Osipov (1983) studied algologically pure cultures of *Microcystis aeruginosa* and *Anabaena variabilis*, and axenic cultures of *A. variabilis* and *Nostoc muscorum*. The algal biomass increase over time was highest during the exponential growth phase, when there was the most intense photosynthesis, and approximately zero during the lag phase. The filtered COD increase over time was high during the lag phase and highest (29.8 mg/L-d) when there was greater mortality. An inverse correlation was observed between the algal biomass increase and the filtered COD increase over time for the axenic cultures, but due to the influence of bacteria, this was not clear in the algologically pure cultures.

3 LAKE MEMPHREMAGOG

3.1 General characteristics

Lake Memphremagog (lat. 45°06' N, long. 72°17' W) is a long (40 km) and narrow (2.4 km mean width) meso-oligotrophic lake lying on the Quebec Vermont border. Although the Canadian portion of the lake's watershed is little developed, nearly 70% of the 1689 km^2 watershed is drained by three Vermont rivers the Clyde, the Black, and the Barton, which enter the lake at its southern end These rivers carry agricultural runoff and sewage from several small towns, and contribute 84% of the phosphorous loading into the lake. A north-south decreasing nutrient gradient may be responsible for observed gradients in primary and secondary productivity (Ross and Kalff, 1975).

The lake is morphometrically divided into 3 basins on the basis of depth The general characteristics of each basin are given in Table 1 (Watson, 1979)

Table 1. General Characteristics of Lake Memphremagog

Basin	Area (x10^{7}m^2)	Volume (x10^{8}m^3)	Mean Depth (m)*	Depth of Mixed Layer (m)
South	4.4	3.2	7.0	7.0
Central	2.2	10	51.0	10.5
North	1.0	2.8	13.5	9.5

*(Ross and Kalff, 1975)

3.2 Algae in Lake Memphremagog

3.2.1 Algal species variation

Watson (1979) conducted a detailed examination of the phytoplankton dynamics in Lake Memphremagog. The findings are presumed to be still valid for the lake as present nutrient levels are not appreciably different from those previously observed (Ross and Kalff, 1975; Watson, 1979). Watson observed that in spring, all stations exhibited high biomass concentrations of *Diatoma tenue* var. elongatum, which was rapidly succeeded by *Oscillatoria Redekei* as temperatures increased. This was accompanied by *Ceratium hirundinella*, *Melosira italica* subsp. *subarctica*, and *Oscillatoria* cf. *rubescens* in the south basin; *C. hirundinella* and *Fragilaria crotonensis* in the central basin; and *F. crotonensis*, *Rhizosolenia eriensis*, and *Botryococcus Braunii* in the north basin. In the late autumn, a significant increase in *M. italica* subsp. *subarctica* occurred in the south basin, and was observed much later in the central basin. Water column instability, due to wind and temperature effects, caused the populations of blue-green *O. Redekei* to suffer, being supplanted in areas by surface blooms of *Anabaena flos-aquae*.

The netplankton species ($>35\mu$m) were characteristically periodic in occurrence although *Cryptomonas rostratiformis*, *Asterionella formosa*, and *Fragilaria crotonensis* were often present. The nanoplankton ($<35\mu$m) species: *Rhodomonas minuta*, *Cryptomonas Marssonii*, *C. erosa*, *C. reflexa*, and *Chrysochromulina parva* occurred in almost all samples and were frequently significant contributors to the total biomass. The relative proportion of percent nanoplankton biomass decreased significantly over the

season with increased trophic level. Zooplankton grazing, although considerable, caused only short term imbalances in the nanoplankton. With increased total biomass there was an increase in the number of species observed but a significant decrease in the community diversity and evenness.

3.2.2 Phosphorous influence

Total phosphorous (TP) levels were found to have little influence on the relative proportions of netplankton or nanoplankton in the lake, although the data indicated an indirect effect on the size distribution. Under conditions of lower phosphorous levels, the prominent spring blooms of *Bacillariophyta* and *Cyanophyta* were reduced or absent, as were the autumn peaks of *Cryptophyceae*. The relative importance of the *Chrysophyta* was unchanged but there was no significant relation with TP. TP was found to have little relation with short term fluctuations in species composition.

4 MEMPHREMAGOG 1990/1991 SAMPLING CAMPAIGN

4.1 Sampling sites

Five sites were chosen for sampling on Lake Memphremagog (Figure 1). Pender and Indian sites are situated at the southern tip of the lake in the shallow southern basin. Border site is located on the Canada-U.S. border and is also within the area of the southern basin. Central site is located at about the level of the Limnology Research station, roughly where the central basin is deepest. The fifth sampling site, North, is located in the north basin halfway between Central site and the northern tip of the lake, where it is drained by the Magog River. The sites were chosen to investigate north-south differences along the length of the lake. Although mixing occurs within each of the three basins, the basins do not mix between themselves. As Central site was located at the deepest point on the lake, both epilimnion and hypolimnion samples were taken from this point. Three sampling sites were chosen in the southern basin, two sites at the tip, because this area was considered likely to be more active due to the greater population density around the southern end of the lake and the relative shallowness of the basin.

4.2 Sampling schedule

During the 1990 preliminary sampling season, samples were taken approximately every two weeks from July until the fall turnover in late September/early October. The 1991 sampling season commenced at the beginning of May, after the spring turnover, and

samples were taken every 10 days to two weeks until the end of July. Sampling could not be continued until the fall turnover, as planned, due to equipment difficulties

4.3 Sampling equipment

Data collection was often weather dependent Water samples and *in situ* measurements were taken from the boat once it was anchored at the site Secchi depth measurements were taken with a Secchi disk, while pH and temperature were recorded by a pH meter with the probe lowered to the desired depth Integrated epilimnion samples were taken from the first five meters of the water column with a polyethylene tube. Depth samples were taken with a Van Dorn bottle lowered to the desired depth. Samples were stored in rinsed polyethylene bottles, until the return to the station where they were transferred into prepared acid-washed amber glass bottles with PTFE lined caps. Bottled samples were stored at 4°C until transported back to Montréal

5 METHODS

5.1 Preparation of samples

5.1.1 THMFP and chlorine demand samples

For the preparation of the filtered THMFP and chlorine demand samples, the lake water was filtered with 0.45 μm glass fibre filters that had been prewashed four times with distilled water to remove any organic carbon. Prior to sample preparation, the 250 mL metric round amber bottles were washed with chromic acid, following method #1070 in Standard Methods (APHA *et al*, 1989) and oven baked at 218°C for three hours. To the bottles were added 5 mL of pH 7 phosphate buffer to stabilize the pH, and an appropriate amount of dosing solution. The dosing solution of chlorine used was saturated chlorine water with approximately 4.98 mg Cl_2/L as titrated according to Standard Method #4500-Cl B. Generally 2 to 4 mL of chlorine water was added to each sample bottle, depending upon the expected strength of the sample, such as to leave a residual of only 1 mg/L. The bottles were then filled with sample such as to leave no air space. Reagent blanks contained only the phosphate buffer and the sample water. Control blanks were filled with Millipore water instead of distilled water so as to not exert any chlorine demand. Millipore water was generated using a combination of the Milli-RO4^R and Milli-Q^R systems. After prefiltering and reverse osmosis removed all particles from the water, it was stored in a reservoir before the next stage. This involved the use of activated carbon filter, ion exchange, and Millipack 0.22 μm filter cartridges

to remove organics and ions from the water. Samples were stored for 48 hours at 20°C in the dark. At this point the chlorine demand samples were analyzed following Standard Method #4500-Cl B. The chlorine residual in the THMFP samples was neutralized with approximately 2 mL of a 0.02 N solution of sodium thiosulfate. The samples were stored in the dark at 4°C until analysis.

5.1.2 Organic carbon samples

Dissolved organic carbon (DOC) samples were filtered with 0.45 μm glass microfibre filters in a glass filtration apparatus to reduce any possibility of organic contribution from plastic vessels. Only 10 to 15 mL of sample were required for organic carbon analysis. The samples were contained in small chromic acid washed glass vials. The glassware preparation procedure for the total organic carbon (TOC)/DOC samples was the same as that for the THMFP samples. Samples were preserved with one drop of concentrated nitric acid and stored at 4°C until analysis.

5.2 Analysis of the THM samples

5.2.1 Preliminary experiments with the GC/MS

The THMs were extracted from the samples by automated purge and trap (Tekmar ALS 2016, LSC 2000) prior to determination by gas chromatography using Standard Method #6230 B. The initial gas chromatograph (GC) had a mass spectrometer (MS) as a detector. In order to take advantage of this, the intention was originally to

investigate the presence of other organic halides such as dichloroethane, trichloroethane, dichloroacetic and trichloroacetic acid, and even possibly halonitriles in addition to the four THMs. In the analyzed samples, however, only chloroform was found to be present, although there were occasionally trace amounts of the other THMs.

Unfortunately, the Varian Saturn GC/MS, with its high sensitivity, was very often contaminated. The source of the contamination proved to be the 10 μg/L standards with which attempts were being made to tune the instrument. The flow rates required by the purge and trap were far too high for the MS and were causing the contamination. Attempts were made to operate the purge and trap at lower flow rates. In order for this to be successful, a cryogenic cooling system was needed for the GC to cool it to -50°C. The low temperatures and long GC elution times were supposed to compensate for the low flow rate through the column. This method, however, was extremely time consuming due to the analysis time required for each sample and very expensive due to the large quantities of liquid nitrogen that were required. Eventually, the GC/MS was abandoned for a conventional Varian model 3700 GC with an electron capture detector (ECD).

5.2.2 Preparation of the instruments

The pressures of the helium carrier gas and the nitrogen makeup gas were 80 psi (551.6 kPa). Only ultrapure gases were used and these were first filtered through oxygen traps before entering the instruments. The flow rate of helium through the purge and

trap unit was 40 cm^3/min. The purge and trap valve and line temperatures were set at 100°C and the ready temperature was set at < 30°C. The purge and trap method used was a modified version of the EPA method #624 with a 12 minute purge. No dry purge was used as there was a moisture control module (MCM) to eliminate entrained water from the system. The desorb stage at 180°C lasted 5 minutes. The trap was baked afterwards for 7 minutes at 260°C.

The flow rate of the helium through the column (VOCOL DB-624 capillary column) was approximately 9 cm^3/min or roughly 14 psi (96.5 kPa) column pressure. The flow rate through the detector of the combined gases could not exceed 30 cm^3/min. The temperature of the ECD was set at 300°C and allowed to drift somewhat as the temperature control was not precise. The GC method started with the oven temperature at 30°C for 8 minutes. The GC method was started automatically by the integrator when the purge and trap entered the desorb stage. The oven temperature then increased at 15°C/min to 120°C, where it remained steady for 2 minutes. Originally, the oven temperature increased to 210°C to ensure that there would be no residue in the column. This had to be reduced when it was discovered that at higher temperatures the portion of the column inside the detector experienced bleeding of the packing material.

5.2.3 Analysis procedure

The Tekmar LSC2000 has 16 individual injection ports with 5 mL volume glass sample vials. A maximum of 15 samples were analyzed during each complete run (one

port was always kept for water blanks only, to avoid risks of contamination). One complete run lasted roughly 12 hours. The ambient temperature and the degree of ventilation in the room controlled the amount of time required for the system to return to its ready temperature and influenced the run times. The vials were cleaned with Millipore water and baked for 2 hours at 450°C in a muffle furnace. The sample was pipetted into the vials with disposable borosilicate glass pipettes. The pipette was rinsed three times with Millipore water, then three times with the sample before actually taking the sample volume. The bottles were vigourously shaken prior to opening to redissolve any volatiles that might have left solution.

Each day a few 100 μg/L standards ($CHCl_3$ in methanol) were analyzed to check for detector drift. If the standards were not within 10 % of the known concentration and reproducible, the instrument would be recalibrated. After this a Millipore water blank was run to check for residue or entrainment on the trap or in the GC column. Regular weekly recalibration of the instrument was performed and a new standard curve generated (Figure 2) A six point calibration curve was used. The initial range was higher but proved not to be necessary. At this time a number of samples were repurged and re-analyzed to check the efficiency of the purge process. During the purge stage, the vent on the purge and trap would be plugged to check the system for leaks. The purge and trap does not develop leaks very readily although it is very sensitive to the presence of any leaks in the system. When no leaks are present in the system the pressure buildup will stop the bubbling within the vials.

5.2.4 Detection limit and confidence interval

The detection limit and confidence interval were calculated using the following equations (IUPAC):

$$D_I = \frac{(x_I - x_B)}{m}$$

$$C_I = k \left\{ S_B^2 + S_i^2 + \frac{((1 - x)/m)^2 S_m^2}{m} \right\}^{1/2}$$

where x_I = smallest discernable signal
x_B = mean of blanks
m = analytical sensitivity (slope of linear regression)
i = intercept
k = 3
S_B = standard deviation of mean
S_i = standard deviation of intercept
S_m = standard deviation of slope

The detection limit calculated from successive runs was found to be 3.23 μg/l. The standard deviation for the repeated 100 μg $CHCl_3$/L samples was less than 1.08 μg/l. The confidence interval, calculated from several series of standards run on different days, also accounted for the error contribution from detector drift. The confidence interval was found to be 21.2 μg/L.

5.2.5 System efficiency

Dore *et al* (1982) found that the conversion of resorcinol, as a precursor, to THMs was 91.5% based on the mass balance. Resorcinol was used to test the overall efficiency of the system. Known concentrations of resorcinol were prepared and analyzed following the same methodology as that for the samples. Recovery of the

THMs relative to the original amount of resorcinol was 88.2%. Based on the findings of Dore *et al* (1982) this would appear to indicate that the overall process had an efficiency of 96.4%

5.3 Analysis of the other parameters

5.3.1 Organic carbon samples

The organic carbon samples were analyzed on a Dohrman DC-80 carbon analyzer. This instrument used the persulfate-ultraviolet oxidation method. The analysis was conducted with the instrument calibrated in the 10 to 400 mg/L range. The reactor fluid and the calibration standards were made according to the procedures given in the operating manual. Each sample volume of 100 μL was injected by syringe into the instrument which was started simultaneously. At least three repeat injections were performed for each sample.

5.3.2 Water quality parameters

The turbidity measurements were done on a Hach 2100 turbidimeter. A 25 mL sample was inserted, in a dedicated vial, into the instrument. The calibration was done with sealed vials containing standard suspensions. The suspended solids and alkalinity measurements were performed following Standard Methods (APHA *et al*, 1989).

5.3.3 Nutrient data

Chlorophyll *a*, total nitrogen and phosphorous, secchi disk and temperature data were obtained from the Limnology Research Group at McGill. Total nitrogen samples were digested with persulfate and measured on a ultraviolet spectrophotometer (Smith *et al, in press*). The total phosphorous samples also underwent persulphate digestion, while the final blue colour was also read on a spectrophotometer (Johnson, 1971) The procedure for chlorophyll *a* was developed by Bergman and Peters (1980).

6 RESULTS AND DISCUSSION

In a complex natural system like Lake Memphremagog, it was not surprising that no obvious cause-and-effect relationship was found between any single associated parameter and the THM concentrations observed. Given the interdependency between the parameters, it was impossible to draw concrete conclusions from the data as to the exact nature of the factors influencing the THM formation potential (THMFP). However, an attempt has been made to present a hypothesis on the possible relationships existing within the lake between the parameters and the THMFP.

6.1 Chloroform variation over space and time

6.1.1 Pender and Indian sampling sites

The seasonal variations in the trihalomethane formation potential (THMFP) concentrations at the Pender and Indian sampling sites are shown in Figures 3 and 4 (Appendix B). The only THM detected in the chlorinated samples was chloroform ($CHCl_3$). The variations observed at each site were quite similar. This was not surprising given that these two sites are in close physical proximity to each other.

At Pender, a large peak was observed in both the filtered and unfiltered samples late in the 1990 season at 1808 (dates are given as ddmm). During 1991, peaks were noticed at 0506 and 2606 in the unfiltered THMFP, with the first peak coinciding with a maximum in the filtered THMFP. The peaks observed during the early 1991 season

(almost 200 μg/L at 2606) were not as great as that observed during the late 1990 season (over 300 μg/L at 1808).

At Indian during the late 1990 season there was a similar THMFP peak at 1808 in the unfiltered sample (over 280 μg/L). The THMFP of the filtered sample decreased from a probable maximum of 180 μg/L at 1808 to 120 μg/L at 2309. The difference observed between the filtered and unfiltered THMFP is supposedly due to the algal biomass only, which makes a greater contribution overall although the ECPs are supposedly more reactive (Briley *et al*, 1980). During the early 1991 season, a small increase in THMFP to 0506 was observed in the unfiltered sample, coinciding with a peak in the filtered sample. A large peak (190 μg/L) was also observed in the unfiltered sample at 2606.

Although it is not possible to know whether the late summer peaks present in 1990 would also have been present in 1991, there is a strong possibility that this might have been the case as it is not surprising to find higher THMFP when algal growth peaks during the late summer (Karimi and Singer, 1991). An examination of the chlorophyll *a* data for the periods in question indicate that there were high concentrations during the late summer and early autumn of both 1990 and 1991 (Figures 28 to 33, Appendix D). The THMFP peaks observed likely represent precursor increases due to large releases of algal extracellular products (ECPs) and increased algal biomass during growth.

Examining the 1991 season, the initial THMFP is expected to have been mostly from humic material entering the lake with the runoff, augmenting that produced in the

lake. The first observed THMFP peak occurred during the period of the spring (or early summer) blooms when the dominant alga is *Diatoma tenue* var. *elongatum* and probably represents a precursor release from algal biomass and ECP during the exponential growth phase. Algal release of ECP is highest during the exponential growth phase (Sakevich and Osipov, 1983), which might explain the observation of only the single filtered THMFP peak at 0506. The large peak, appearing only in the unfiltered sample a few weeks later is likely to be the contribution of mainly biomass during the late stationary growth/death phases, especially as there is a shift in dominant algal species to *Oscillatoria redekei* and other blue-greens around this period. One would expect, then, that the major ECPs would be polysaccharides, glycolic acid, and polypeptides (Watanabe, 1980).

On the basis of similar levels of observed chlorophyll *a* and other nutrients during the late summer of 1990 and 1991, one could expect that a THMFP peak should exist in late summer 1991 of a similar magnitude in concentration as 1990 (Hoehn *et al*, 1978; Veenstra and Schnoor, 1980; Alecón-Herrera *et al*, 1992). The high THMFP levels observed at summer's end are likely the result of a combination of the maximum algal growth levels, a shift in species domination due to changing conditions, and a decrease in species diversity with increasing algal populations in the lake (Watson, 1979).

6.1.2 Border sampling site

The seasonal variation at the Border sampling site is shown in Figure 5 (Appendix B). There was a late season maximum in THMFP in the unfiltered sample at 1808, although this was not as high as that observed at Pender and Indian (185 μg/l versus roughly 300 μg/L). The THMFP peak in the filtered sample, however, occurred at 0409 instead of at 1808. This was possibly due to the phosphorous deficiency at Border in the period prior to this. Stress conditions could have caused the algae to feed heterotrophically on the previously released ECPs such that they become unavailable as precursors. This might explain the low concentration of THMFP (140 μg/l) observed in the filtered sample for 1808. The delayed peak at 0409, possibly due to the decreased N to P ratio at that period, could then have been the result of a large posthumous release of ECPs (Sakevich *et al*, 1980).

During the early 1991 season, the variation of THMFP over time was very similar for both the filtered and unfiltered samples. In both cases, the THMFP increased gradually to a maximum at 1506. There was no second, larger unfiltered peak observed a few weeks later as at Pender and Indian. The peak in the unfiltered sample appeared later than at Pender and Indian and the concentration was slightly lower than that at the two other southern basin sites.

The filtered THMFP maximum occurred over the 0506 to 1506 period at Pender and Indian, whereas at Border there was a sharper peak of a slightly lower concentration at 1506 (145 μg/L versus 160 μg/L). Although it is possible that the observed peak at

Border at 1506 was actually the result solely of the precursors from the exponential growth phase, it is not likely, because an expected peak from precursors released during cell lysis was not observed at any time during the subsequent sampling periods. A more probable explanation is that there were no clearly defined growth stages for the algal population at Border as a whole and that the delayed peak observed was actually the overlapping influence of the precursors from the growth and death stages.

6.1.3 Central sampling site

The seasonal variation of the THMFP at Central is shown in Figure 6 (Appendix B). The unfiltered peak during late 1990 covered the 1808 and 0409 sampling dates and was smaller than the peaks observed at the southern sites (160 μg/L). The filtered peak appeared to be slightly shifted to 0409, which could be a response to a phosphorous limitation during the mid-summer period, similar to the Border site. The lower THMFP concentrations could also be due to a lower level of algal growth, due to nutrient deficiency, which the low chlorophyll *a* level at the same period would suggest.

During the 1991 season, the variation of the filtered and unfiltered THMFP appeared to follow the same pattern as Pender and Indian. The first peak of the unfiltered sample, during the period of suspected algal exponential growth, occurred at 0506 and was of the same magnitude as those at Pender and Indian, while the second peak at 2606 was smaller (170 μg/L versus 190 μg/L). The peak for the filtered sample was of a similar concentration as that at Border (145 μg/L), although occurring earlier.

6.1.4 North sampling site

The seasonal variation of the THMFP at North is shown in Figure 7 (Appendix B). Although little can be said about the relatively low THMFP levels during the late 1990 season, one can conjecture that they are the result of heterotrophic feeding by the algae in response to the phosphorous limited conditions at the time and of reduced population levels of algae as indicated by chlorophyll *a* levels.

The variation in the 1991 THMFP levels at North is similar to that observed at Pender, Indian, and Central. Although the early unfiltered THMFP peak is of the same concentration as that at Central (165 μg/L), the filtered peak is greater (157 μg/L), roughly equal to those at Pender and Indian. This seemingly small contribution by the algal biomass during the exponential growth period is not reflected during the later growth/death stages where the unfiltered THMFP is of the same concentration as Pender and Indian (190 μg/L).

6.1.5 North-south differences

If similar THMFP trends are assumed for late summer 1991 as occurred during late 1990, the expected late summer peak would be significantly larger than the earlier summer peaks at Pender and Indian, but approximately the same size or smaller at the other sites. This may be due to shifts in dominance between the algal species accompanying *O. redekei* in the various basins in response to varying levels of nutrient availability. There might also have been an influence in the southern tip of *Anabaena*

flos-aquae, as the shallower southern tip would be more likely to have instability in the water column due to temperature or wind effects.

Figures 8 and 9 (Appendix B) are the THMFP monthly averages for all sites, unfiltered and filtered, respectively. Generally, the late season 1990 THMFP at Pender and Indian can be seen to be greater than at the other sites. During early 1991, however, while this appears to be also suggested by the data, the differences between the sites are small. This may be due to the fact that the chlorophyll *a* levels measured between the sites during early 1991 are less variable than those during late 1990. Chlorophyll *a* levels observed at the northern sites during the late 1990 season are lower than at the southern sites at the same time, although they are similar to northern levels observed during the early 1991 season. This suggests that the lower THMFP observed may be due to a less abundant algal biomass rather than a less reactive nature of the algae present.

Comparing the filtered and unfiltered samples, it appears that Pender and Indian had greater contributions to the THMFP from the algal biomass than the other sites during early to mid-summer 1991 (assuming the difference between the filtered and unfiltered THMFP can be attributed solely to biomass). This may have been due to a greater degree of feeding on the ECPs by heterotrophic bacteria at the southern tip of the lake. The direct impact, especially on the southern basin, of human activities on THMFP cannot readily be identified as being separate from the algal contribution. However, an indirect impact on THMFP, perhaps due to human contribution of nutrients into the lake, is quite likely, given the relatively small volume of water contained in the

southern tip.

Overall, the THMFP concentrations found in Lake Memphremagog were similar to those found by other researchers. Hoehn *et al* (1984) found THMFP in the 200 to 700 μg/L range in Crater Lake. Edzwald *et al* (1985) found reservoir levels of TTHMFP in the 200 to 400 μg/L range, while Veenstra and Schnoor (1980) found lower levels of $CHCl_3$ (120 to 260 μg/L) in a river.

6.1.6 Variation over depth at Central site

Figures 10 and 11 (Appendix B) show the seasonal variation of THMFP at Central site for different sampling depths (unfiltered and filtered, respectively). As each layer of the stratified lake theoretically mixes completely within itself, an examination of the epilimnion and the hypolimnion will give an indication of the vertical variation of THMFP within the lake. While the 1990 samples were taken in the epilimnion and the hypolimnion, the 1991 samples were taken at 4 depths to investigate any variations in THMFP as the depth of the boundary between the layers changed. There was also the possibility of different algal species dominating at different depths, depending upon individual light requirements (Watanabe 1980), although this did not appear very likely as the trophic zone was not extremely deep in the lake.

The unfiltered samples indicated a major difference between the THMFP of the layers during the supposed period of exponential growth. This was likely due to the fact that the biomass contribution during this period was probably only available in the

trophic zone: the zone of light penetration and active photosynthesis. No significant difference was observed between the layers during the period thought to be the cell lysis stage. Algal cells would have either settled or migrated out of the epilimnion over time such that a release of THM precursors upon cell lysis would have been available over a much larger portion of the water column. Once settled out, the cells would not have been resuspended back into the upper layer.

The filtered samples generally show no significant difference between the layers during the early and late summer. The only real difference observed was between the samples taken at the 5 m and 20 m depths during the exponential growth period. This was likely the result of the elevated levels of photosynthetic activity at the time, but could have indicated the presence of heterotrophic bacteria grazing on the ECPs.

7 VARIATION OF ASSOCIATED PARAMETERS OVER SPACE AND TIME

7.1 Organic carbon

The seasonal variations of total and dissolved organic carbon (TOC, DOC) are plotted with the respective THMFP observed at each site in Figures 12 to 21 (Appendix C). The TOC variations over time at the Pender and Indian sites were quite similar. Over the mid-summer period, Pender had slightly higher TOC values, in the 6.5 to 9 mg/L range (average 7.6), while Indian was in the 5.5 to 8 mg/L range (average 6.6). High TOC concentrations were observed at both sites at the beginning of the 1991 season. The TOC levels decreased from 11 to 12 mg/L to hover in the 5 to 6.5 mg/L range, with a peak in the mid-summer. The high initial concentrations were likely allochthonous material due to runoff entering the lake and resuspension of bottom material during turnover. During the late 1990 season, there was a TOC peak observed at 1808, while the THMFP was at a maximum. While this was perhaps a reflection of higher algal activity, it is likely that the TOC observed was not solely due to phytoplankton activity, as this activity has been found to be not significant in explaining seasonal variations in TOC (Storch and Saunders, 1978).

DOC seasonal variation closely follows the unfiltered THMFP trend. Both Pender and Indian, during the early summer, have high initial DOC values. After turnover, this drops off sharply, down to the 5 to 8 mg/L range. Two peaks were observed, at sampling dates 0506 and 2606, as had been generally found for THMFP.

This is in contrast to the gradual decrease over the season of the TOC levels and the small observed mid-summer peak occurring a few weeks later than the DOC peaks. In late summer, the DOC variation observed was similar to that of the TOC, with maximums at 1808 of similar magnitude

Border was the only site where similar trends for both THM and organic carbon concentration were observed over time. Both TOC and DOC levels at Border were generally similar to those at Pender and Indian, in the 4 to 11 mg/L (TOC) and 4 to 8.5 mg/L (DOC) ranges During the early season, there was a peak at 1506 for both THMFP and TOC, while a DOC peak over the 0506 and 1506 sampling dates corresponded to the filtered 1506 THMFP peak. During the late season, TOC and DOC increased over August and September.

Although the DOC concentration at Central was similar to Pender and Indian in both variation and magnitude, the change in the TOC levels followed the same general trend as Border The TOC level declined sharply after runoff, with a peak during the early summer, and a gradual increase over August and September similar to that at Border The DOC concentration, after the initial decrease, remains steady through the early summer until the slight increase at 2606. The late 1990 summer measurements indicate a generally increasing level of DOC over the late summer and autumn. None of the TOC/DOC peaks coincided with THM peaks. However, the large TOC peak at 1506 could be the large algal contribution to the organic carbon pool associated with the late stationary growth phase (Fedorak and Huck, 1988).

North has similar ranges of TOC/DOC as other sites. The TOC behaviour follows that of the THMFP, with both having peaks in 2606 and gradual increases over August and September. Overall, the variation at North was closer in behaviour to Pender and Indian than Border or Central. At North, there was also a gradual TOC decrease during the early summer with a mid-summer TOC peak occurring roughly two weeks after the DOC peak. The DOC levels during the late summer peaked at 1808, as at most sites, except Border, which is shifted later.

The monthly averages (Figures 22 to 27) give a better idea of the seasonal variation. TOC and DOC generally followed similar trends. The exception was Central, where DOC declined from a high in May, while TOC was increasing between May and June before decreasing. The TOC behaviour was generally the same as for the DOC levels with a maximum occurring in May. Central is likely to exhibit a different pattern of TOC variation from the other sites because it is much deeper, and therefore the larger water volume possibly dilutes any TOC contribution from runoff and the resuspension of bottom material during the spring. The monthly averages also suggest that the 1990 TOC levels may have been marginally higher than those in 1991. The organic carbon levels in Lake Memphremagog are moderate to high compared to values found by other researchers: Veenstra and Schnoor (1980) found TOC levels of 4 to 15 mg/L, Hoehn *et al* (1984) found DOC levels of 1.9 to 4.3 mg/L, and Edzwald *et al* (1985) found non purgeable TOC levels of 3 to 6 mg/L.

7.2 CHLOROPHYLL *a*

The variation over time and space of chlorophyll *a* is shown in Figures 28 to 33 (Appendix D) The variation in chlorophyll *a* observed during the 1991 season was quite similar for all sites: a chlorophyll *a* peak at 1506, followed by a gradual decrease in concentration to 2307, after which it increases sharply. One can hypothesize that these represent early and late algal blooms.

There is a similar pattern in 1990, although it is less sharply defined and has more variation between the sites. The North and Pender sites showed much less seasonal variation in 1990, with North staying between 2 to 4 μg/L and Pender keeping quite high over the season between 5 to 7 μg/L. Chlorophyll *a* values in 1990 and 1991 appeared to be of roughly the same magnitude, in the 2 to 8 μg/L range (except for large increases at Pender for the end of the 1991 season).

While there is no obvious relationship with the THM levels found, the observed chlorophyll *a* peaks generally occur one sampling period (roughly two weeks) after the supposed algal exponential growth peaks contribution to THMFP (at 1506 and 0409). It may be conjectured that these peaks occurred during the stationary growth phase where biomass concentrations were high but ECP release was low. Also in late 1990, the chlorophyll *a* levels for Pender, Indian, and Border sites were high, corresponding with higher THMFP levels, while Central and North had low chlorophyll *a* and also low THMFP levels. In early 1991, there was little difference between sites, but Pender had higher chlorophyll *a* and THMFP levels than the others, although the difference between

Pender and the site with the next highest concentration, Indian, was not large

7.3 Total Phosphorus

During the 1990 sampling season, the seasonal variations of total phosphorus (TP) at Pender, Indian, and Border were similar to each other as were those at Central and North (Figures 34 to 39, Appendix E). The TP at the southern sites experienced a maximum in June, decreased during July, and rose again slightly in August and September. At Central and North, the phosphorous levels decreased slightly over the season, but were essentially stable from May until September

During the 1991 sampling season, the variation of the monthly averages for phosphorous at each site was similar to that of 1990, but generally more subdued. There was an overall decrease in TP over the first half of the season, although Pender and Indian both had smaller peaks in June than 1990 and much larger ones in August, coinciding with the early and late summer algal growth periods. Overall, there was less difference in total phosphorus levels between sites for 1991 than for 1990 The Pender levels of total phosphorus in 1990 and 1991 were roughly the same, although the 1991 levels were slightly higher than those for 1990 at the other sites.

No relationship was observed between the changes in phosphorous concentrations and THMFP, although it is likely that THMFP levels were influenced by the lower total phosphorus amounts available. This could possibly cause a shift to a less reactive species rather than simply lower populations of the existing species, since there is little

suggestion of that in the chlorophyll *a* levels. During 1991 the Pender, Indian, and Border sites had small phosphorus peaks roughly at the period of exponential growth, with smaller peaks at Pender and Indian during the cell lysis stage. During late summer 1990, TP increased at Pender and Indian around the 1808 sampling date and at Central and Border just prior to this. The monthly averages indicate similar trends between TP and THMFP. Pender and Indian sites peak during August, Central site is stable during the late summer, and North increases over August to September.

There was no real relation observed between total phosphorus and chlorophyll *a* levels. In 1990, early total phosphorus peaks were not reflected in chlorophyll *a* levels, which remained steady. Then while total phosphorus remained steady after mid-summer, chlorophyll *a* levels increased at all sites. During the early 1991 season, chlorophyll *a* peaked two to three weeks after total phosphorus. Both levels appeared to decrease until the end of July, when there was a large TP increase at Pender and Border, but no significant change at the other sites. In the same period the chlorophyll *a* concentration increased significantly at Pender and Indian and to a lesser degree at the other sites.

7.4 Total Nitrogen

The monthly averages are used here for greater clarity when discussing the seasonal variation between sites (Figures 40 to 45, Appendix F). The Pender and Indian sites generally had the highest total nitrogen (TN) concentrations, while North had the lowest. On average, total nitrogen levels were higher in 1991 than in 1990 (range of

300-700 μg/L compared with 250-550 μg/L) early in the sampling season, but August and September levels were similar (except Pender with high August TN levels).

The variation was also quite different between the 1990 and 1991 seasons. For 1990, all sites started with fairly high levels and decreased. Three sites, Pender, Indian, and Central, rebounded in July, dropped in August, only to increase again in September. Total nitrogen concentrations at the Border and North sites reached a minimum in July, then gradually increased towards the end of the season.

TN Levels in 1991 started much lower than those in 1990, and increased to June, generally peaking during the exponential growth period, approximately two weeks after the THMFP peaks. This suggests that the high levels of nitrogen are consumed during algal growth and the smaller increase occurring roughly a month afterwards was the release of nitrogen back into the water after cell lysis. Blue-green algae can be large releasers of nitrogenous substances such as amino acids and polypeptides (Hellebust, 1974). The TN levels at Border, however, peaked at over 700 μg/l at 0506 and declined thereafter. A possible explanation for this could be that algal growth and the production of THM precursors at Border occurred in overlapping stages over the whole season rather than in two distinct blooms as was suggested. This would mean that the nitrogen uptake and return to the water from dead cells would be difficult to discern.

During 1990, it was harder to see the relationships as Pender, Indian, and Border all had increased total nitrogen and THMFP peaks in the same period. At North, the later occurrence of the THMFP peak was perhaps due to low total nitrogen levels. At

Central, an inverse total nitrogen to THMFP relationship was observed during the late growth period. It is likely that other factors were playing the dominant roles in this instance.

Generally, sites with higher total nitrogen levels were also higher in chlorophyll *a* levels. Although there was no obvious relationship, similar trends in behaviour were observed for both parameters during 1990 and 1991. For 1990, both chlorophyll *a* and total nitrogen decreased to a minimum in mid-summer, and then gradually increased until the fall turnover, with a large total nitrogen peak at Pender site in July. This was reflected in a small chlorophyll *a* peak occurring at the same time. In 1991, both TN and chlorophyll *a* levels peaked in June, early in the summer, and then declined over time. The sharp chlorophyll *a* increase at the end of the summer, however, was not reflected in total nitrogen levels except at the Pender sampling site.

7.5 Nitrogen to Phosphorus Ratios

Lake Memphremagog is a phosphorous limited lake. This is fairly clear from the nitrogen to phosphorus (N to P) ratios, which are generally above 20, and sometimes well above that (Figures 46 to 51, Appendix G). Looking at monthly averages, the N to P ratio trends appear to be almost opposite for 1990 and 1991. During 1990, there were fairly high initial ratio values of 28 to 38, which fell in June such that part of the lake (south basin) became no longer phosphorous limited. The N to P ratio then gradually increased to its original value over the rest of the summer, peaking in July or

August. For the 1991 season, the ratio started lower (18 to 30), and increased to June or July before decreasing to generally the same levels as in the spring.

This seasonal variation was influenced greatly by total phosphorus peaks in June 1990, which depressed the ratio, and total nitrogen peaks in June 1991 which elevated it. The very large TP peak observed in August 1991 was balanced by a corresponding large TN peak at the same time. This greater availability of nutrients would explain the high increase in chlorophyll *a* levels between July and August of 1991. Resuspension of nutrients that had settled out of the water column is a possible explanation for the source of peaks. However, the peaks were not observed at Indian, which might be expected, as the two sites are quite close. It is more reasonable to propose that the nutrients were contributed by a few point sources at the southern tip of the lake, either Newport or one of the three rivers, Black, Barton, or Clyde.

The 1990 data appear to indicate that at 1808, Border, Central, and North were all severely phosphorous limited (N to P ratios of 38 to 43). These values drop during the next period (to 28 to 30 for Border and Central, and from 43 to 38 for North). This was likely the reason that while Pender and Indian had filtered and unfiltered THMFP peaks at 1808 (N to P ratio around 25), Border and Central had the filtered THMFP peaks delayed by two weeks and North had no real filtered peak to speak of. This temporary phosphorous deficiency during the exponential growth phase could have caused temporary heterotrophic feeding by the algae on the ECPs released, particularly since the nitrogen and phosphorous levels at Border, Central, and North were already rather low

at the time.

In 1991, no individual patterns of variation in N to P ratio were observed between the sites. This was not surprising since the total phosphorus and total nitrogen seasonal variations were similar for all sites. Levels of both during early season were higher relative to 1990 Ratio values stayed in the 25 to 38 range all season except during the very beginning and end of the sampling year where some of the southern sites dropped down to 20 or below

7.6 pH and Alkalinity

On-site data for the pH levels in the lake were available only for 1990 (Figure 52, Appendix H). The pH generally remained in the 7.5 to 8 range. There was little overall variation between sites and over time. The exception was a sharp drop in pH at 1808 for all sites occurring at the same time as the highest unfiltered THMFP peaks. The larger THMFP peaks coincided with smaller pH reductions. A possible explanation is the slightly lower alkalinity levels for 1808 which, coupled with high light intensity and high pH, could have induced conditions whereby active photosynthesis would be limited by CO_2 levels. This situation favours the release of glycolic acid, the most common one librated by algae (Hellebust, 1974; Watanabe, 1980), which might cause a temporary reduction in pH. The pH variation between sites at 1808 mirrored that of alkalinity.

Alkalinity levels generally did not exhibit much seasonal variation (Figure 53, Appendix H). During the mid- to late summer of 1990, it hovered in the 52 to 60 mg/L

as $CaCO_3$ range, while it remained in the 50 to 55 mg/L range for the early to mid-summer period of 1991. The exception was the Pender site (Figure 54), which displayed a fair degree of variation in both late 1990 (between 55 to 65 mg/L) and early 1991 (50 to 62 mg/L). During the early 1991 season, Pender had alkalinity peaks at 0506 and 2606, which corresponded to the unfiltered THMFP peaks observed. The increase in alkalinity to 0506 was likely due to increased algal activity, although in the case of Pender, it may also have been influenced by human activities. The southern tip where the Pender site is situated is relatively shallow and does not contain a large volume of water so that point sources may have a significant impact.

Although 1990 appears to have had higher alkalinity levels than 1991, this may not actually have been the case, as the periods covered were not exactly the same for the mid-summer levels for each year. The higher ranges at all sites during the mid- to late summer of 1990 may have been the result of increased levels of algal activity since this is the period of greatest algal activity.

7.7 Suspended solids and turbidity

Figures 55 to 61 (Appendix H) show the variations in suspended solids and turbidity over the 1990 and 1991 sampling seasons. Suspended solids (SS) concentrations for 1990 and 1991 were roughly in the same range, generally 0.5 to 3 mg/L. During the mid- to late summer of 1990, although there were no significant differences between sites, the southern sites appeared to have slightly higher SS levels than Central and

North. Although there was no great seasonal variation over the period examined, the behaviour was the same for all sites and there appeared to be a gradual increase in SS occurring over August and September.

During the early to mid-summer of 1991, there were similar trends in seasonal variation observed between Pender, Indian, and Border, and for Central and North. There was no variation over space between the southern sites. The SS levels there peaked at 1506, fell gradually to 2307, and then appeared to increase again. The behaviour in 1990 and 1991 at Border, Indian, and Pender appeared to follow patterns similar to those of chlorophyll *a*, which might be expected if algae were supposed to be the primary source of suspended solids in the water column. This is not the case for Central and North, both of which have turbidity levels increasing over the season to maximums at 2606. The initial peak at 1506 at the southern sites possibly reflected the contribution of particulate matter to the lake by spring runoff. The particulate matter would not have settled as readily in the shallower southern basin and might therefore have been more present in the upper layer sampled. All sites have a second unfiltered THMFP peak at 2606 that is larger than the initial 0506 peak, except Border which peaks at 1606. This was possibly the late stationary growth/death stage of the first algal bloom with a release of precursors as a result of cell lysis.

The late summer results of 1990 indicate a turbidity peak at or just after 1808, similar to chlorophyll *a*, with the peak coinciding with THMFP observed levels. In 1991, Pender, Indian, and North all had peaks at 0506, while Border peaked at 1506,

and all sites had high turbidity levels at 1007 (5 to 6 NTU). The first peaks coincided with THMFP peaks. The maximum turbidity levels observed a few weeks after the 2606 THMFP peak were not necessarily surprising, since it is likely to be turbidity due to the contribution from dead cells. Unfortunately, the SS sample from the same date as the turbidity sample was contaminated and therefore unusable, but given the association between the two parameters, one would expect to have also observed SS peaks for all sites at 1007. For both 1990 and 1991, there was generally not a great deal of difference in turbidity levels between sites. Turbidity levels during 1990 appear to have been lower than the 1991 levels (0.5 to 3 NTU compared to 1 to 6 NTU range)

7.8 Secchi depth

There was a considerable amount of variation in secchi depth measurements from one sampling date to the next for all sites (Figures 62 to 67, Appendix I). This may not be entirely due to variations in lake water quality as secchi readings are also influenced by light intensity (time of day, cloud cover), wind effects, and the degree of calmness of the water. Such readings are much more subjective than other data.

The monthly averages indicate that during 1990 there was a clear difference between the sites with increasing secchi depth reading from the southern-most tip of the lake to the north. This indicates an increase in the degree of potential light penetration into the water column. The difference between north and south was not as clear in 1991 This was partly because the Pender, Indian, and Border secchi disk readings were higher

than in 1990, while those at Central and North were roughly the same (in 1990, 2 to 5 m; in 1991, 2.5 to 5.5 m) during the early and mid-summer. By the late summer, however, there was a definite north-south difference again.

Pender and Indian had increased secchi readings in July, at the same time as a decrease in THMFP and chlorophyll *a* levels. Oddly, there were also high levels of turbidity at all sites, although lower secchi disk readings would have been expected while turbidity was high.

7.9 Tabulated values

The water quality data measured during the 1990 and 1991 seasons cannot really be compared because they do not cover the same periods. The 1990 sampling season covered mid to late summer, while the 1991 season covered generally early to mid-summer (Table 2). For alkalinity, there was a definite increasing north-south gradient during 1990 and 1991 with Indian, Border, and Central sites roughly the same. The 1990 pH levels exhibit the same behaviour. There was an observed north-south gradient in suspended solids measured for 1990, but there appeared to be no trend in 1991. There was no real variation observed in turbidity levels. Secchi depth readings can be compared between 1990 and 1991, as they covered roughly the same period. There was a north-south gradient and 1991 secchi values appeared to be higher than those during 1990.

Table 2. Variation of water quality parameters

Site	Alkalinity (mg/L $CaCO_3$)	SS (mg/L)	pH	Turbidity (NTU)	Secchi (m)
Pender					
1990	62 ± 3	2.2 ± 0.5	7.73 ± 0.33	1.9 ± 1.0	2.3 ± 0.5
1991	55 ± 6	1.7 ± 0.7		3.0 ± 1.5	3.1 ± 0.5
Indian					
1990	57 ± 2	2.1 ± 0.9	7.69 ± 0.31	1.5 ± 0.9	2.8 ± 0.6
1991	53 ± 4	1.8 ± 0.7		2.6 ± 1.4	3.4 ± 0.4
Border					
1990	57 ± 3	1.6 ± 0.3	7.69 ± 0.39	1.5 ± 0.8	3.2 ± 0.4
1991	53 ± 1	1.5 ± 0.7		2.5 ± 1.6	3.8 ± 0.6
Central					
1990	56 ± 2	1.4 ± 0.6	7.64 ± 0.64	1.3 ± 0.5	3.8 ± 0.6
1991	53 ± 1	1.8 ± 0.8		2.6 ± 1.7	4.3 ± 0.8
North					
1990	55 ± 2	1.1 ± 0.4	7.56 ± 0.75	1.4 ± 0.5	4.2 ± 0.8
1991	52 ± 1	2.5 ± 2.2		2.7 ± 1.9	4.5 ± 0.6

Note: Values given are the averages ± the standard deviation over the sampling season

7.10 Temperature

Temperature profiles indicate the changing thickness of the mixed layer (epilimnion) over time in response to a change in temperature (Figures 68 to 70, Appendix J). At spring overturn, the entire water column is considered to mix within itself. This actually occurs during the whole season in the south basin, which is quite shallow (mean depth 7 m), and even at Border, which is deeper (mean depth of 10 m) As temperatures increase, the water column stratifies into layers the epilimnion, the

metalimnion, and the hypolimnion. With temperature change over the season, the thickness of the epilimnion will gradually increase and squeeze the metalimnion (region with change in temperature of roughly 1°C/m) such that the temperature profile in the lake becomes sharper.

This can have an effect on algal activity and THMP as density differences prevent mixing between the layers. Nutrients or algae leaving the trophic zone, due to settling out or in response to stress conditions, will no longer be productive as they will not be recirculated into the upper region of the water column where active photosynthesis occurs. It is necessary to know the changes in the depth of the mixed layer to examine depth effects. During the early season a 10 m depth is well in the hypolimnion while by late summer 15 m is barely considered still hypolimnetic.

The seasonal variation of water surface temperature (Figures 71 and 72) indicates that in 1991 the period of maximum algal growth occurred during the period of highest water surface temperature. It also suggests that the end of June would be a likely period to expect the replacement of spring algal bloom by those species making up the large late summer algal blooms. There was no significant north-south temperature gradient observed during the early sampling season although the southern sites appeared to warm up faster, perhaps due to the smaller volume of water.

7.11 Cl_2 Demand

The chlorine demand observed in the late summer samples of 1990 indicate the same behaviour at all sites: a gradual decrease for both the filtered and unfiltered samples over time (Figures 73 to 77, Appendix K). It is odd that at 0208, filtered demand exceeded unfiltered demand, since this is not also reflected in THMFP values. It is unlikely to be due to the contribution of an organic demand during filtration as there are no correspondingly large DOC values. It was more likely because of Cl_2 demand for oxidation purposes prior to serving the demand of the THM precursors. Decreased demand with fluctuations in THMFP could be due to the changing nature of the precursors. Blue-green algae, the dominant species present, excrete more nitrogenous compounds than other algae (up to 30% of N intake) (Hellebust, 1974), but these tend to be precursors more for the non-purgeable fraction of TOX (Trehy *et al*, 1986) and as such may exert Cl_2 demand but not be observed as contributing to THMFP.

7.12 Predicted humic contribution on the basis of colour

Colour data were available only for the mid- to late summer of 1990. The humic contribution to THMFP is predicted using the following equation from Oliver and Thurman (1983):

$$\text{Pred. humic THMFP } (\mu g\ CHCl_3/mg\ C) = 14 * (\text{colour/mg C}) + 17$$

where colour is the spectrophotometric absorbance at 400 nm multiplied by 1300. They found good agreement for those lakes of very low pH, but up to 60% deviation for those

lakes of normal pH 7 range (like Memphremagog), and concluded that the difference was likely due to algal contribution.

There appeared to be a decreasing north-south gradient both in the predicted humic THMFP and the calculated algal contribution (difference between TTHMFP and the humic THMFP) (Figures 78 to 82, Appendix L). All sites had a humic peak at 0208 (0208 to 1808 for Pender and Indian), which was followed by a peak in the calculated algal THMFP. This would appear to indicate a later algal influence than supposed. The unfiltered humic and algal THMFPs were generally in the same range, while there was a significant difference between the humic and algal THMFP for the filtered samples, with the humic contribution being the larger. Both individually had THMFPs of over 100 μg/L.

The humic peak could have been the result of earlier algal activity, assuming that it is from autochthonous sources (detritus) and not allochthonous (runoff). Some researchers (Hoehn *et al*, 1984; Oliver and Visser, 1980) have found that bacteria can alter the character of ECPs, possibly making them more reactive and perhaps altering the ECPs such that they become indistinguishable from humic and fulvic acids.

8 CORRELATIONS BETWEEN PARAMETERS

Attempts were made to find correlations between the THMFP and the investigated parameters: organic carbon, chlorophyll *a*, total nitrogen, total phosphorus, secchi depth, suspended solids, alkalinity, turbidity, and N to P ratio. Filtered and unfiltered samples were treated separately. The graphs of THMFP versus each parameter are given in Appendix N. The correlation matrices for the filtered and unfiltered samples are shown in Tables 3 and 4. Generally, attempts to fit the points to a straight line were not very successful because there was a great deal of scatter in the data. This can be readily seen in the correlation matrix. Although some researchers found correlations between TOC and THMs (Symons *et al*, 1975, found a correlation between non-volatile TOC and total THMs with an r^2 value of 0.98; Glaze and Rawley, 1979, found TOC versus $CHCl_3$ with a correlation coefficient of 0.586), it was very poorly correlated for the period studied. Van Steenderen *et al* (1991) found a low r^2 value with THM versus TOC. The same applies for chlorophyll *a*, although Hoehn *et al* (1978) found a relationship between chlorophyll *a* and THM in the Occoquan Reservoir.

Table 3 Correlation matrix for unfiltered samples

	TOC	chl a	TN	TP	N to P	SS	Alk.	Turb.	Secc.	THM
TOC	1.00	0.45	0.11	0.45	-0.43	0.11	0.22	0.09	-0.22	0.08
chl a		1.00	0.38	0.68	-0.42	0.40	0.09	0.07	-0.40	0.23
TN			1.00	0.59	0.19	0.30	-0.09	0.41	-0.30	0.22
TP				1.00	-0.65	0.24	0.01	0.15	-0.58	0.40
N to P					1.00	-0.05	-0.07	0.14	0.43	-0.25
SS						1.00	0.09	0.56	-0.45	0.33
Alk.							1.00	-0.20	-0.05	0.39
Turb.								1.00	0.05	0.05
Secc									1.00	-0.63
THM										1.00

Table 4. Correlation matrix for filtered samples

	DOC	chl a	TN	TP	N to P	Alk.	Secchi
DOC	1.000	0.264	-0.020	0.133	-0.185	-0.153	-0.168
chl a		1.000	0.382	0.678	-0.425	0.086	-0.403
TN			1.000	0.587	0.190	-0.092	-0.300
TP				1.000	-0.654	0.014	-0.577
N to P					1.000	-0.065	0.434
Alk.						1.000	-0.045
Secchi							1.000

For the lake as a whole the best agreement was found between THMFP and secchi depth (Figures 83 and 84, Appendix M), with correlation coefficients of 0.628 and -0.601 for unfiltered and filtered samples respectively. The THMFP to secchi depth relationship can be clearly seen to be inverse, although the correlation coefficient was not very high. This is due to the degree of scatter present. The relationship formed was similar for the filtered and non-filtered samples:

unfiltered THMFP = -26.49 * depth + 256.44 r = -0.628

filtered THMFP = -29.87 * depth + 245.96 r = 0.601

A multiple regression was performed on the filtered and unfiltered samples between THMFP and the parameters investigated. This gave a better correlation coefficient than any one variable. The regression equation is:

unfiltered THMFP = -126.97 - 0.92 TOC - 7.09 chl *a* - 0.40 TN + 16.25 TP + 5.85 NP + 9.93 SS + 1.94 Alk + 12.40 Turb - 16.78 secchi

r = 0.761

filtered THMFP = -7.26 - 2.62 TOC - 8.33 chl *a* - 0.18 TN + 10.70 TP + 2.47 NP + 2.19 Alk - 18.18 secchi

r = 0.715

The THMFP was also correlated with all parameters for each individual sampling site (Tables 5 and 6). Although the data are still quite scattered (few data points), some possible correlations were found (Figures 85 to 91, Appendix M). Pender and Indian (as well as North, to a degree) had weak correlations with secchi depth for both the filtered and unfiltered samples, although these were better than the correlation for the lake as a whole. Pender also exhibited a reasonable correlation with total

Table 5. Correlation coefficients for THMFP and water quality parameters (unfiltered samples)

	Pender	Indian	Border	Central	North
TOC	0.045	0.023	0.110	0.039	0.141
chl a	0.032	0.138	0.184	0.045	0.313
TP	0.778	0.210	0.221	0.055	0.290
TN	0.032	0.045	0.210	0.134	0.534
N to P	0.371	0.190	0.566	0.045	0.114
Alk	0.489	0.329	0.134	0.017	0.363
SS	0.274	0.237	0.402	0.230	0.786
Turb	0.138	0.170	0.089	0.141	0.387
Secchi	0.619	0.528	0.369	0.387	0.566

Table 6. Correlation coefficients for THMFP and water quality parameters (filtered samples)

	Pender	Indian	Border	Central	North
DOC	0.366	0.084	0.257	0.524	0.155
chl a	0.006	0.068	0.399	0.016	0.015
TP	0.389	0.055	0.465	0.041	0.311
TN	0.014	0.032	0.382	0.148	0.851
N to P	0.344	0.145	0.205	0.148	0.118
Alk	0.268	0.424	0.217	0.049	0.422
Secchi	0.629	0.617	0.210	0.055	0.484

phosphorous (r = 0.778) for the unfiltered sample. There were no strong correlations found for the Border and Central sites. Generally these two sites were very poorly correlated for all parameters. North was correlated with total nitrogen for the filtered sample (r = 0.851) and with suspended solids for the unfiltered sample (r = 0.786).

The predicted algal contribution to THMP was plotted versus chlorophyll *a* (Figures 92 and 93, Appendix M) for the unfiltered sample with a correlation coefficient of 0.382. While this was better than the correlation for total THMFP versus chlorophyll *a* (r = 0.228), it is still low due to scatter in the data. The filtered sample points were very few and highly scattered.

9 CONCLUSIONS

In a natural system such as Lake Memphremagog there was not any one parameter observed that exerted a significant influence on the THMFP of the lake as a whole. It was rather a combination of several of the associated parameters that yielded the closest correlation with the THM concentrations found in the analyzed samples. This was perhaps expected due to the complexity of the system and the fact that some of the parameters were inter-dependent It was not terribly surprising that the correlation between THMFP and secchi depth for the lake as a whole was the closest for any of the parameters. Secchi disk readings are affected by variations in several other parameters.

Some correlations between THMFP and the parameters were found when the sites were examined individually. The correlation between THMFP and TP at Indian site possibly reflected a phosphorous limitation due to lower levels at Indian relative to the rest of the South basin. The correlations found at North site between TN and solids and THMFP were likely due to their low levels. Nitrogen was likely a limiting factor to algal growth and therefore to precursor formation at North.

Contrary to expectations, no direct relationships could be found between the THMFP and the TOC or chlorophyll *a* concentrations. This was likely due to the combined effects of the humic contribution to THMFP and the variations in formation potential due to changes in the algal metabolites. The contribution to the THMFP from humic substances was estimated to be roughly similar to that from algal activity.

The THMFP levels between the various basins of the lake were generally in the same range. Although there was a increasing north-south concentration gradient at certain periods, the overall variation between sites was not statistically significant. This appeared to indicate that there was not a significant contribution to THMFP from human activity.

Although the lake is not considered to be very productive in terms of algal activity, the THMFP present within the lake is still at a level that generally exceeds the US EPA standard of 100 μg/L and could be considered significant. Further study into the nature and causes of the THM precursors will be necessary, particularly if the Canadian Guidelines were to be lowered in future to a similar level as that of the US

GLOSSARY

Algae - Photosynthetic microscopic plants which in excess can contribute taste and odour to potable water and deplete dissolved oxygen on decomposition.

Alkalinity - The capacity of water to neutralize acids, a property imparted by carbonates, bicarbonates, hydroxides, and occasionally borates, silicates, and phosphates. It is expressed in milligrams of equivalent calcium carbonate per litre.

Allochthonous - Humic substances entering a lake from the surrounding watershed through runoff

Autochthonous - Humic substances produced within the lake itself.

Biomass - The mass of biological material contained within a system.

Blooms - Large masses of microscopic and macroscopic plant life, such as green algae, occurring in bodies of water.

Chlorine demand - The quantity of chlorine that would be consumed in a specific period by reaction with substances present in water, if the chlorine supply were not limited. The demand for any given water varies with both time of contact and temperature.

Chlorophyll *a* - Compound present in plant cells resulting in the green colour; used as an indicator of algal concentrations.

Diel effects - Those occurring over a complete light-dark cycle.

Extracellular products (ECPs) - Compounds produced by algae and secreted through the cell walls into solution.

Epilimnion - In a stratified lake, the upper mixed layer of the water where photosynthesis occurs

Humic substances - A general class of heterogeneous, biogenic, refractory, yellow-black, organic substances that are important participants in many geochemical reactions and processes. They consist of humic and fulvic acids and humin.

Hydrophilic - Having a strong affinity for water

Hydrophobic - Having a strong aversion to water

Hypolimnion - The deepest, non-mixing layer of water in a statified lake.

Metalimnion - Intermediate layer between the epilimnion and the hypolimnion, region with a temperature change of roughly 1°C/m.

Organic carbon - Carbon from organic sources; dissolved organic carbon (DOC) is the portion of the total organic carbon (TOC) that is in solution.

Organohalides (OX) - Organic compounds that contain halogen atoms

Phytoplankton - Plankton consisting of plants, such as algae.

Secchi depth - Measurement of the depth of the light penetration into the upper layer of water in a lake.

Surrogate parameters - Those parameters whose concentrations are linearly proportional to the concentration of the target parameter.

Suspended solids - Insoluble solids that either float on the surface of, or are in suspension in, water or other liquids.

Trihalomethanes - Compounds that are derivatives of methane, CH_4, in which three halogen atoms (chlorine, bromine, or iodine) are substituted for three of the hydrogen atoms.

Trihalomethane formation potential - The potential of a compound to react with a halogen, under standard conditions, to form trihalomethanes.

Trihalomethane precursors - Compound that will react, usually with chlorine, to form trihalomethanes.

Trophic zone - The zone in the upper layer of the water in which photosynthesis occurs.

Turbidity - A condition in water caused by the presence of suspended matter

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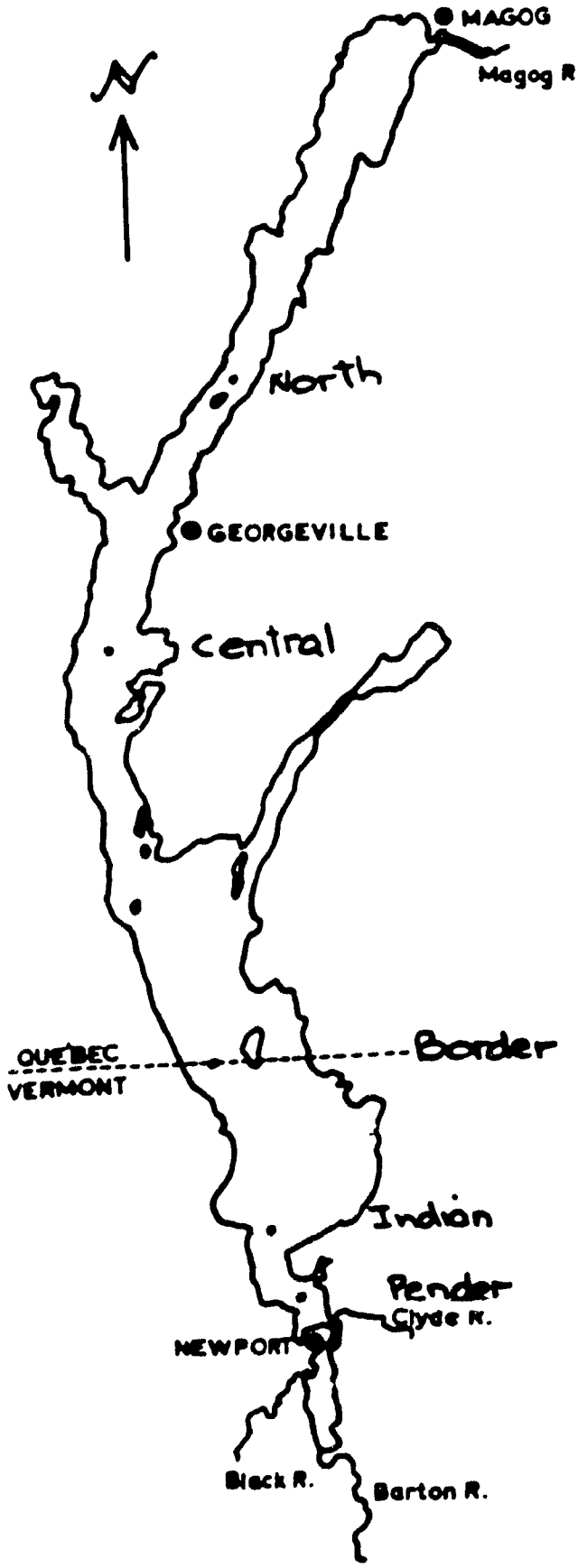
APPENDIX A



Lake Memphremagog Project
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Figure 1. Sampling sites on Lake Memphremagog

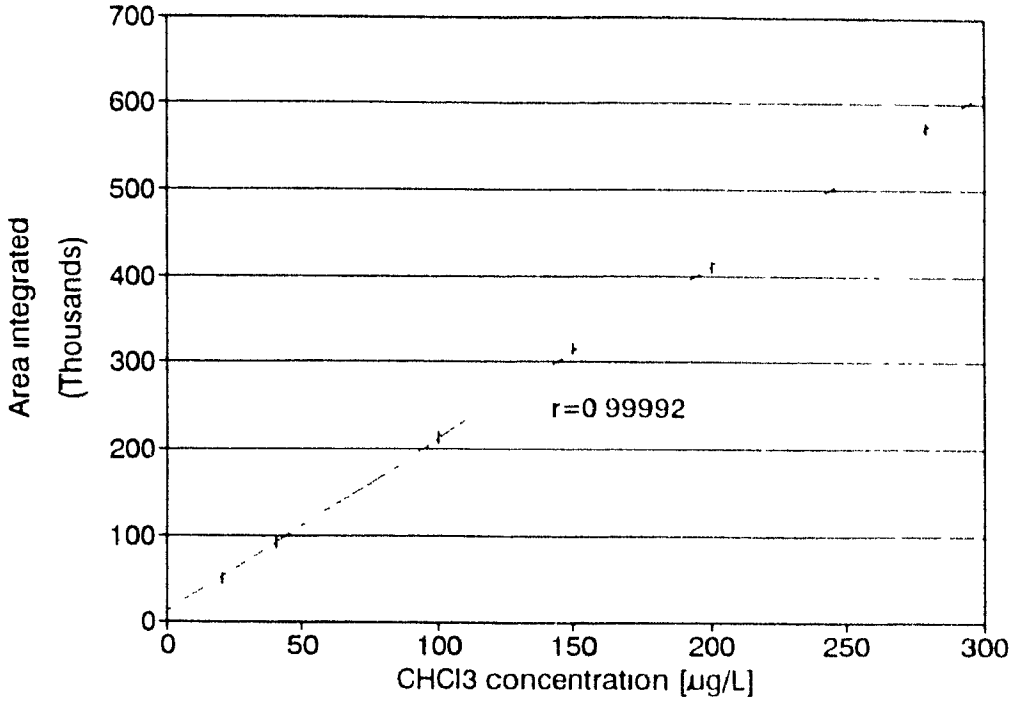

Figure 2. Calibration curve for the analysis of THMFP

APPENDIX B

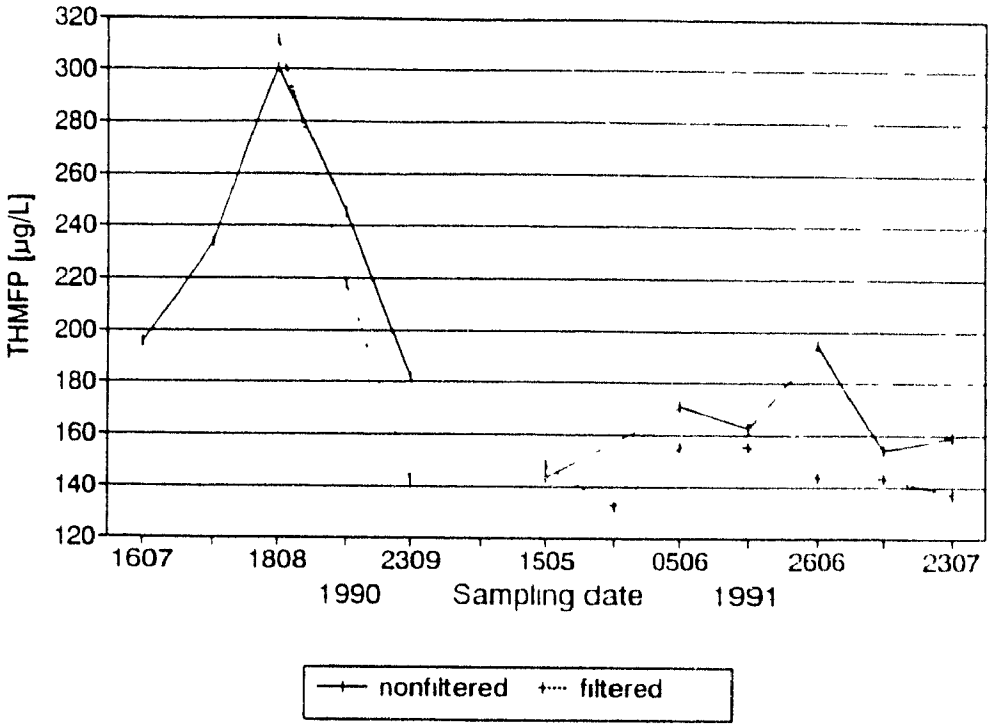

Figure 3. Seasonal variation of THMFP at Pender site

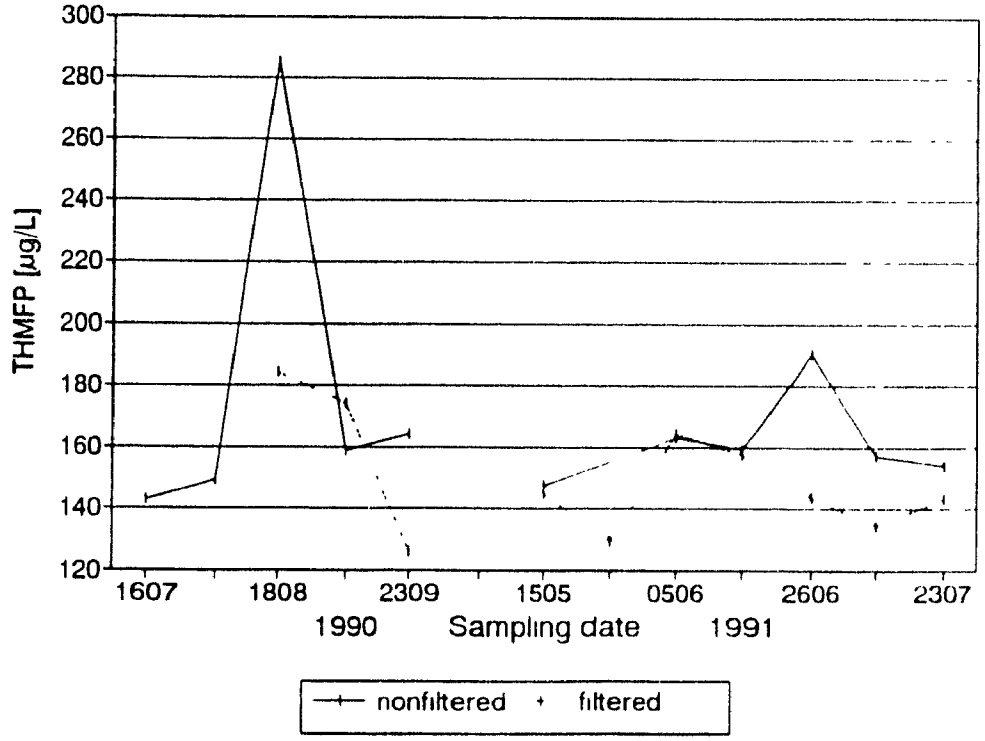

Figure 4. Seasonal variation of THMFP at Indian site

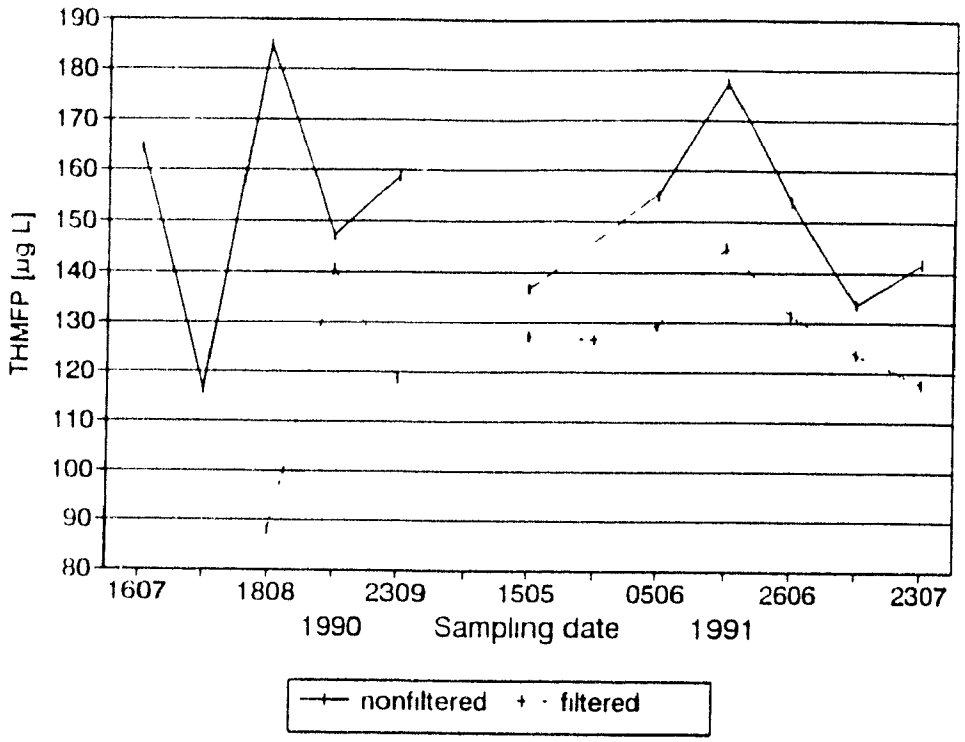

Figure 5. Seasonal variation of THMFP at Border site

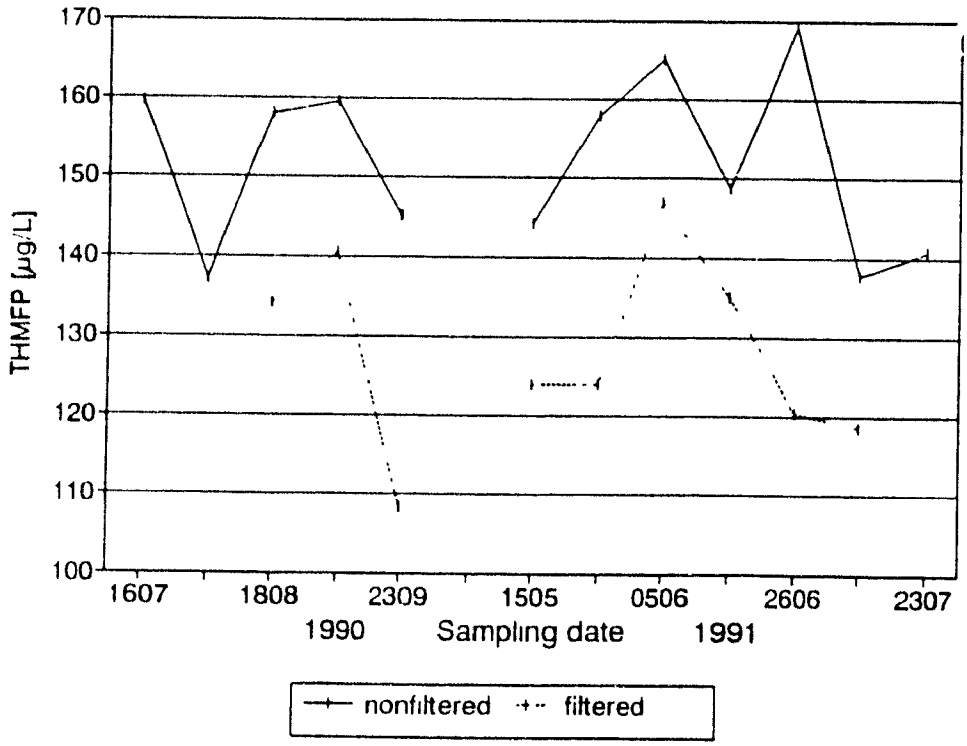

Figure 6. Seasonal variation of THMFP at Central site

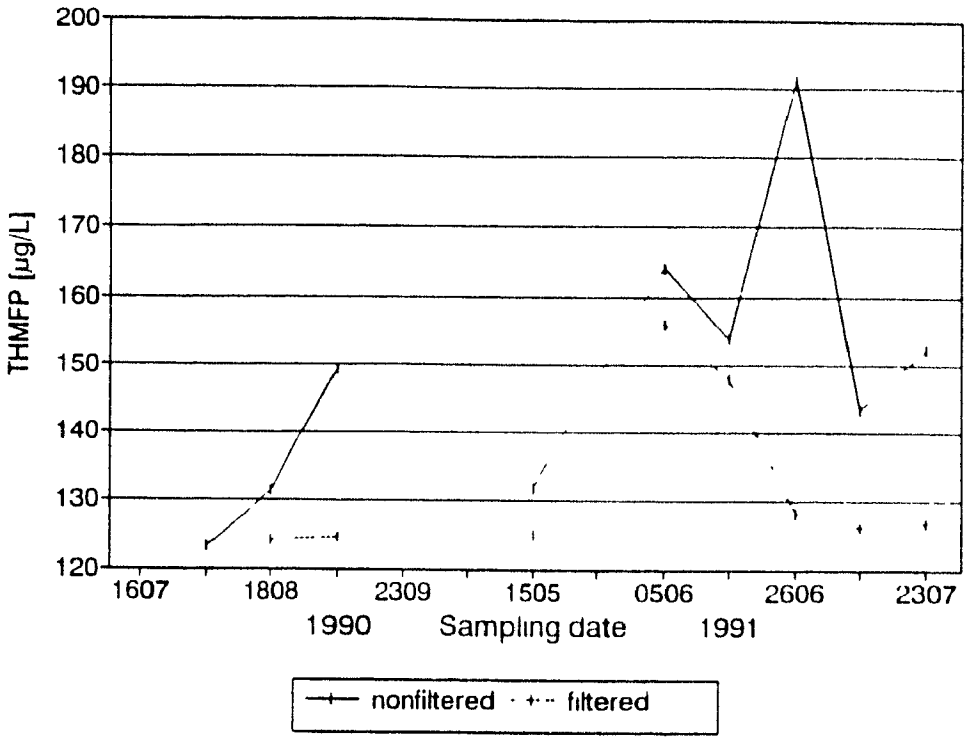

Figure 7. Seasonal variation of THMFP at North site

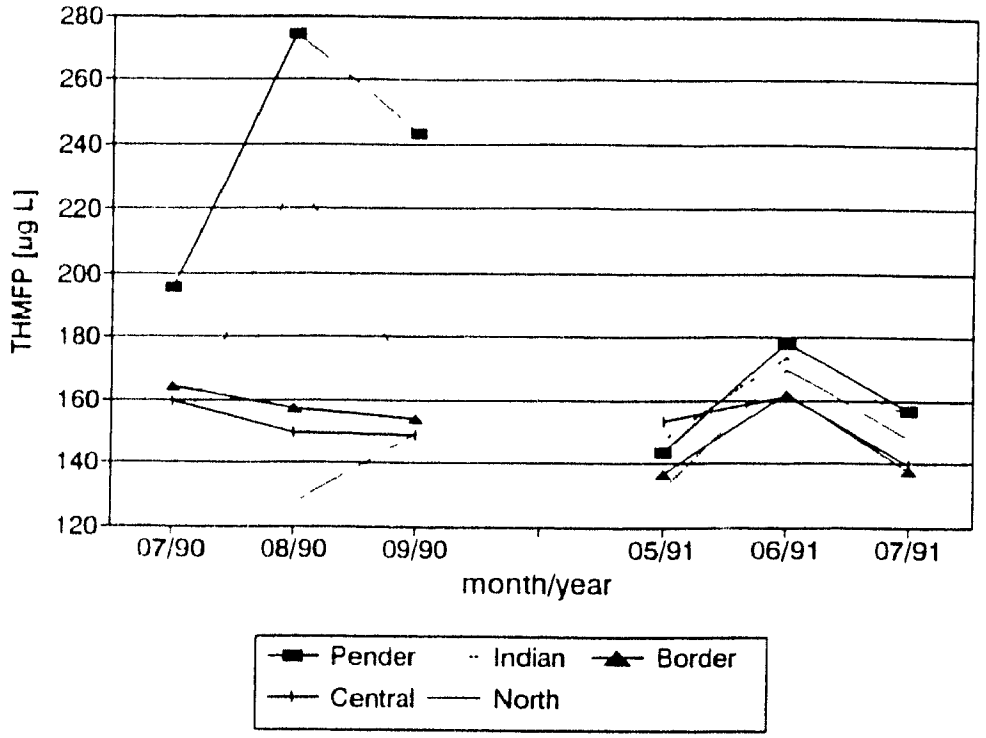

Figure 8 Monthly averages of unfiltered THMFP at all sites

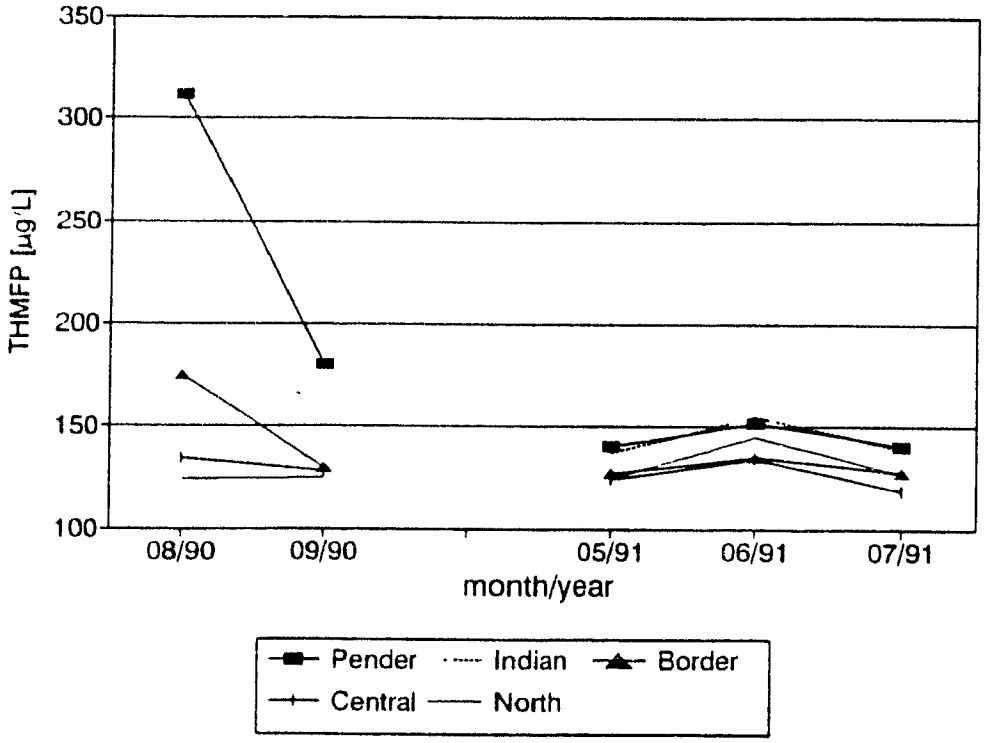

Figure 9. Monthly averages of filtered THMFP at all sites

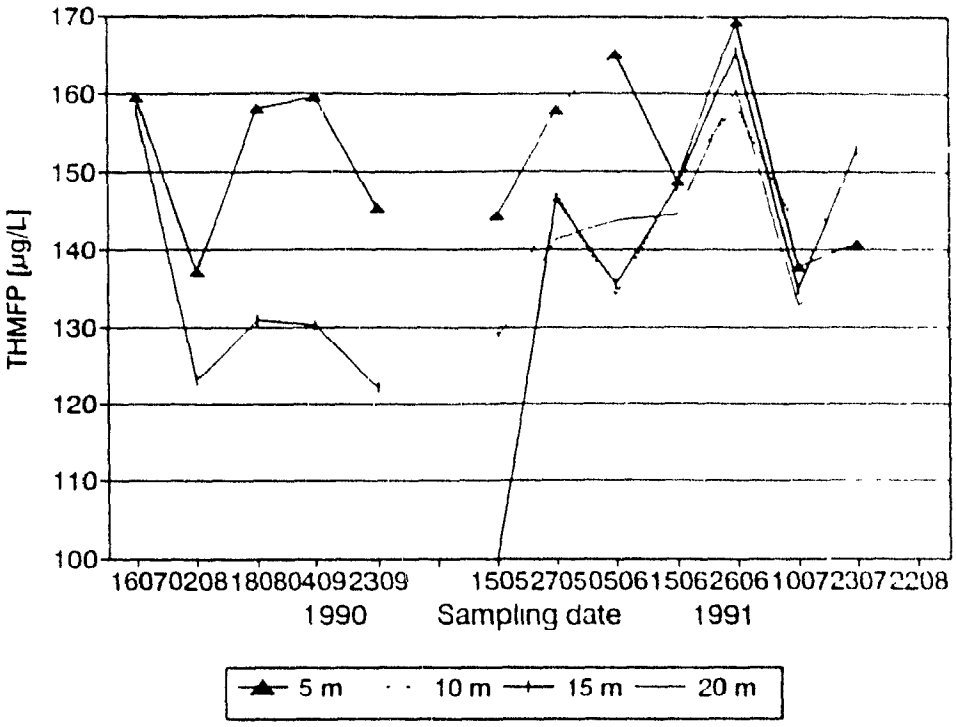

Figure 10. Seasonal variation of unfiltered THMFP at Central site (at 4 depths)

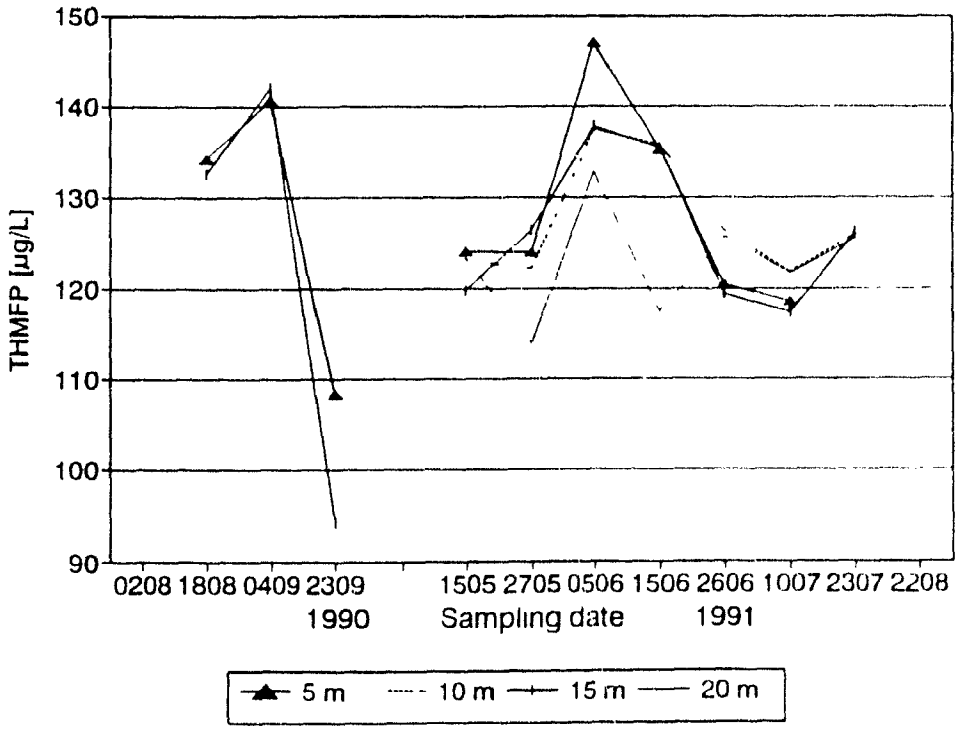

Figure 11. Seasonal variation of filtered THMFP at Central site (at 4 depths)

APPENDIX C

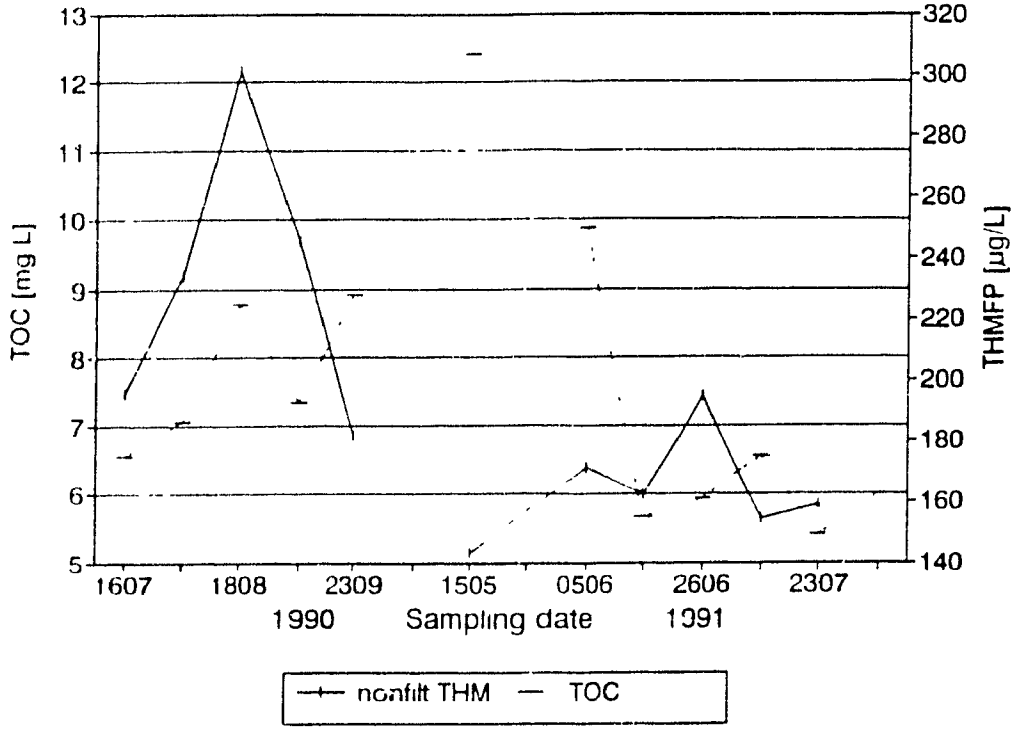

Figure 12. Seasonal variation of TOC and unfiltered THMFP at Pender site

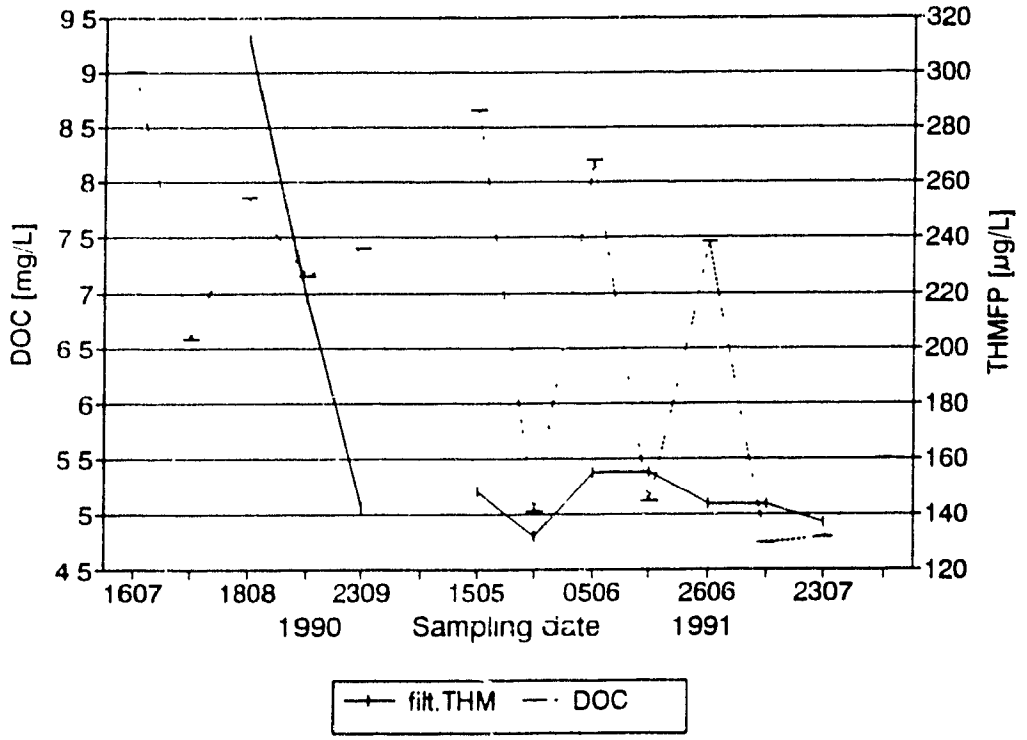

Figure 13. Seasonal variation of DOC and filtered THMFP at Pender site

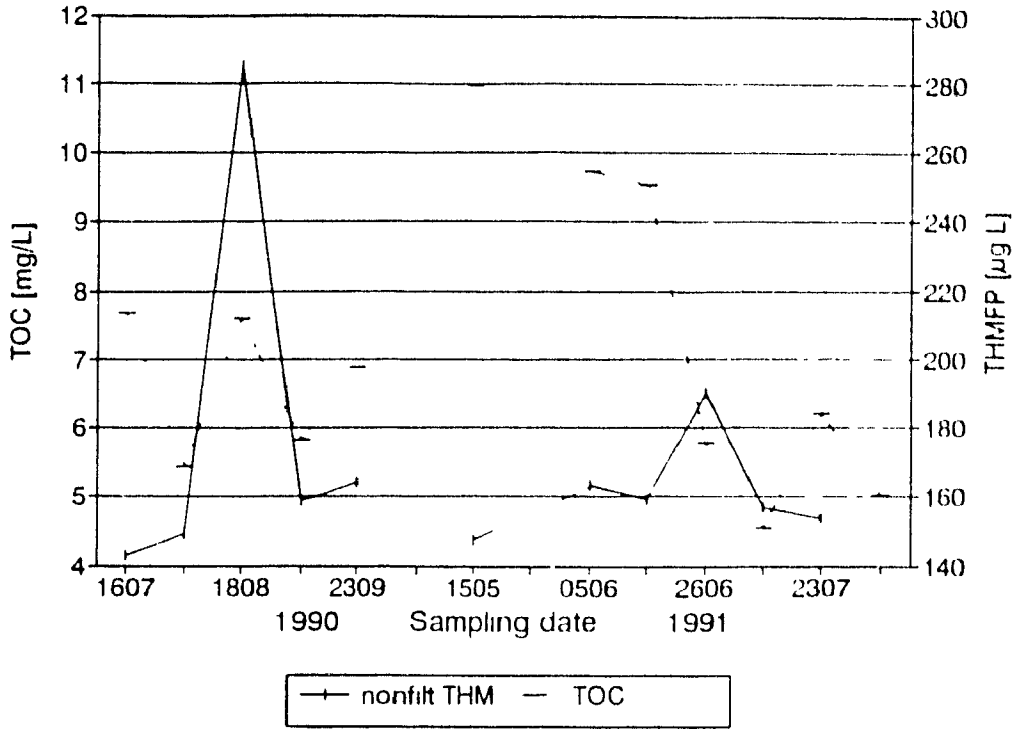

Figure 14. Seasonal variation of TOC and unfiltered THMFP at Indian site

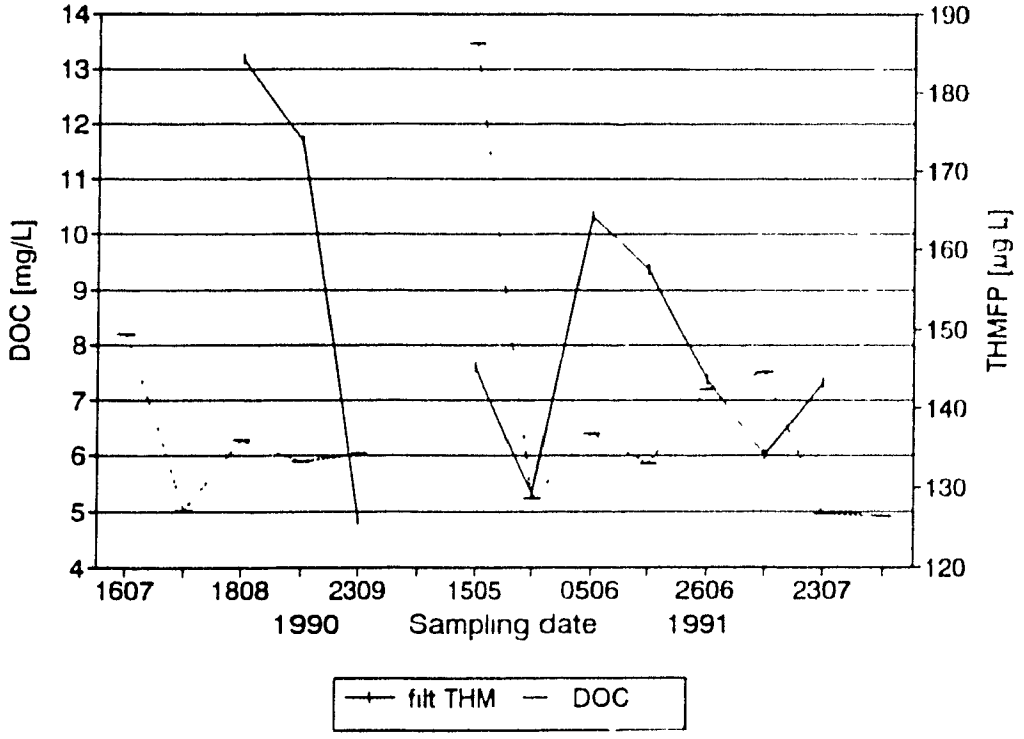

Figure 15. Seasonal variation of DOC and filtered THMFP at Indian site

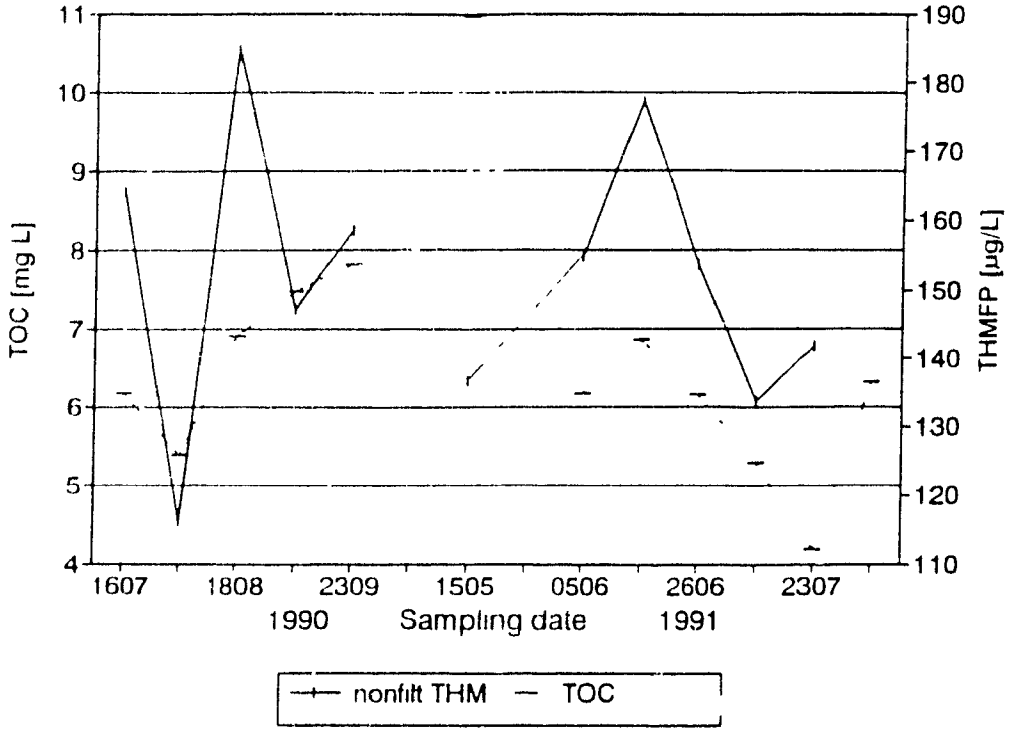

Figure 16 Seasonal variation of TOC and unfiltered THMFP at Border site

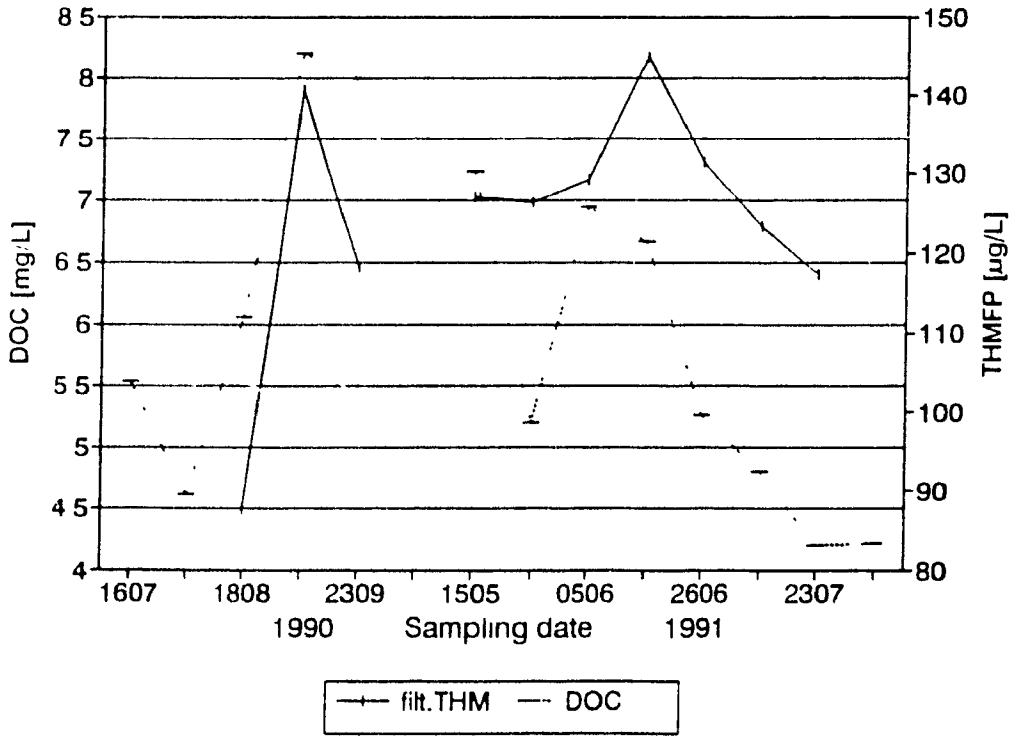

Figure 17. Seasonal variation of DOC and filtered THMFP at Border site

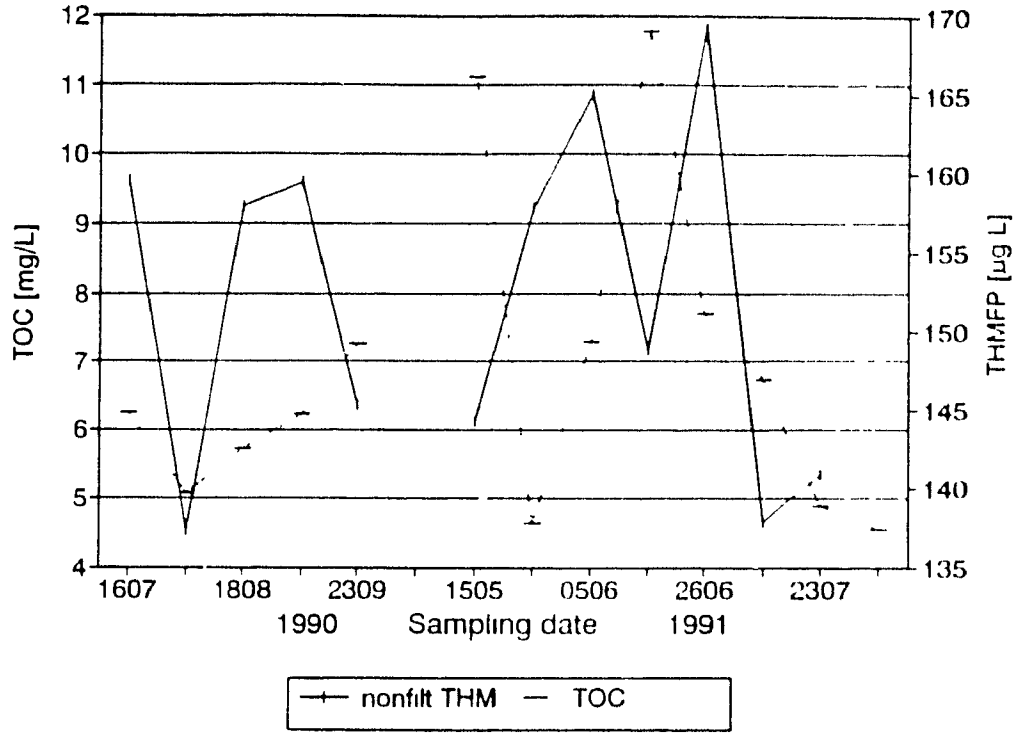

Figure 18. Seasonal variation of TOC and unfiltered THMFP at Central site

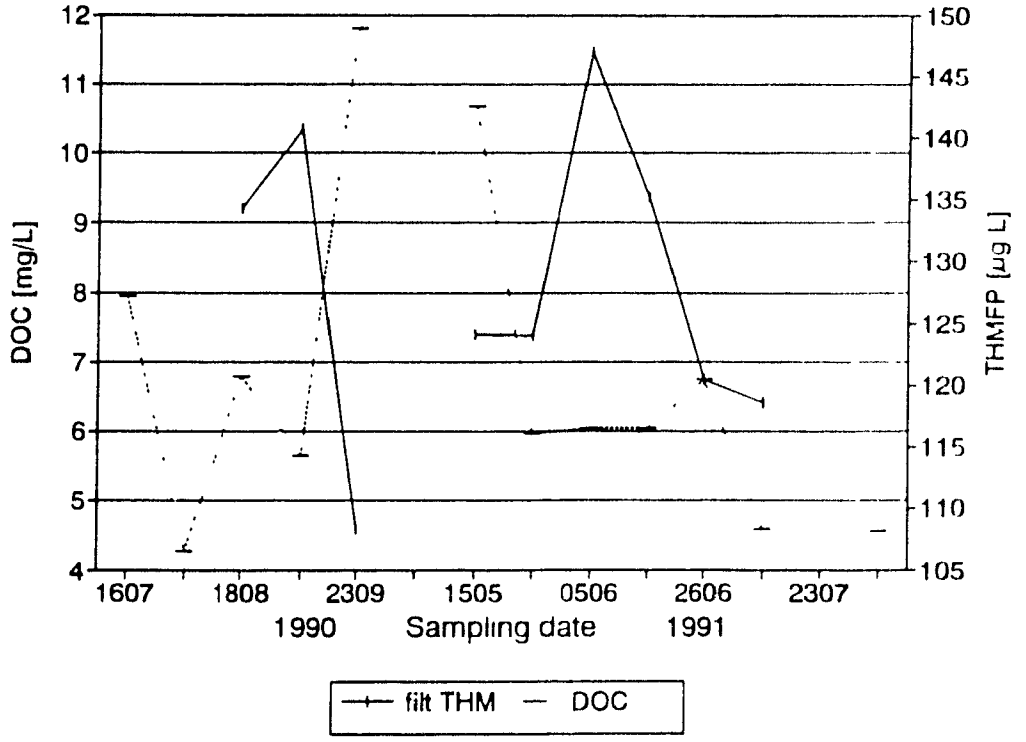

Figure 19. Seasonal variation of DOC and filtered THMFP at Central site

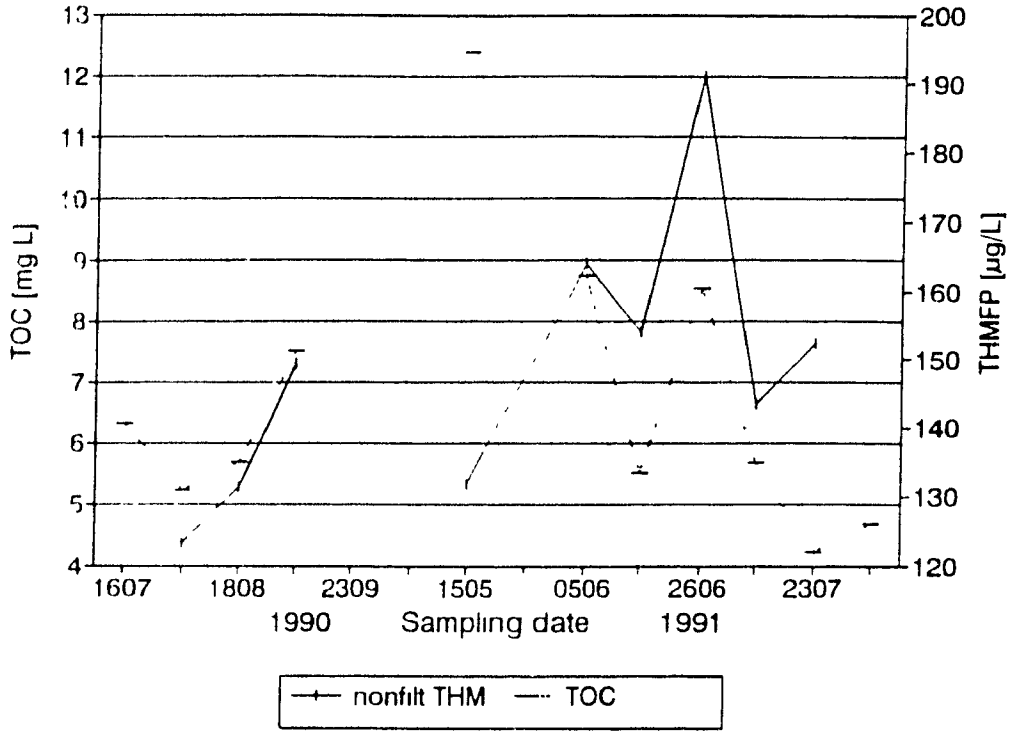

Figure 20. Seasonal variation of TOC and unfiltered THMFP at North site

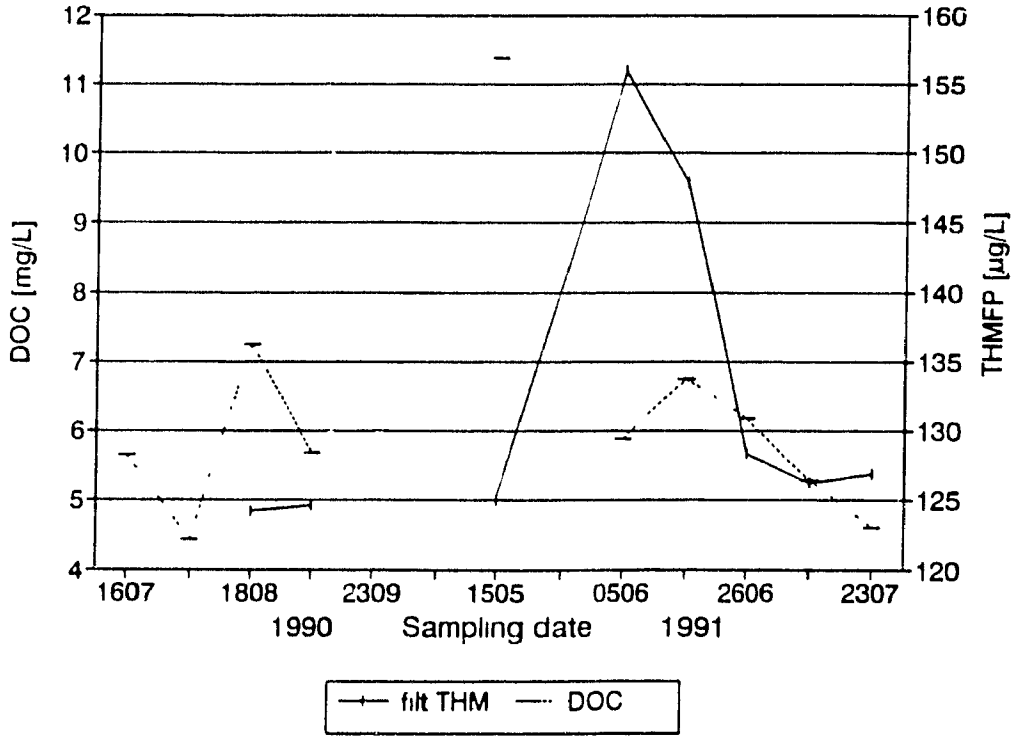

Figure 21. Seasonal variation of DOC and filtered THMFP at North site

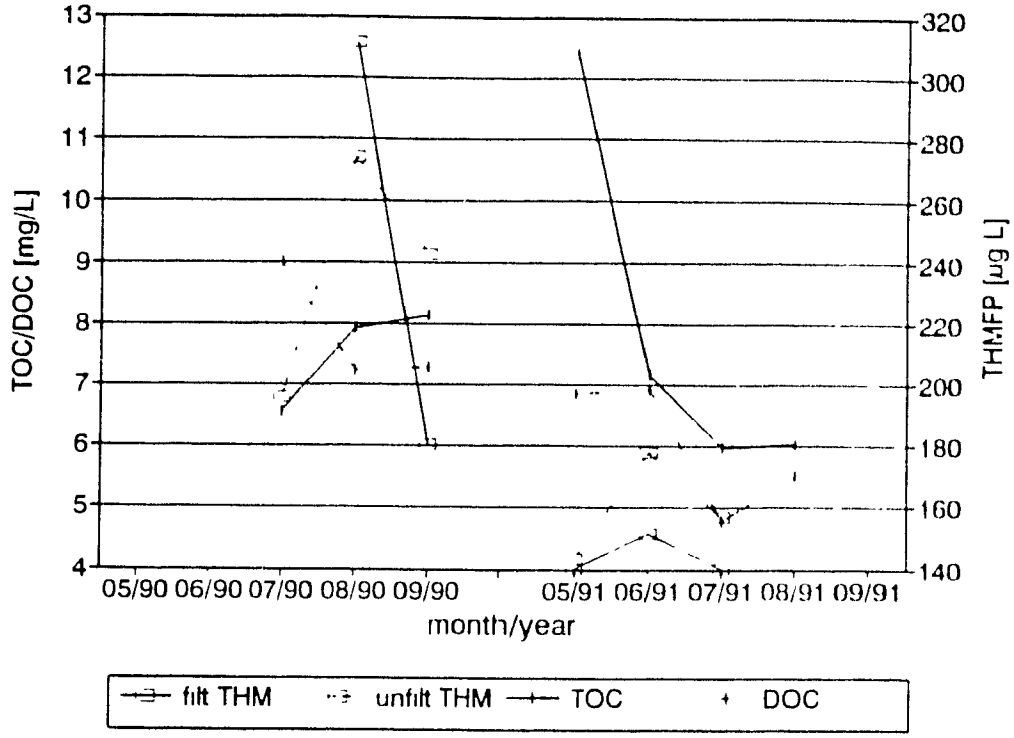

Figure 22. Monthly averages of TOC/DOC and THMFP at Pender site

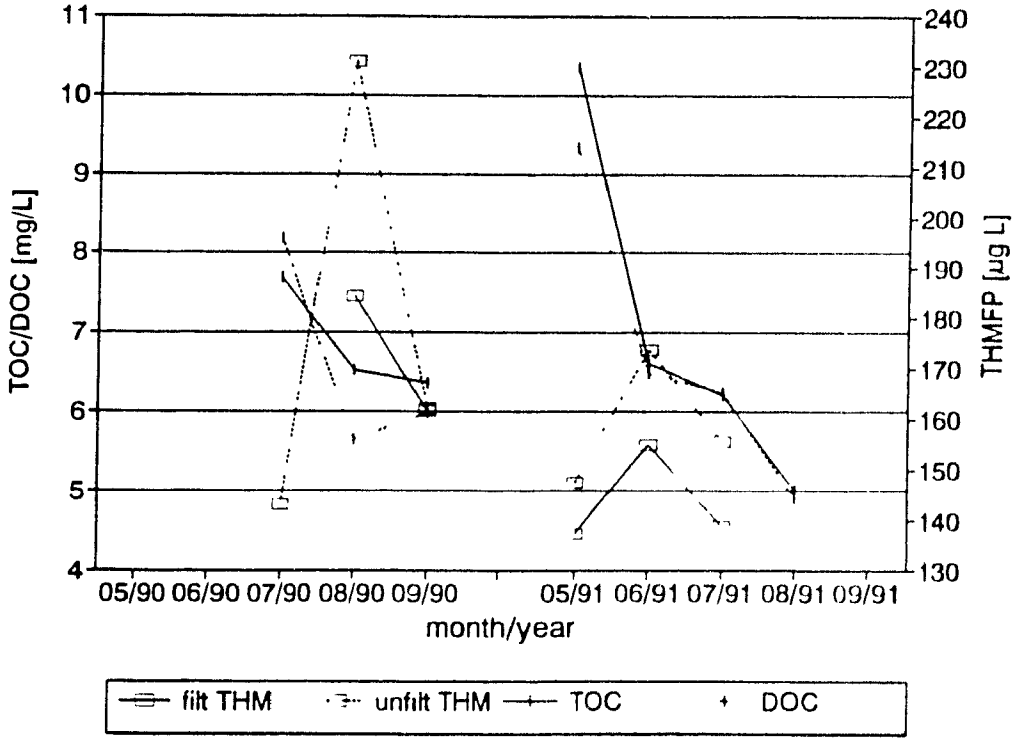

Figure 23. Monthly averages of TOC/DOC and THMFP at Indian site

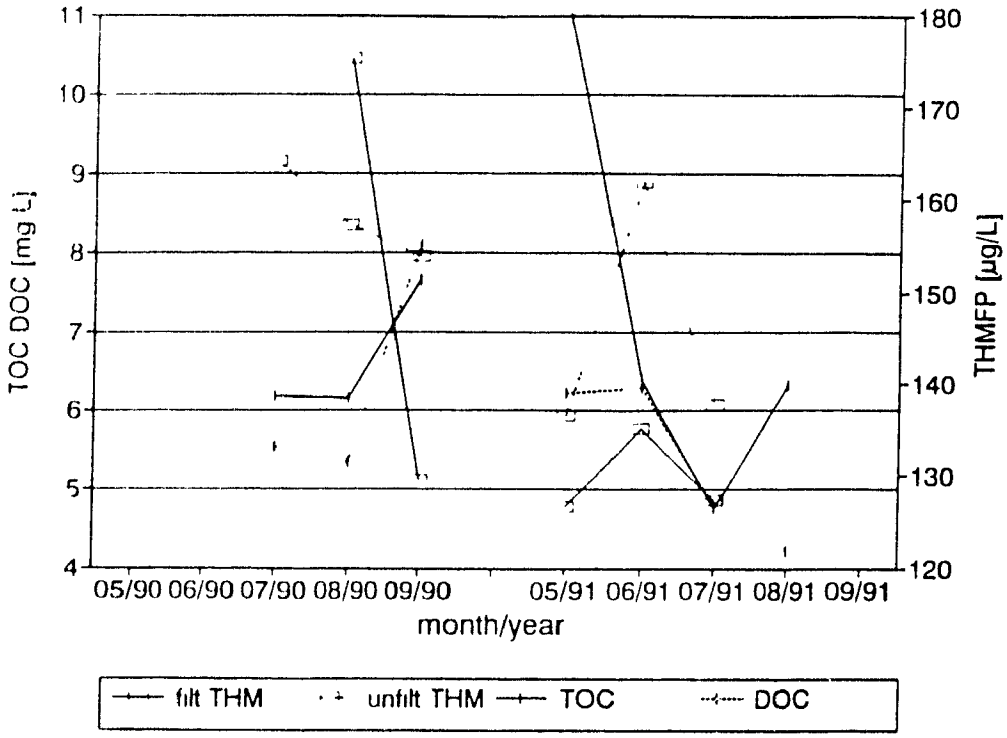

Figure 24 Monthly averages of TOC/DOC and THMFP at Border site

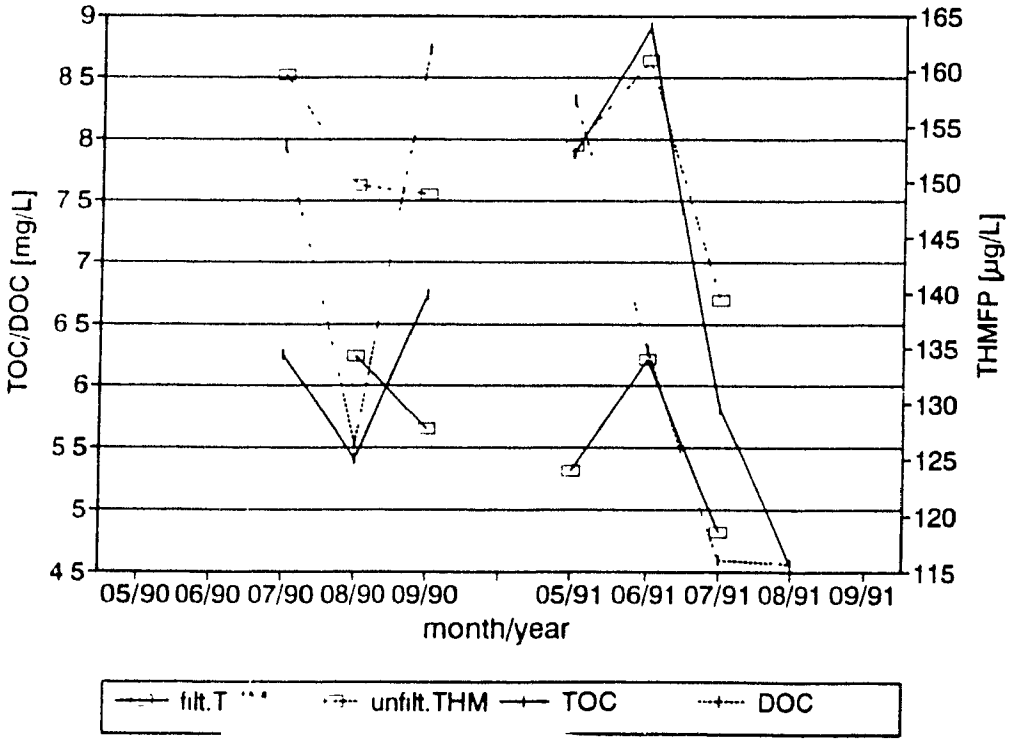

Figure 25. Mon[illegible] THMFP

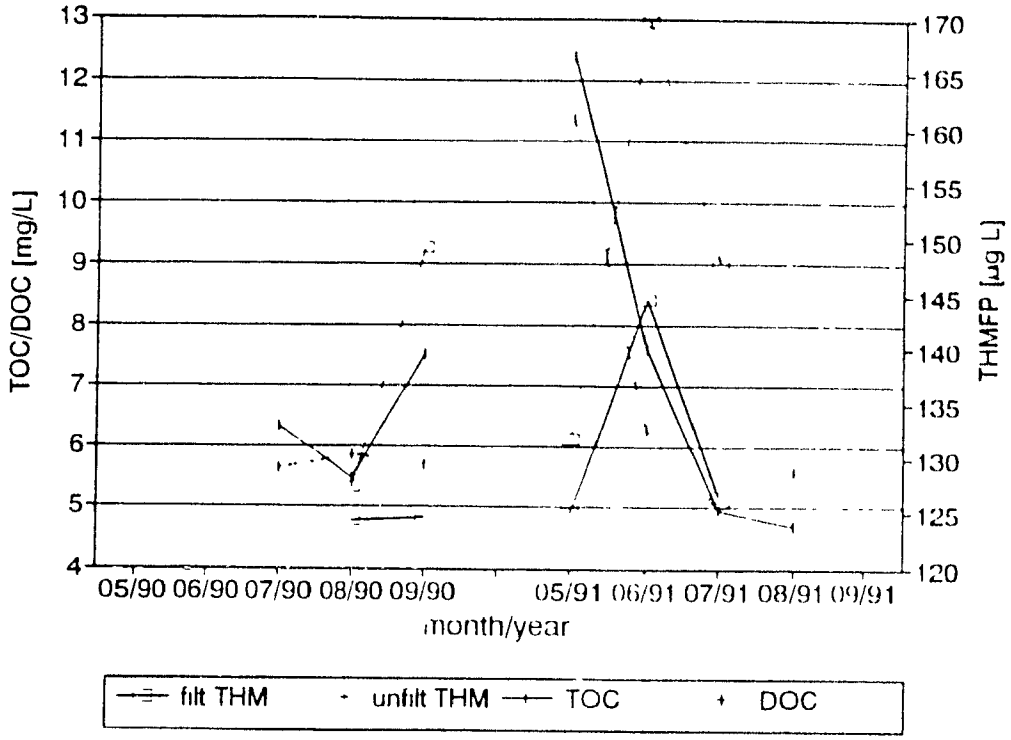

Figure 26. Monthly averages of TOC/DOC and THMFP at North site

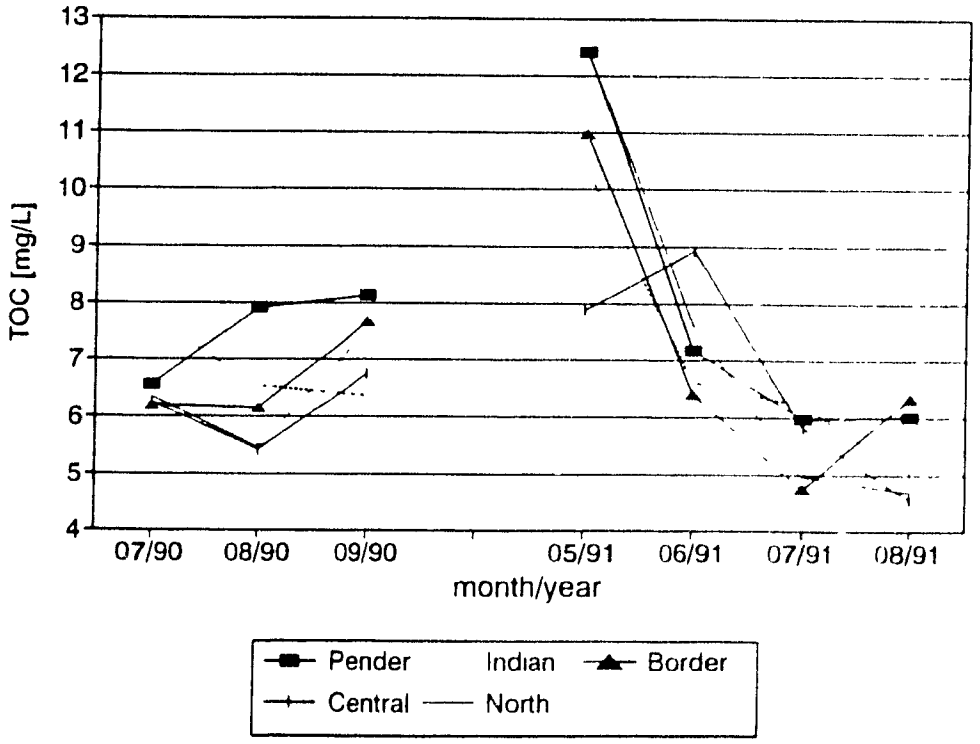

Figure 27. Monthly averages of TOC at all sites (unfiltered)

APPENDIX D

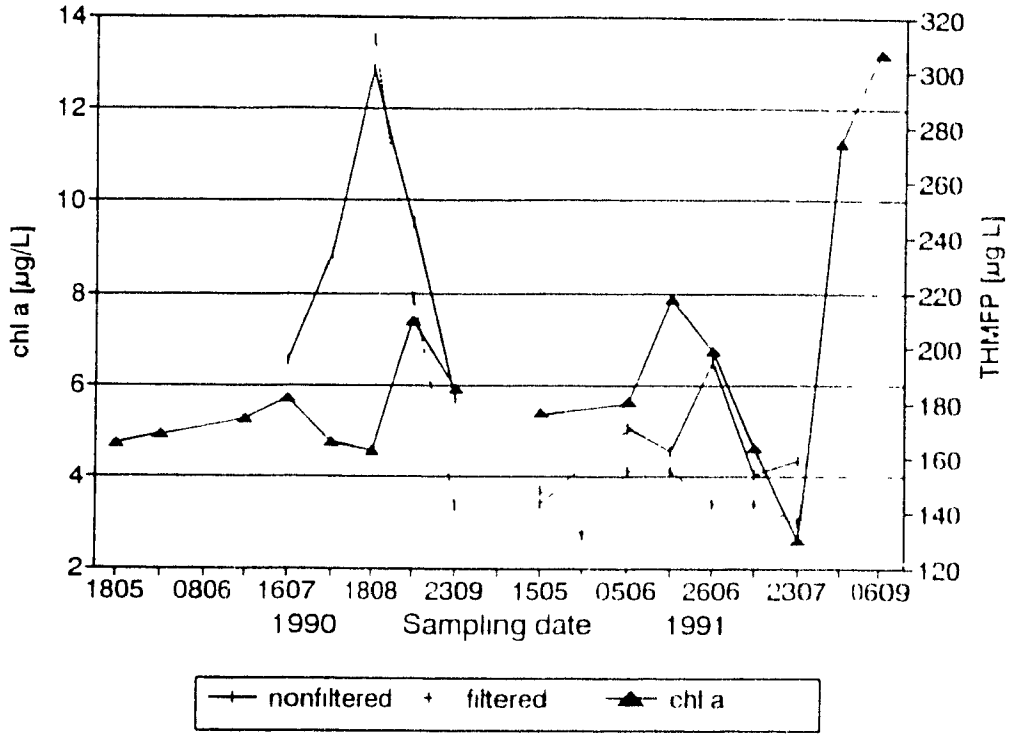

Figure 28. Seasonal variation of chl a and THMFP at Pender site

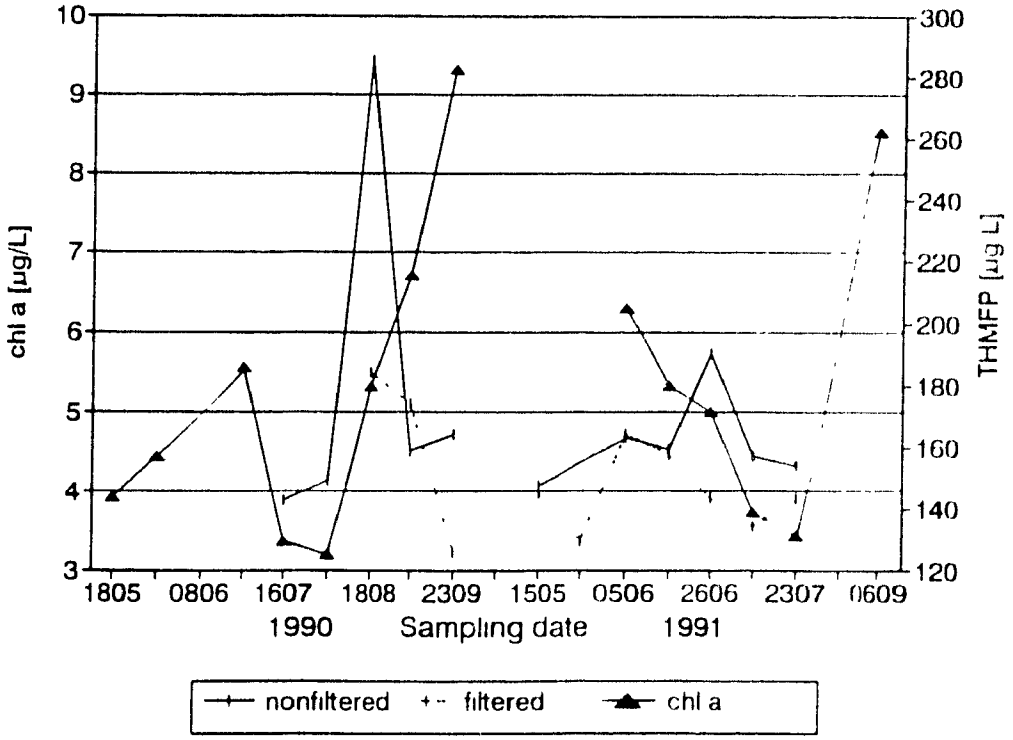

Figure 29. Seasonal variation of chl a and THMFP at Indian site

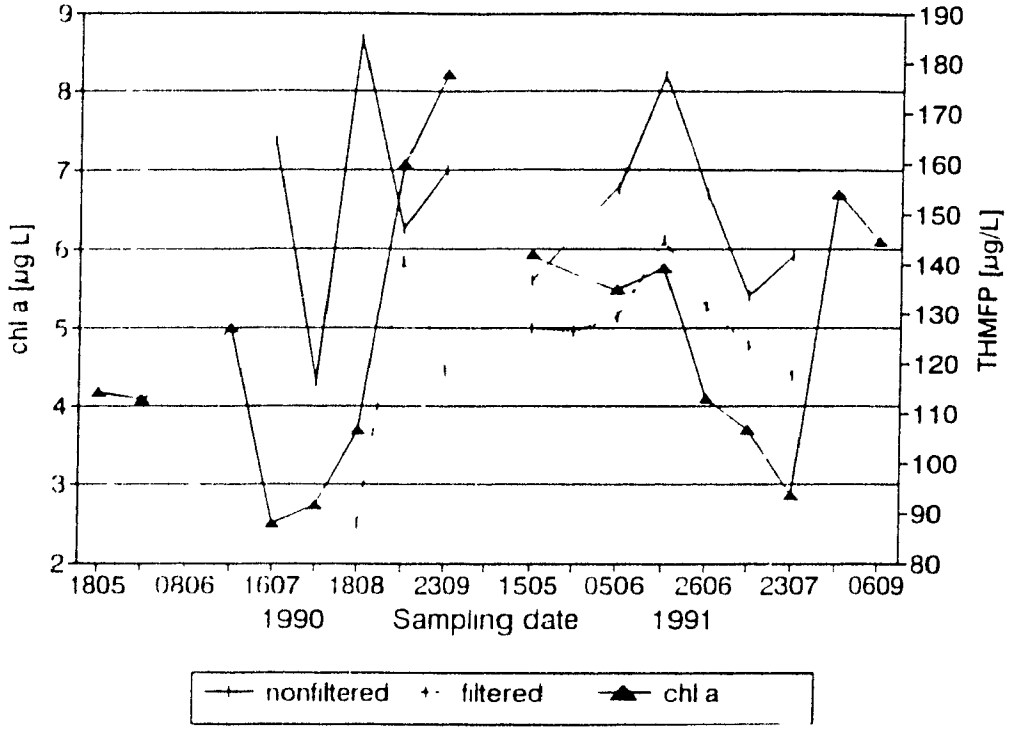

Figure 30 Seasonal variation of chl a and THMFP at Border site

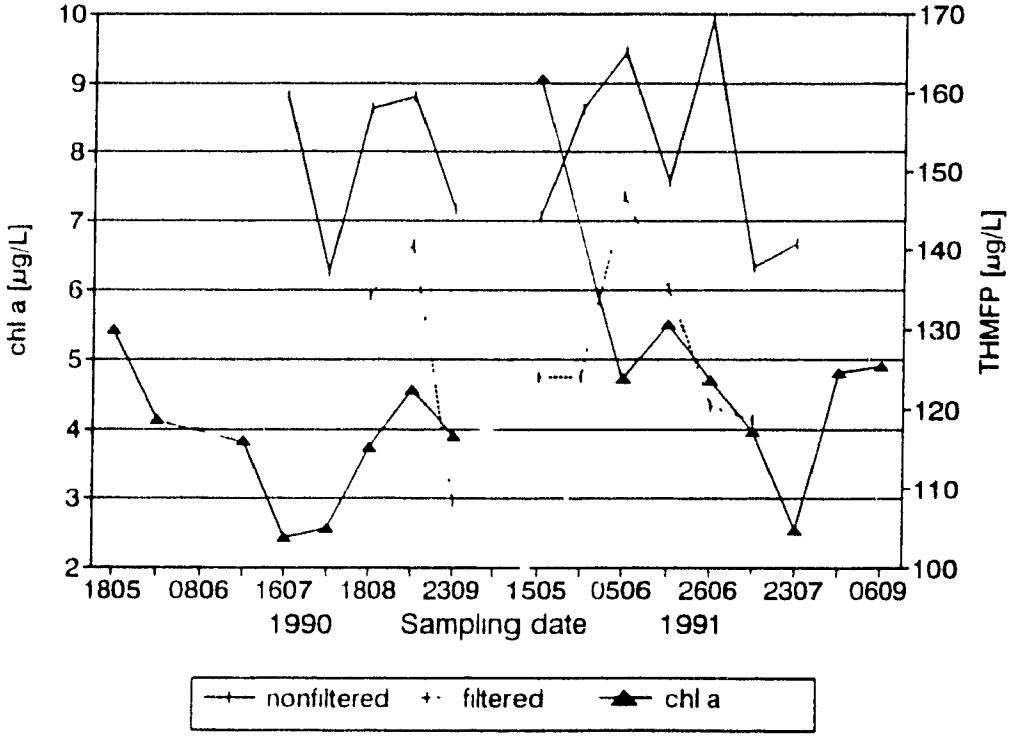

Figure 31. Seasonal variation of chl a and THMFP at Central site

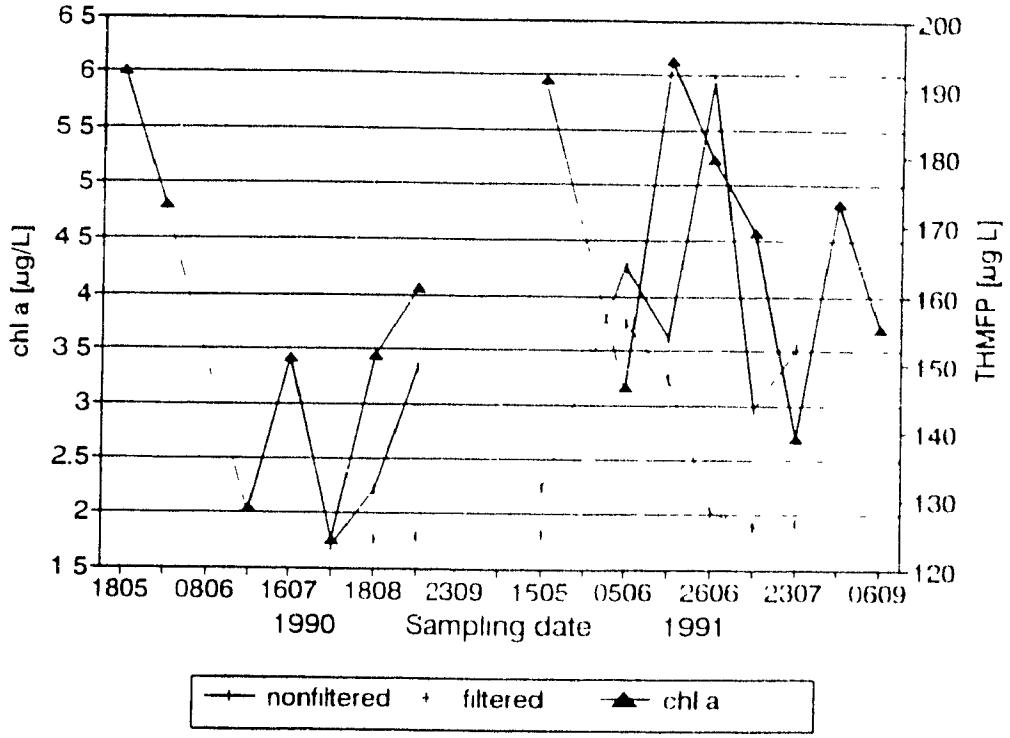

Figure 32. Seasonal variation of chl a and THMFP at North site

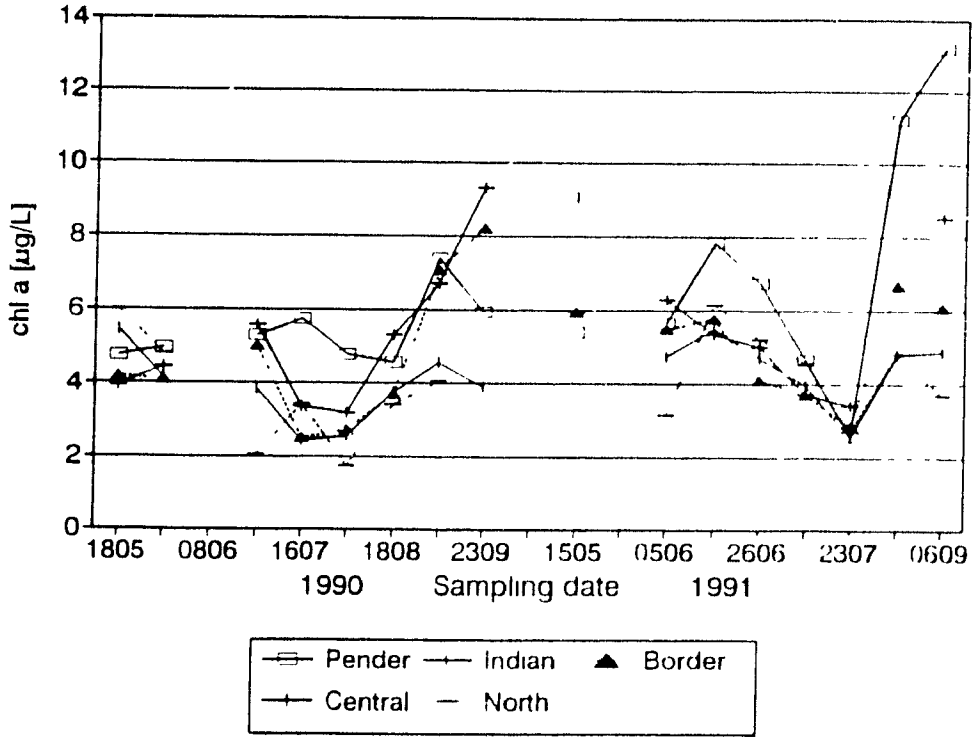

Figure 33. Seasonal variation of chl a for all sites

APPENDIX E

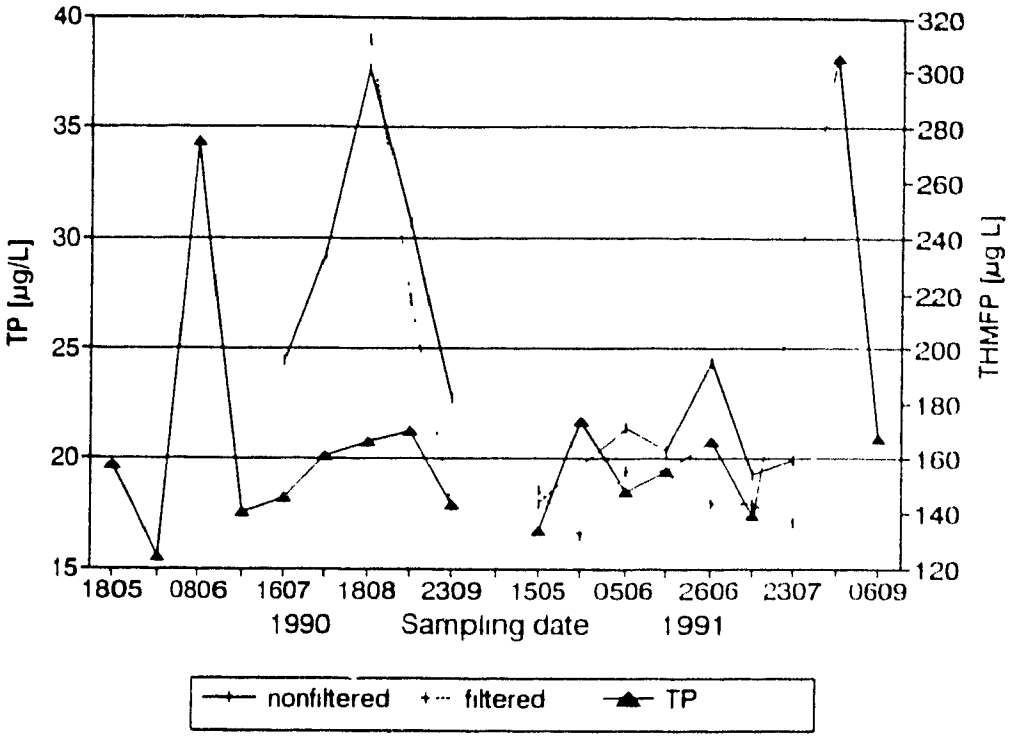

Figure 34. Seasonal variation of TP and THMFP at Pender site

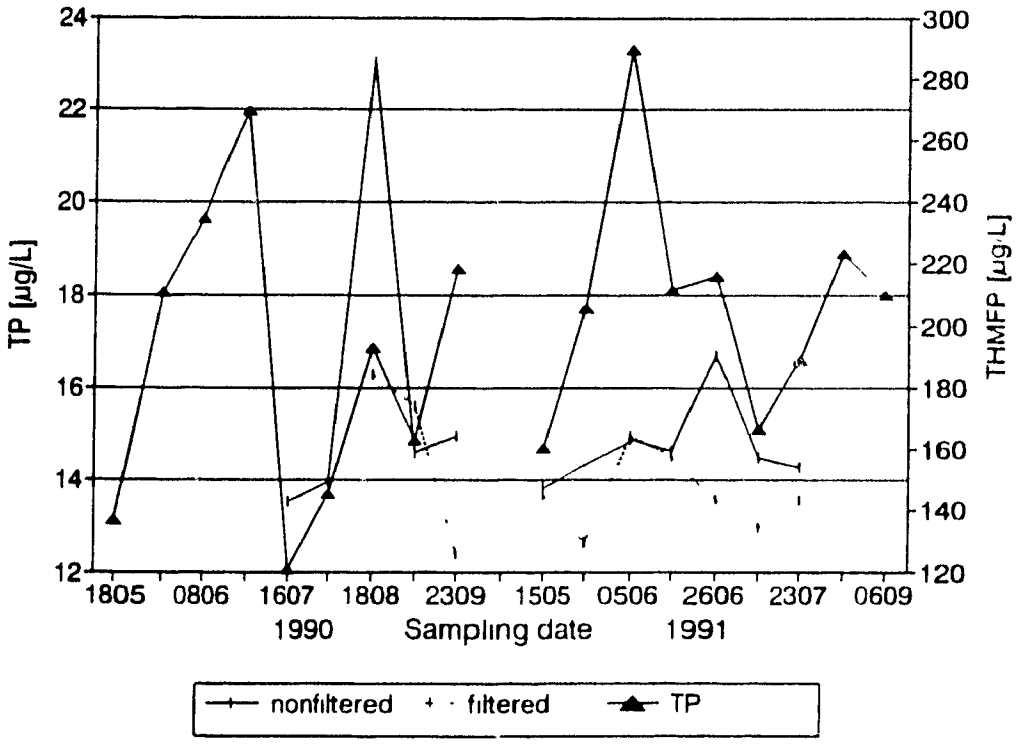

Figure 35. Seasonal variation of TP and THMFP at Indian site

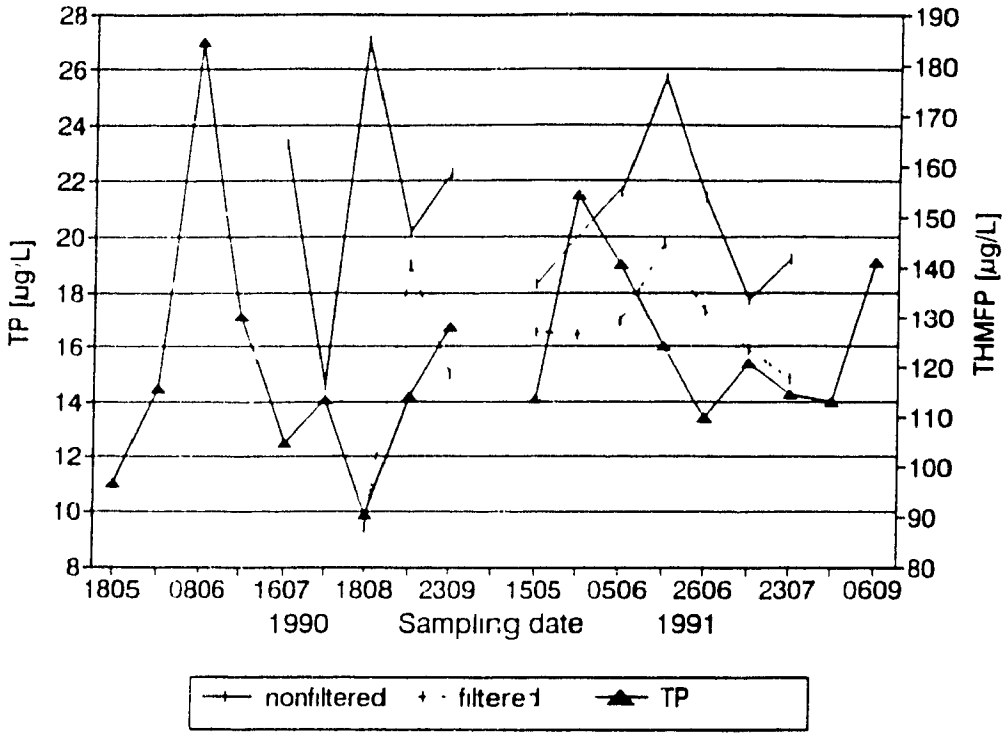

Figure 36. Seasonal variation of TP and THMFP at Border site

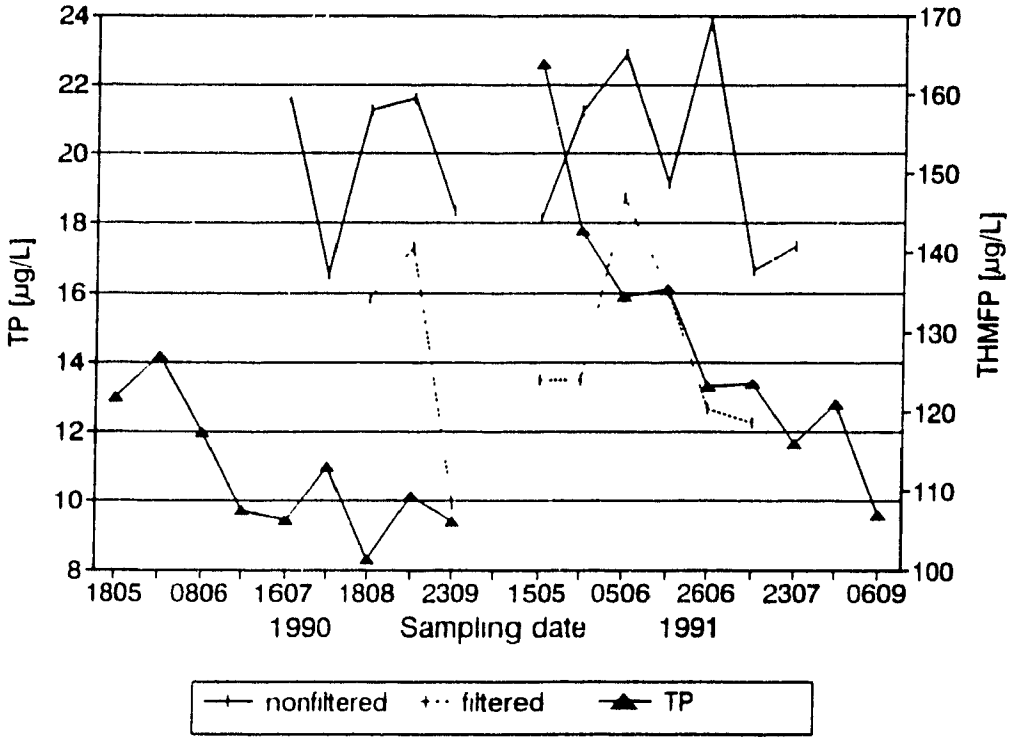

Figure 37. Seasonal variation of TP and THMFP at Central site

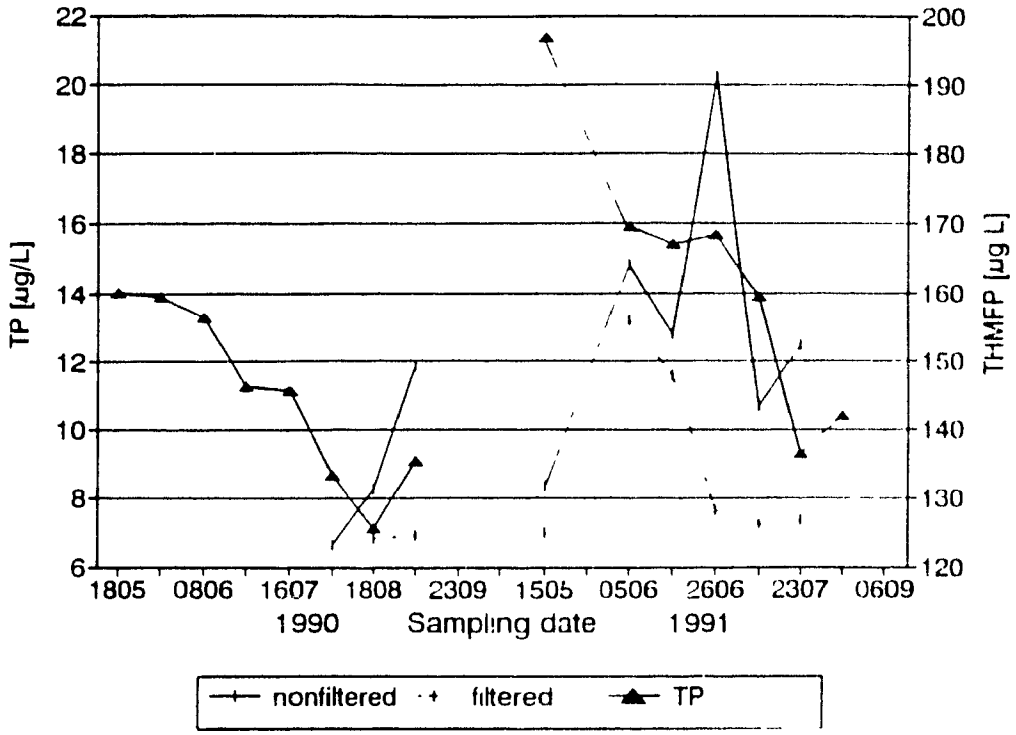

Figure 38. Seasonal variation of TP and THMFP at North site

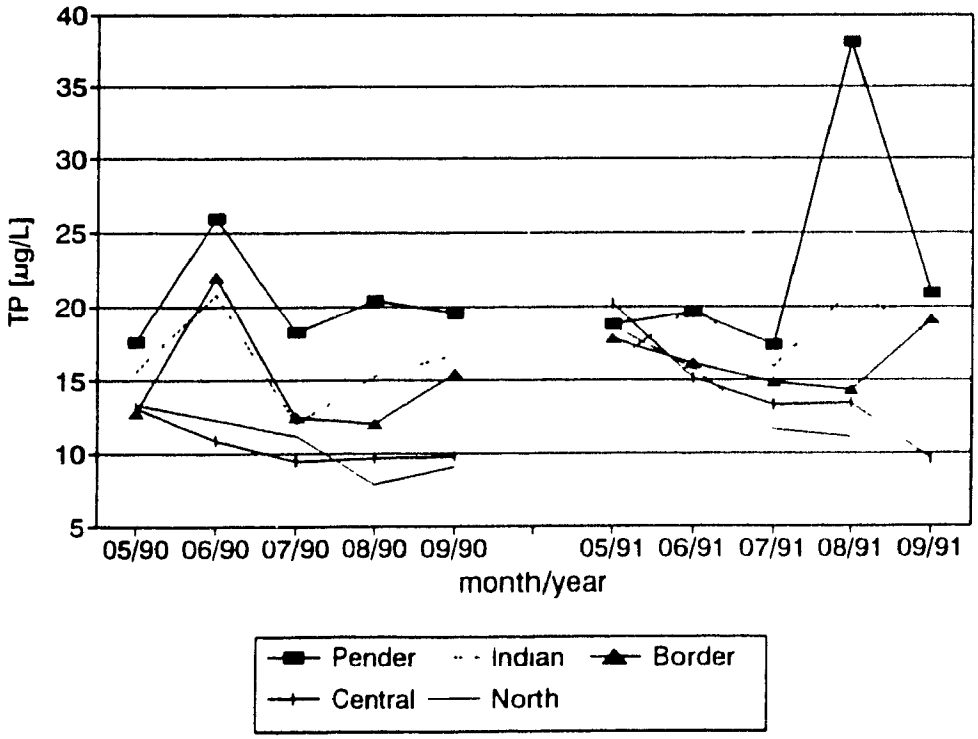

Figure 39. Monthly averages of TP for all sites

APPENDIX F

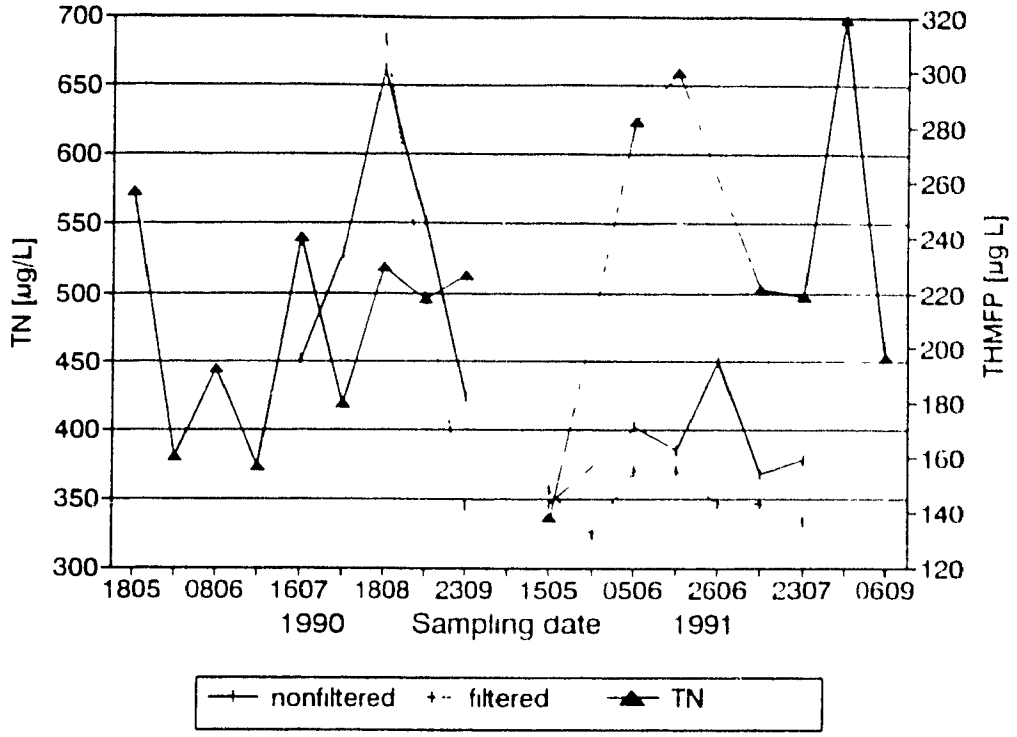

Figure 40. Seasonal variation of TN and THMFP at Pender site

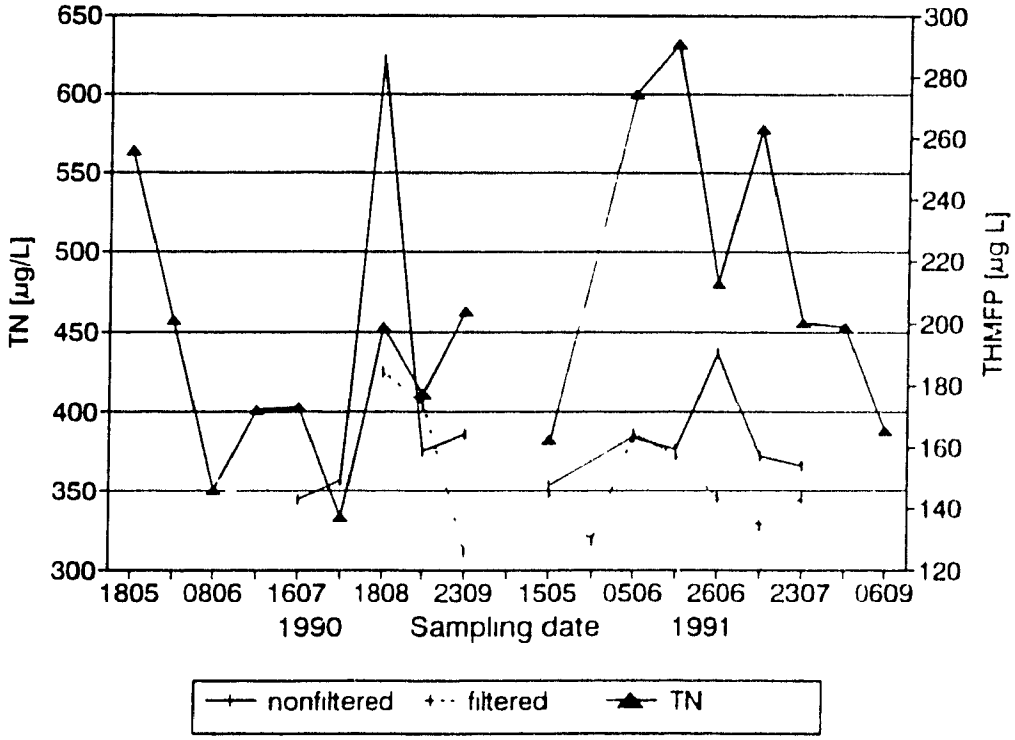

Figure 41. Seasonal variation of TN and THMFP at Indian site

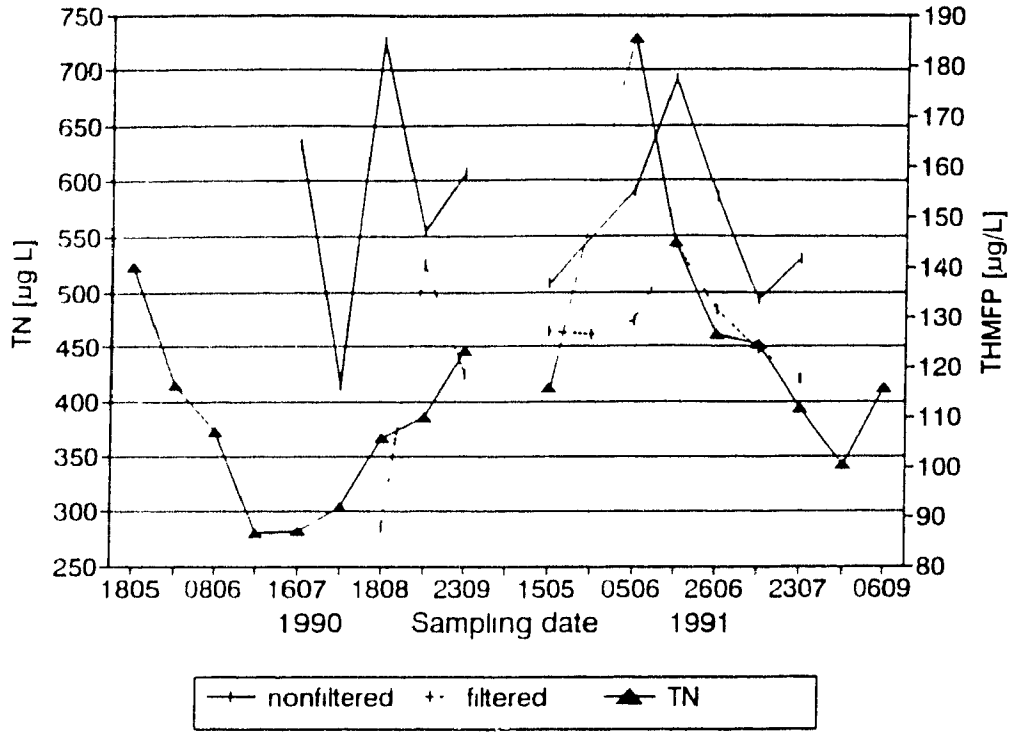

Figure 42. Seasonal variation of TN and THMFP at Border site

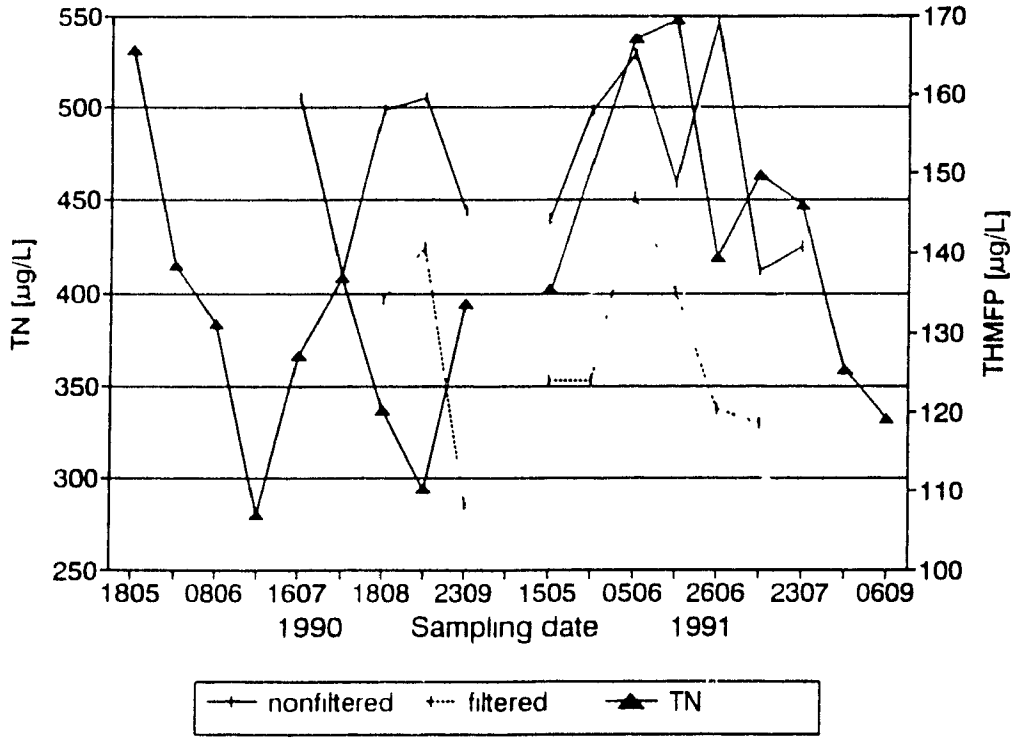

Figure 43. Seasonal variation of TN and THMFP at Central site

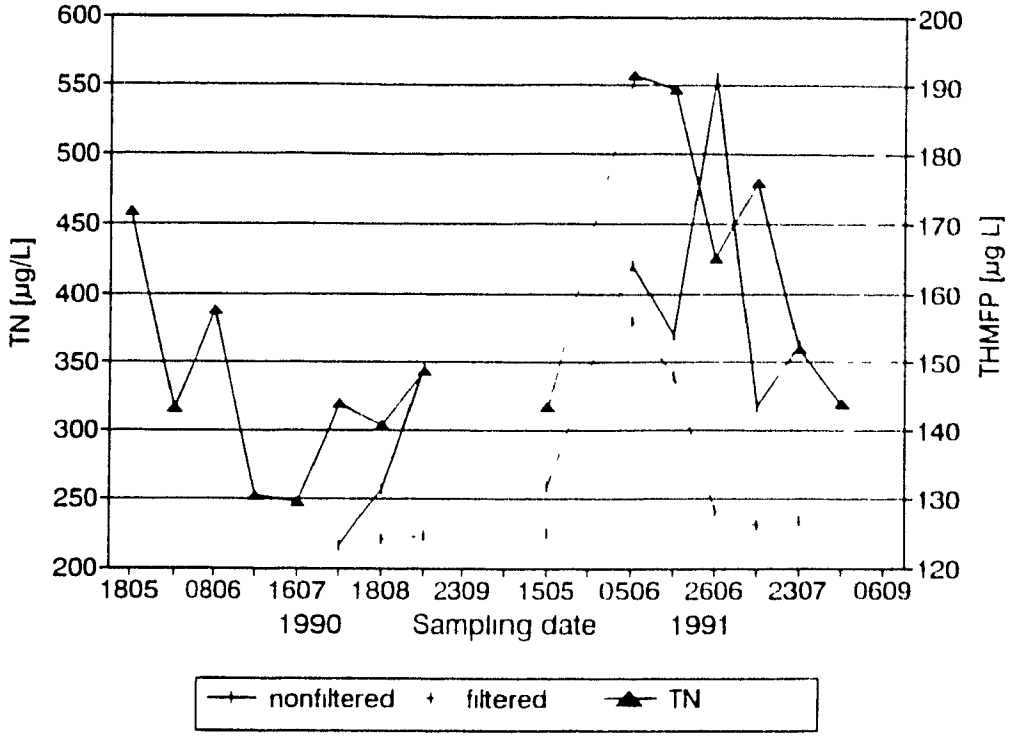

Figure 44. Seasonal variation of TN and THMFP at North site

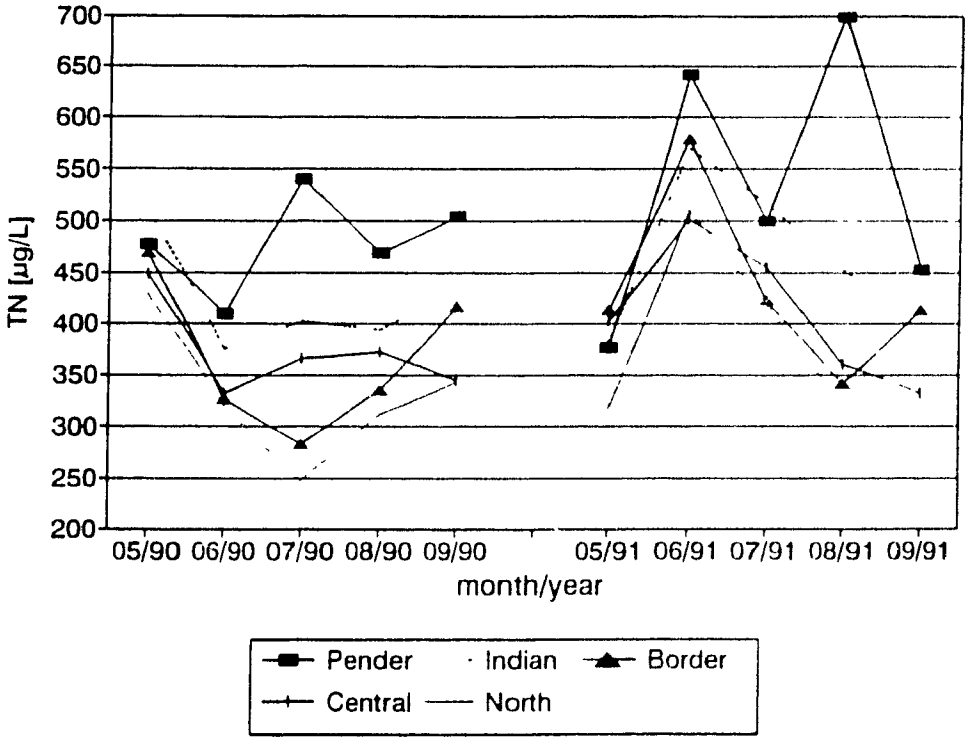

Figure 45. Monthly averages of TN for all sites

APPENDIX G

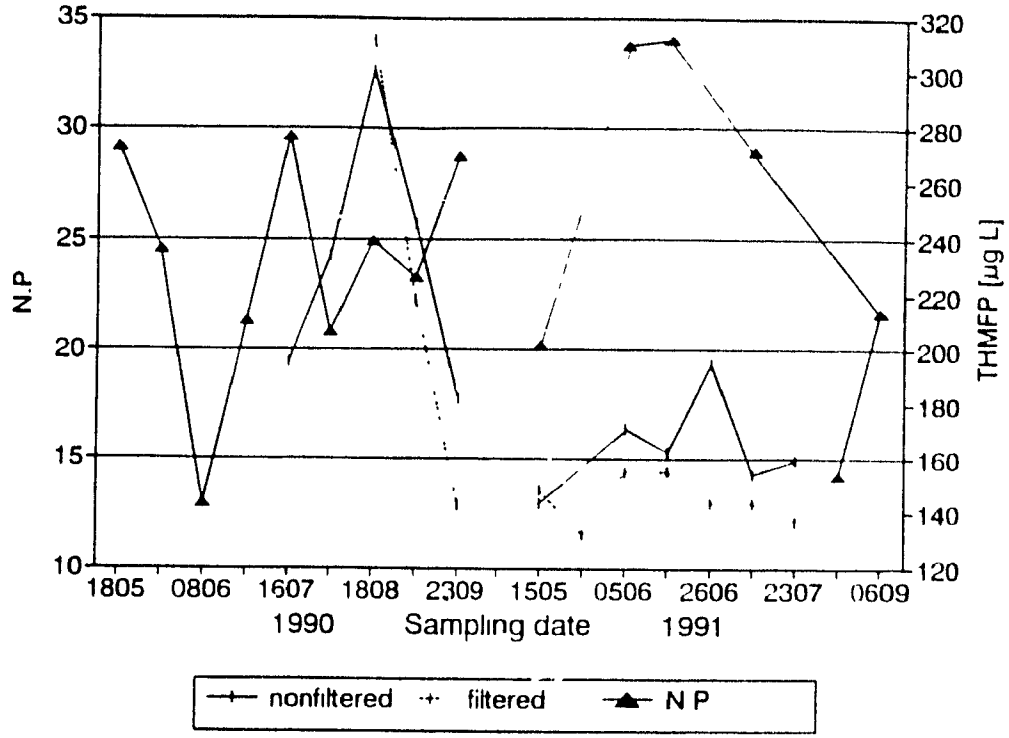

Figure 46. Seasonal variation of the N:P ratio and THMFP at Pender site

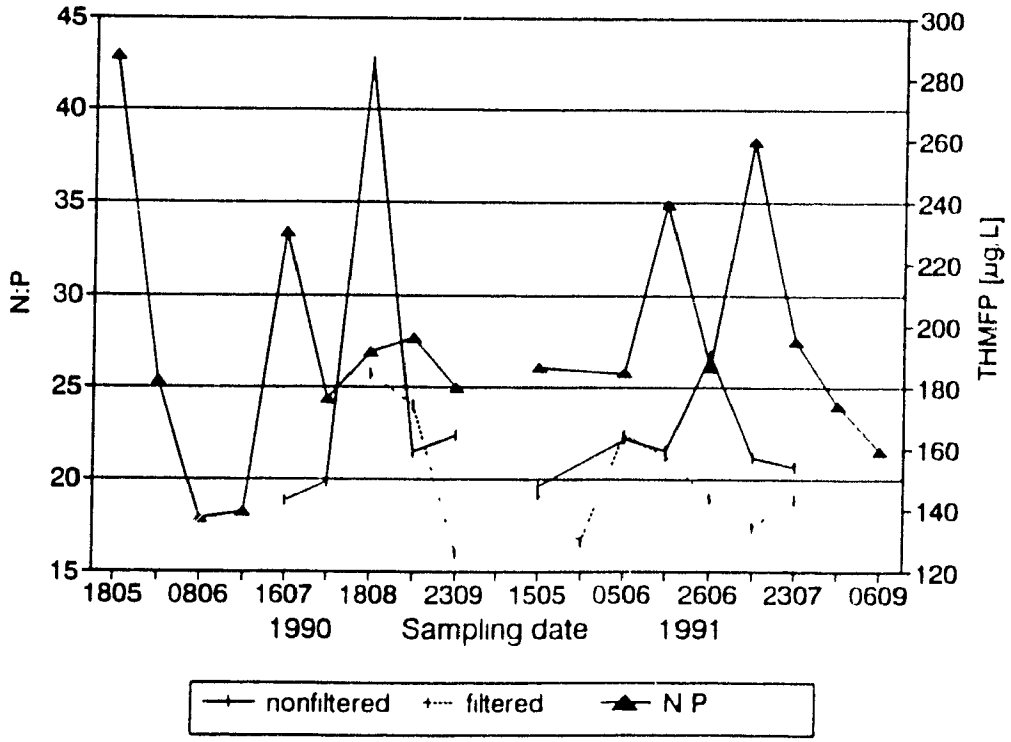

Figure 47. Seasonal variation of the N:P ratio and THMFP at Indian site

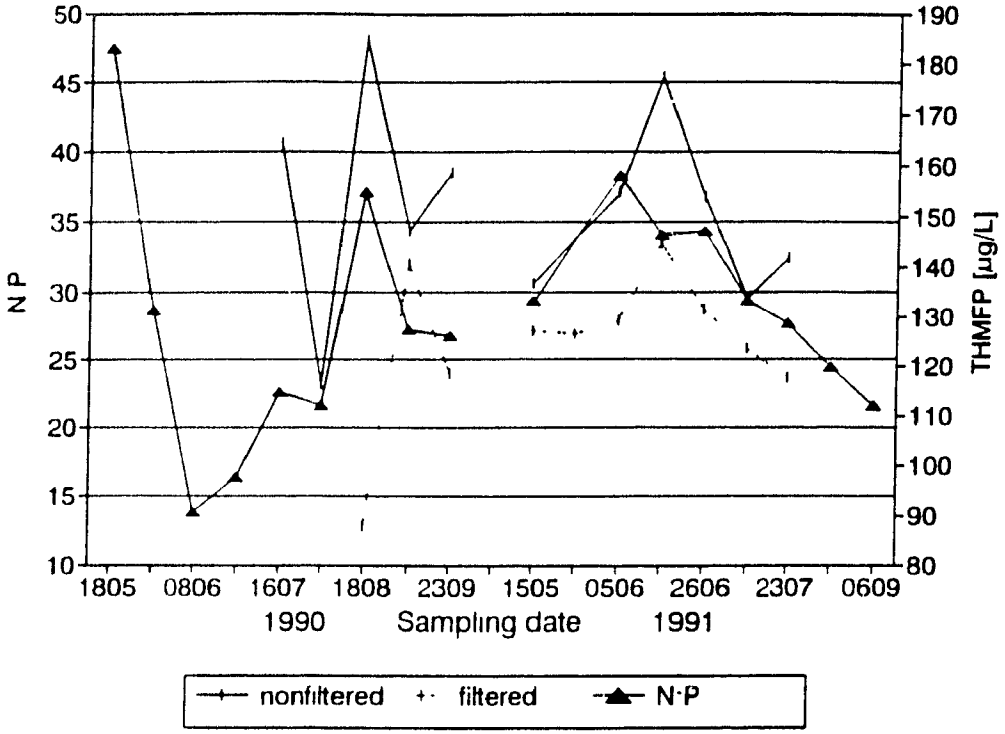

Figure 48. Seasonal variation of the N:P ratio and THMFP at Border site

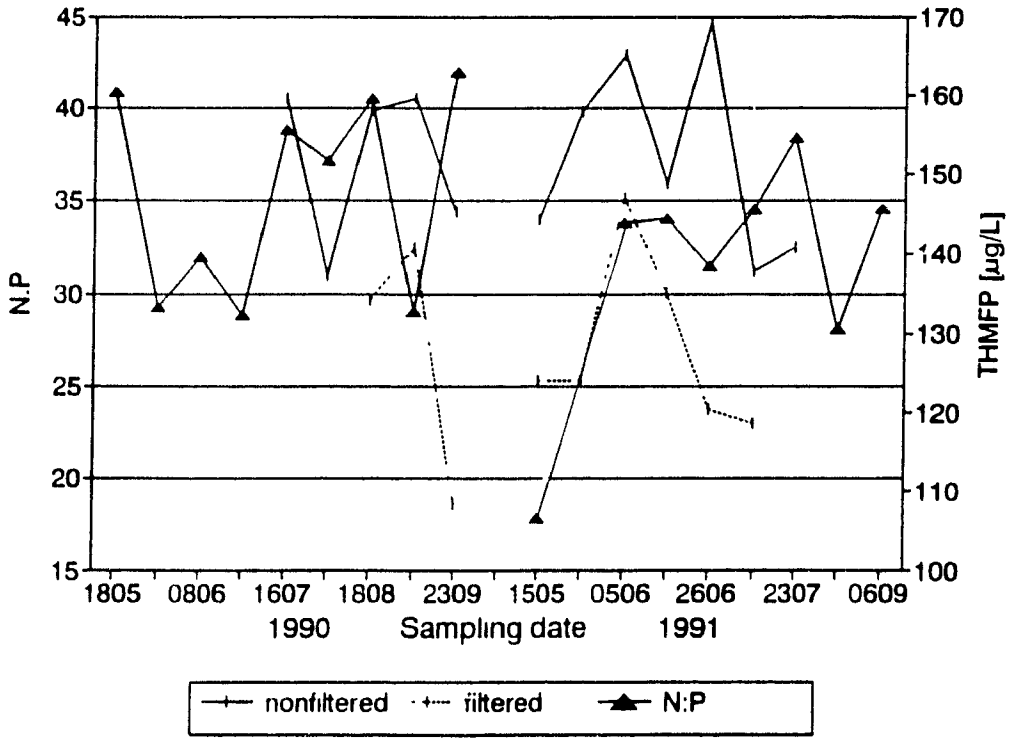

Figure 49. Seasonal variation of the N:P ratio and THMFP at Central site

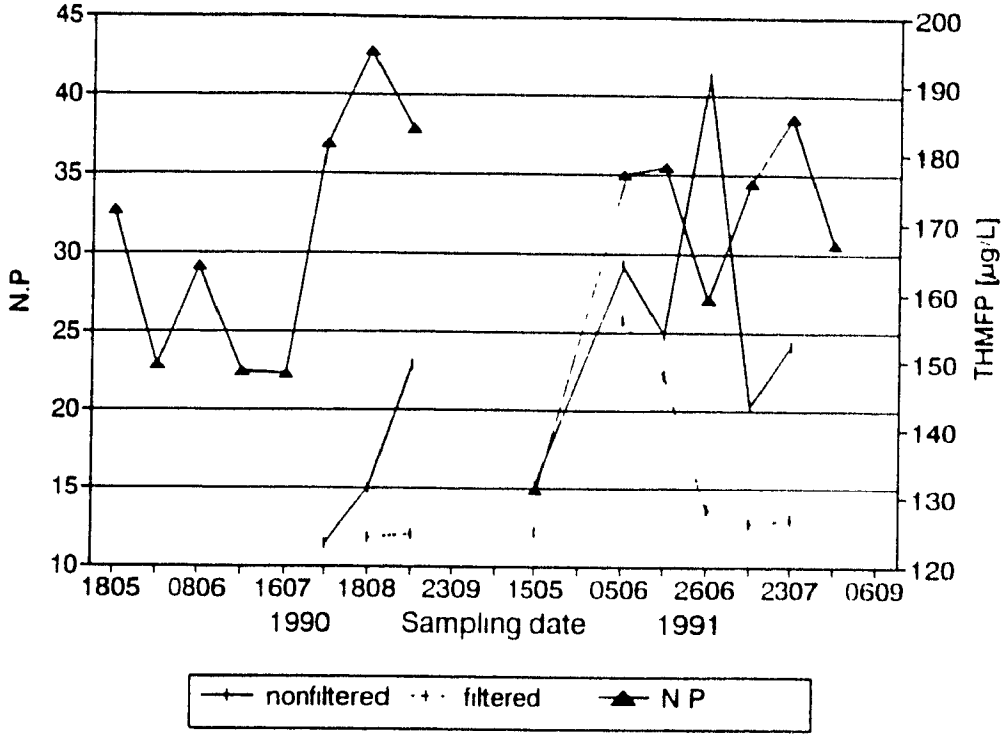

Figure 50. Seasonal variation of the N:P ratio and THMFP at North site

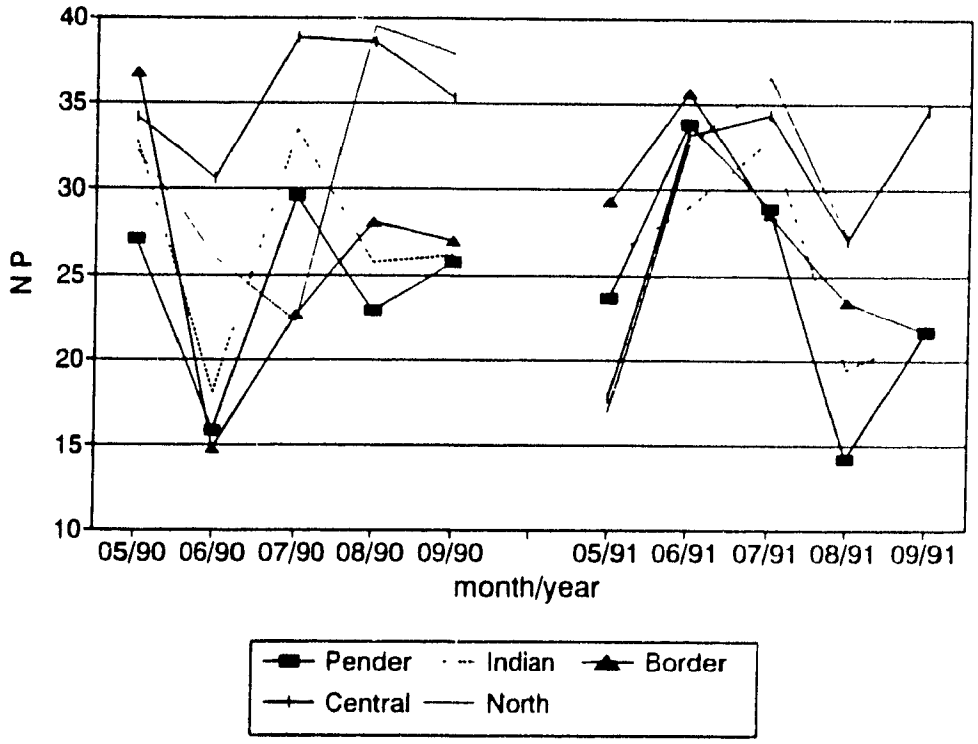

Figure 51. Monthly averages of N:P ratio for all sites

APPENDIX H

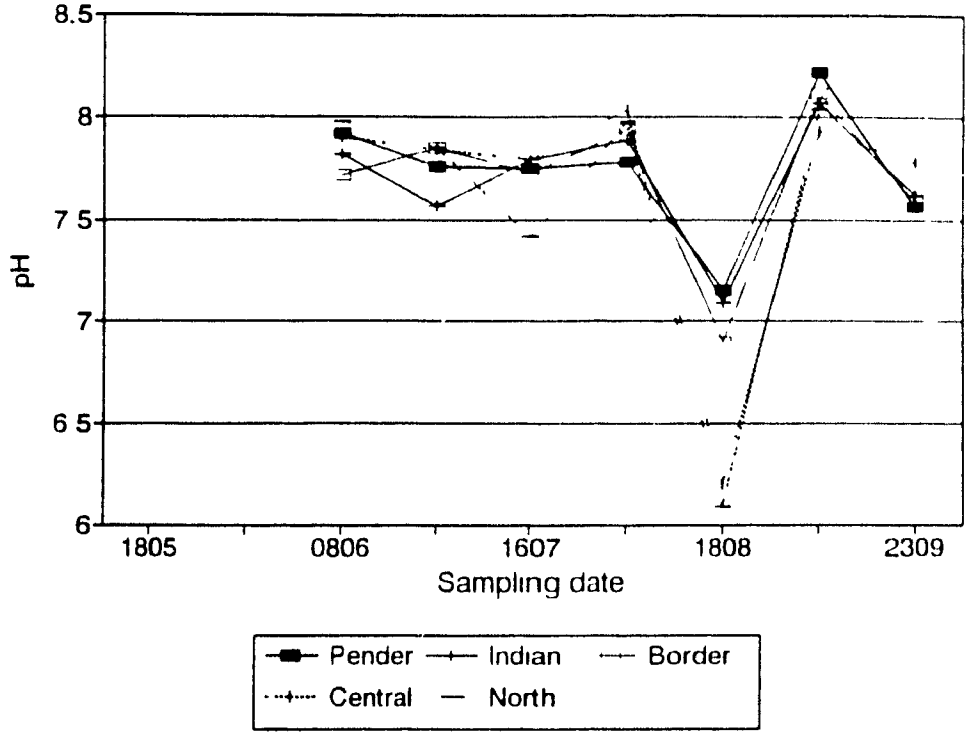

Figure 52. Seasonal variation of pH at all sites (1990 only)

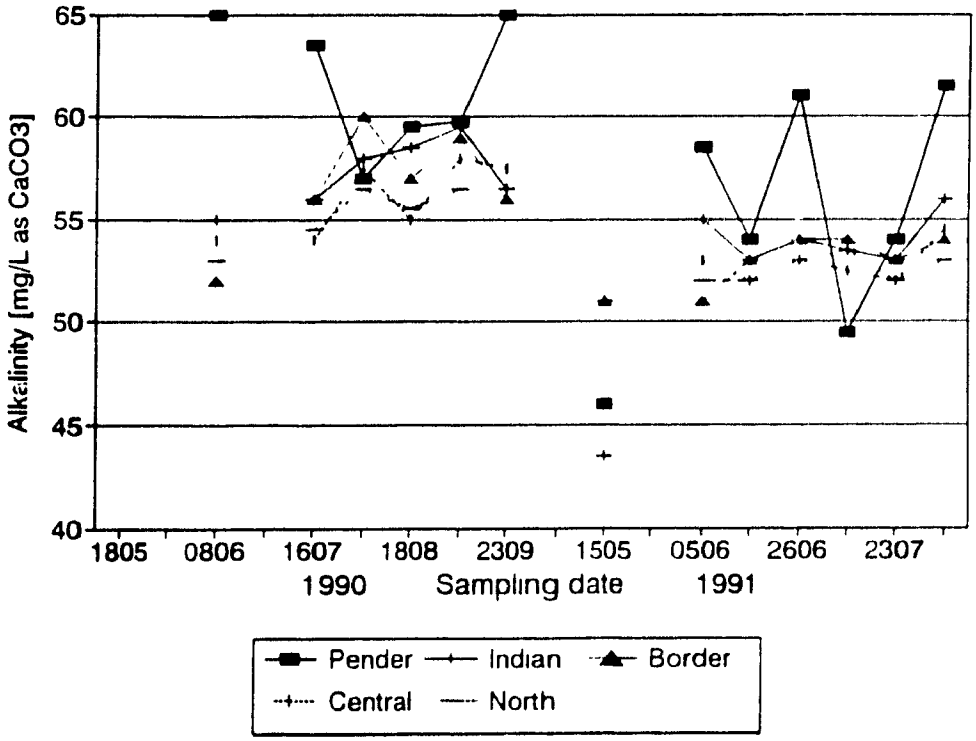

Figure 53. Seasonal variation of alkalinity at all sites

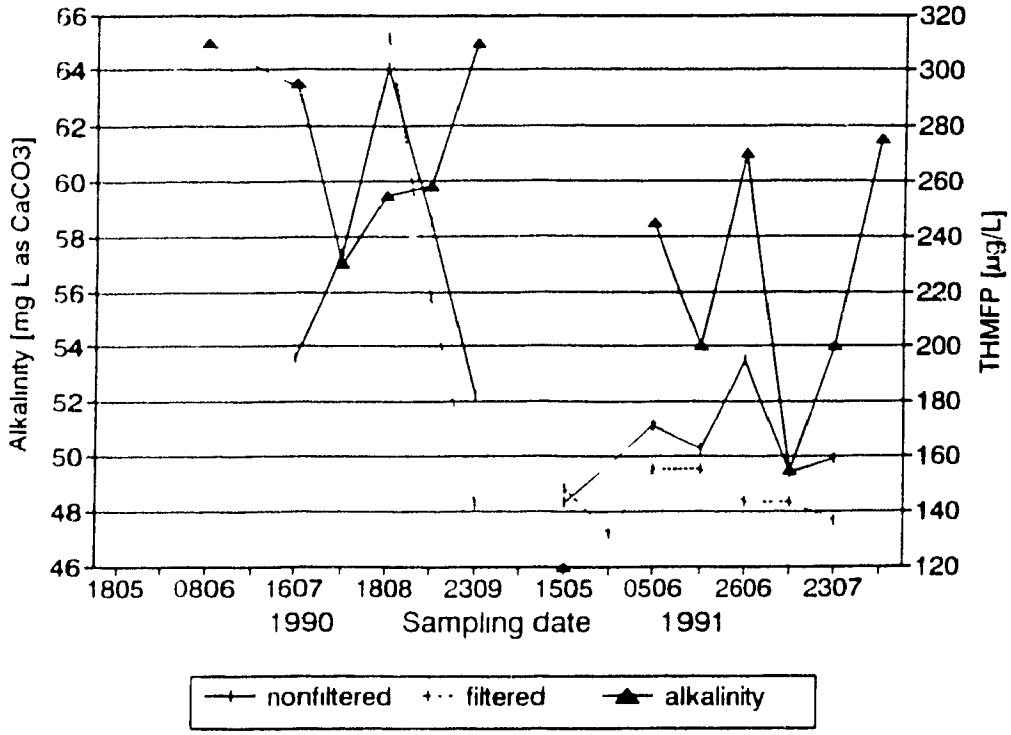

Figure 54. Seasonal variation of alkalinity and THMFP at Pender site

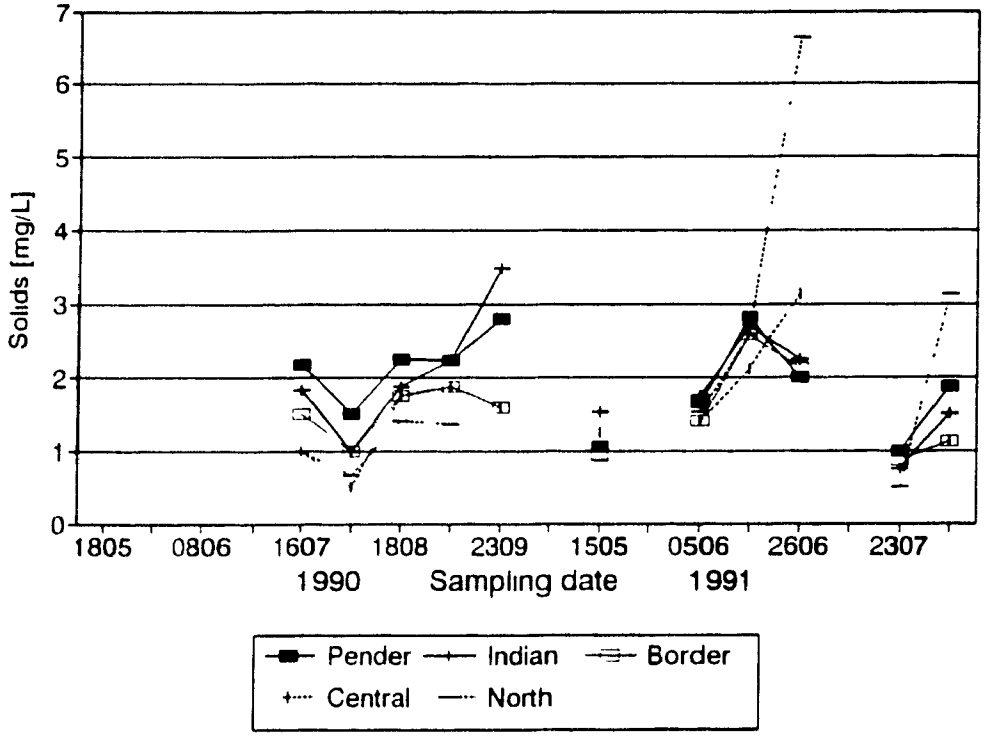

Figure 55. Seasoanl variation of suspended solids for all sites

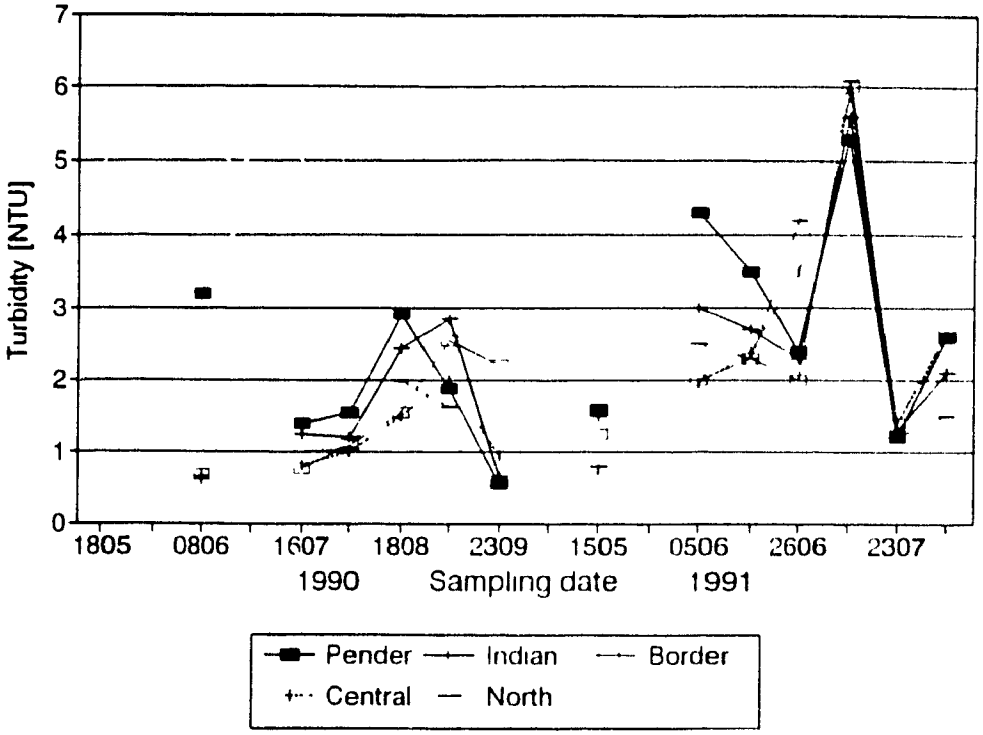

Figure 56. Seasonal variation of turbidity for all sites

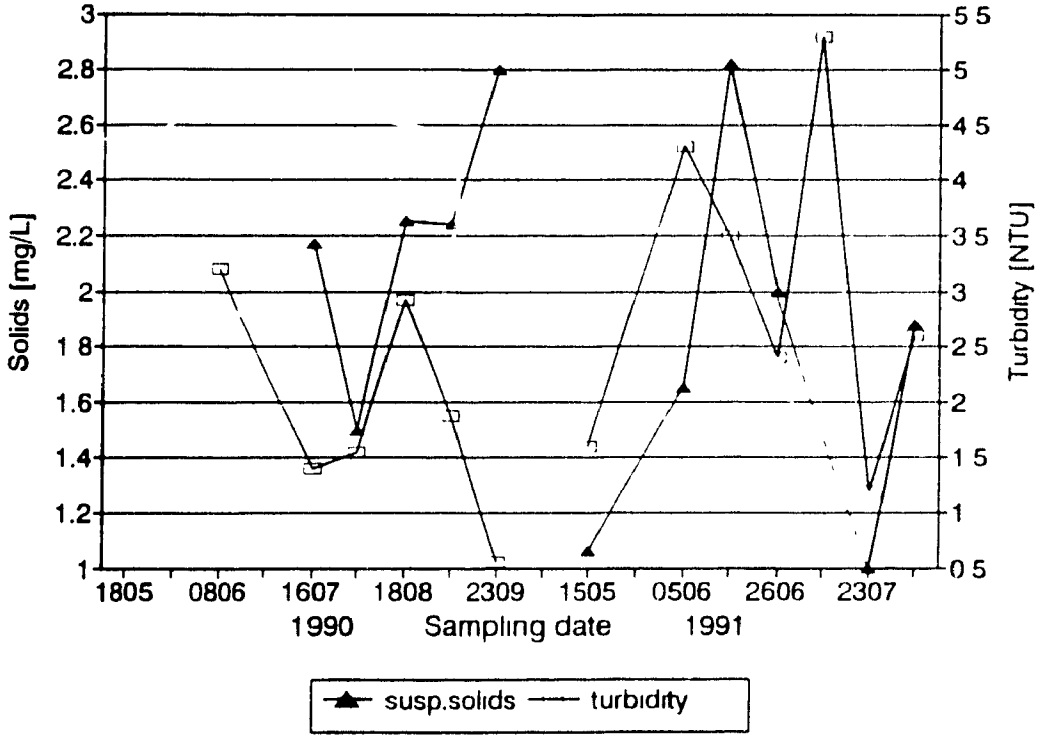

Figure 57. Seasonal variation of solids and turbidity at Pender site

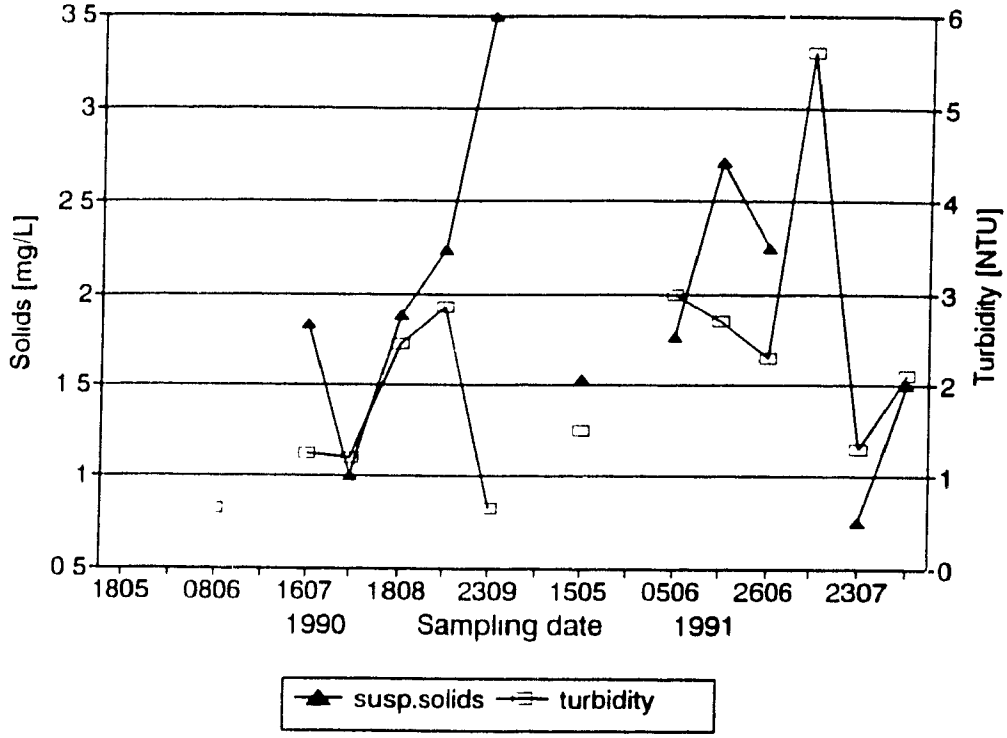

Figure 58. Seasonal variation of solids and turbidity at Indian site

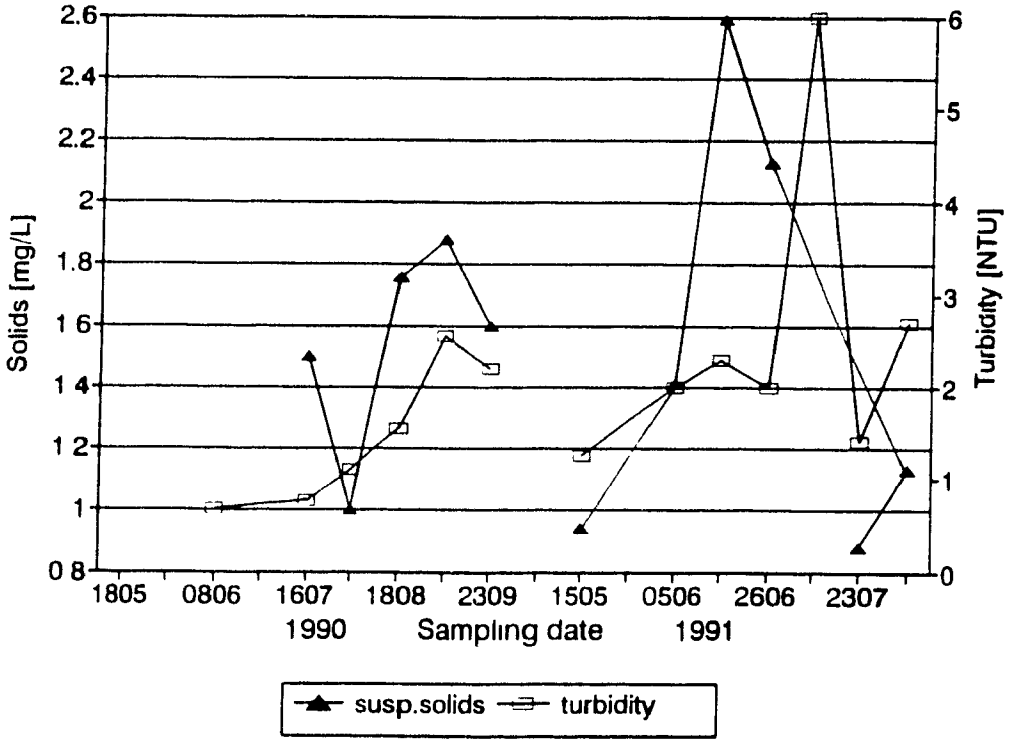

Figure 59. Seasonal variation of solids and turbidity at Border site

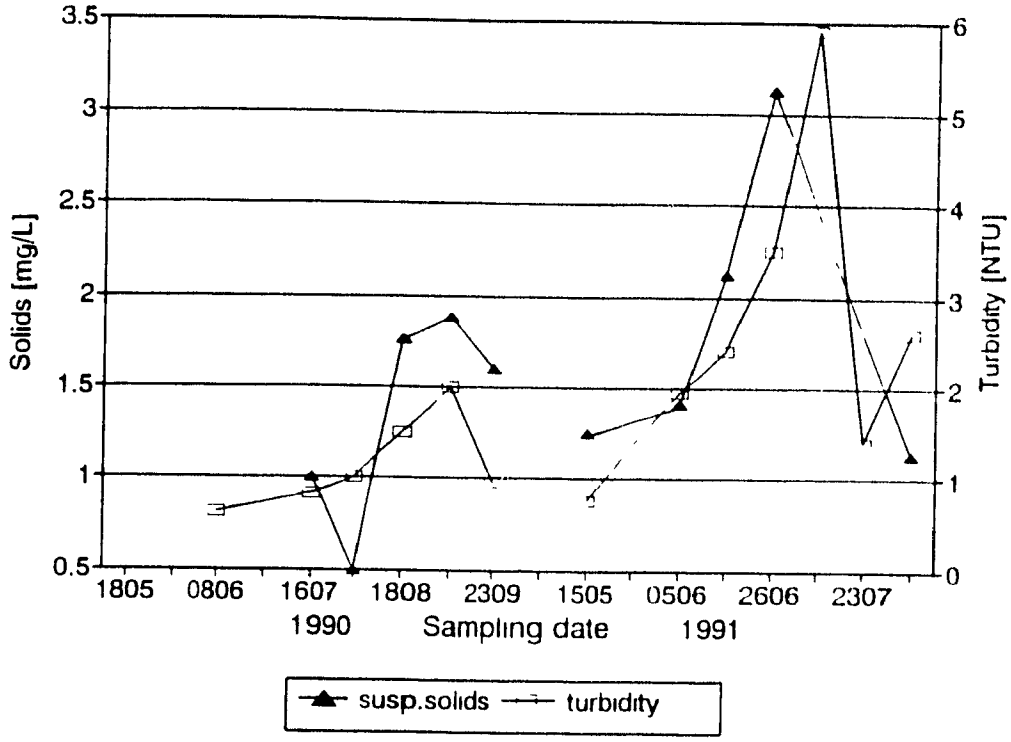

Figure 60. Seasonal variation of solids and turbidity at Central site

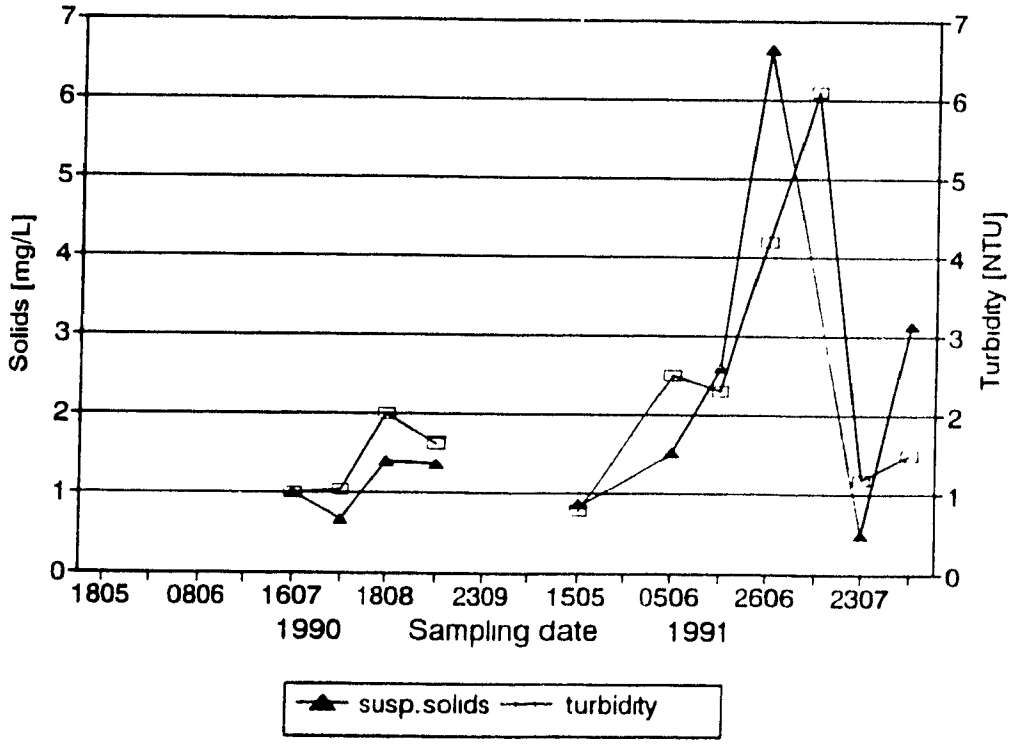

Figure 61. Seasonal variation of solids and turbidity at North site

APPENDIX I

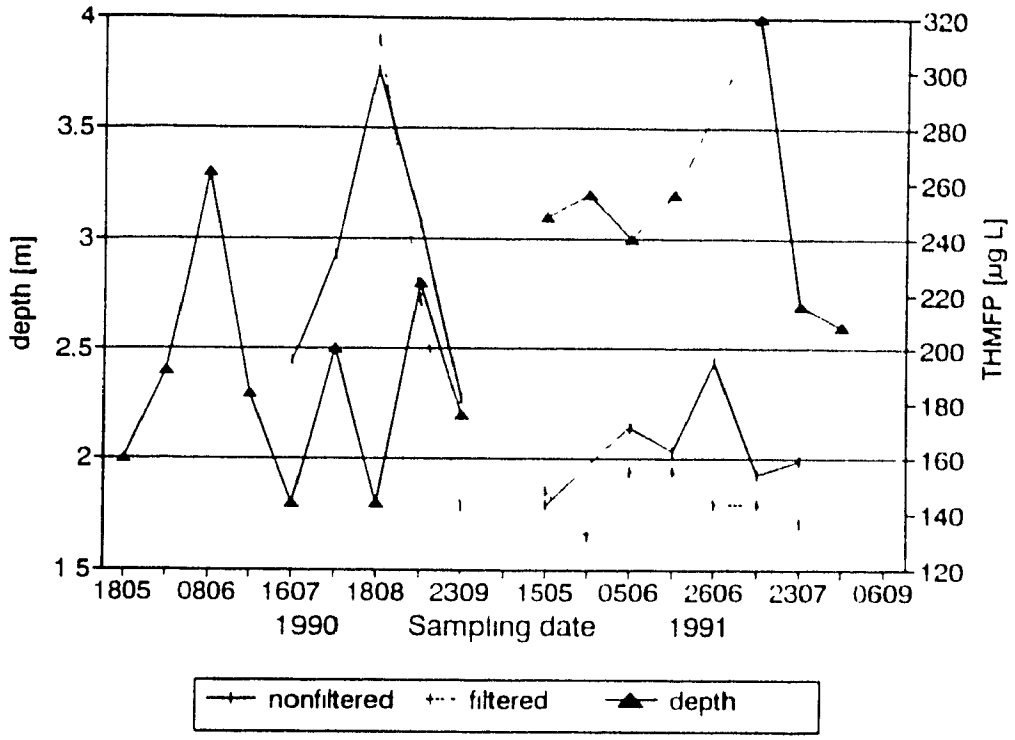

Figure 62. Seasonal variation of secchi depth and THMFP at Pender site

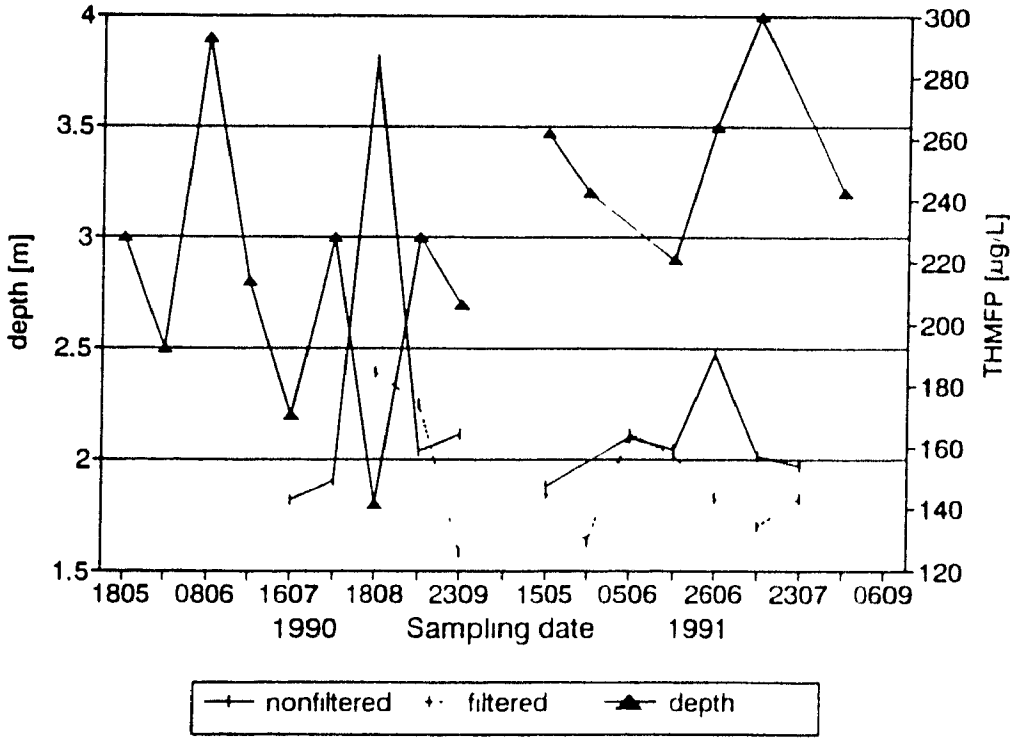

Figure 63. Seasonal variation of secchi depth and THMFP at Indian site

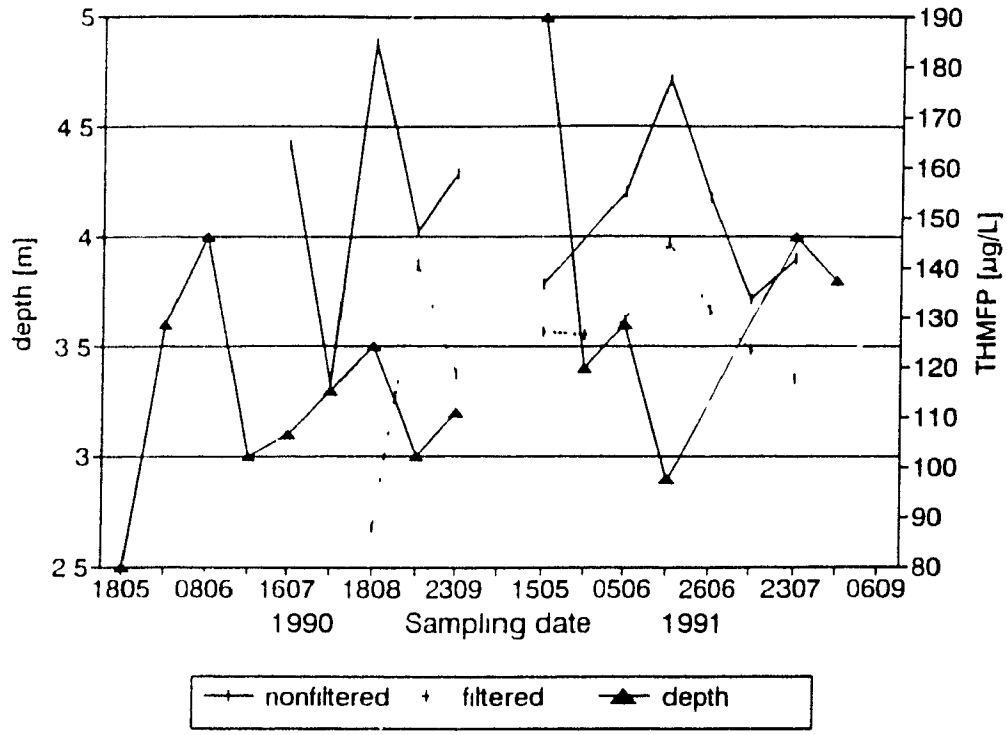

Figure 64. Seasonal variation of secchi depth and THMFP at Border site

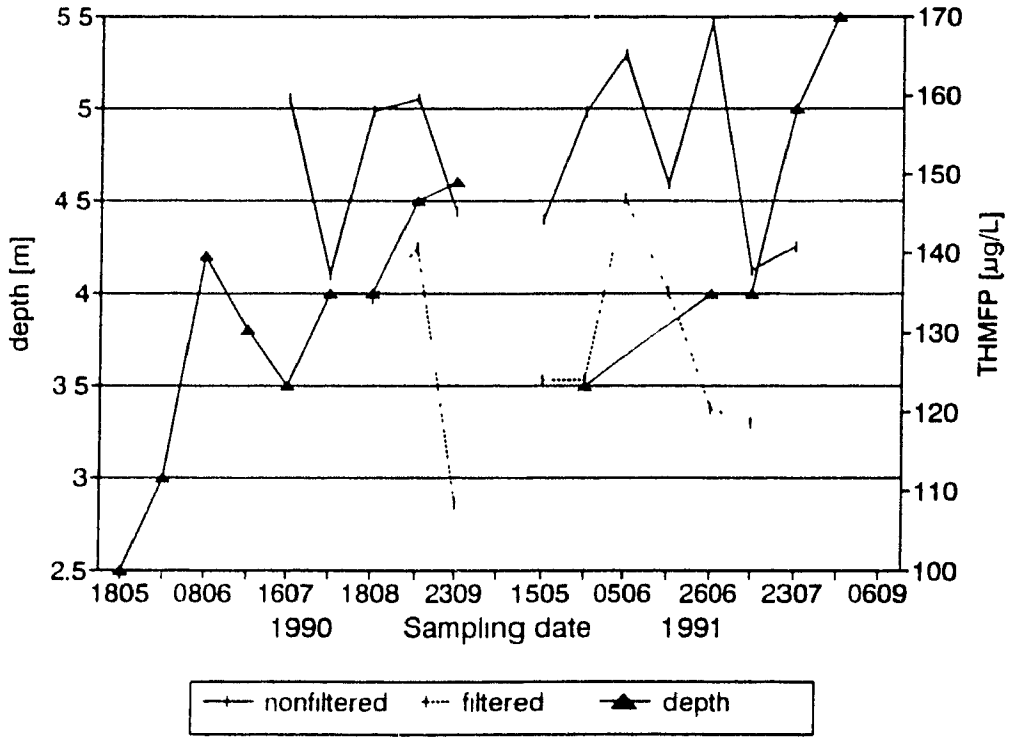

Figure 65. Seasonal variation of secchi depth and THMFP at Central site

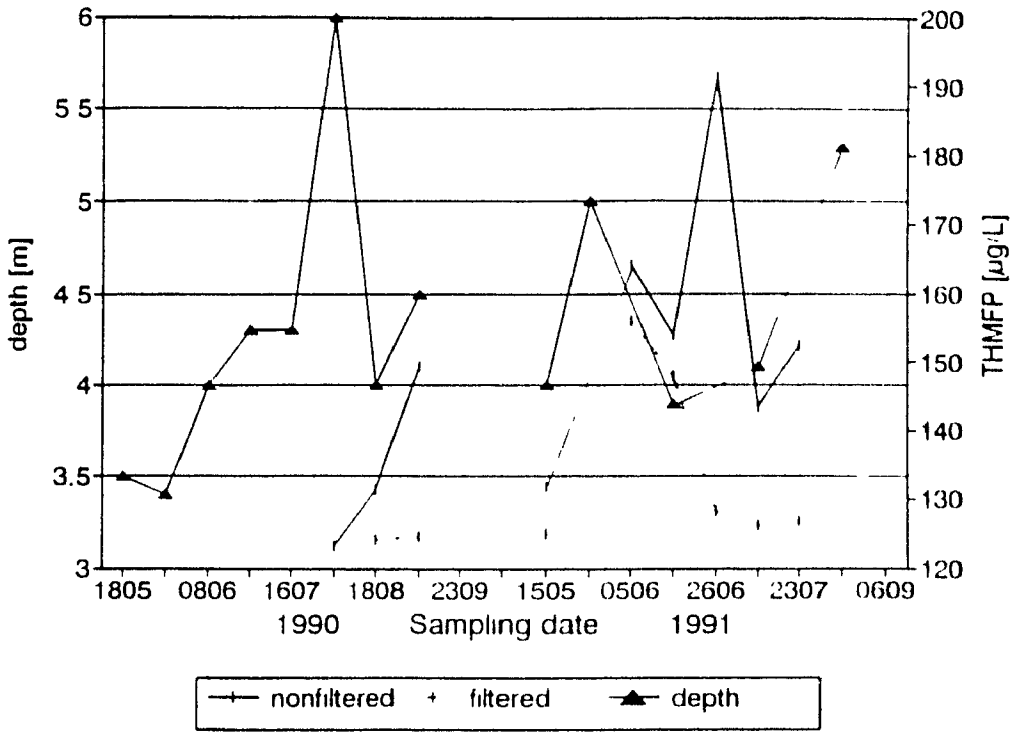

Figure 66. Seasonal variation of secchi depth and THMFP at North site

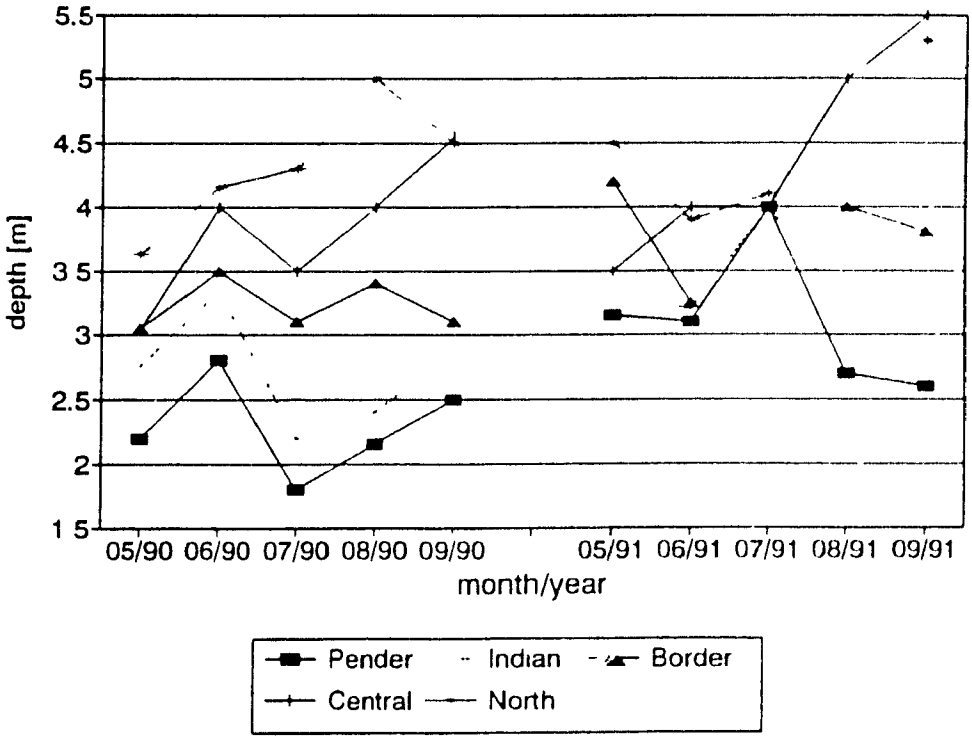

Figure 67. Monthly averages of secchi depth at all sites

APPENDIX J

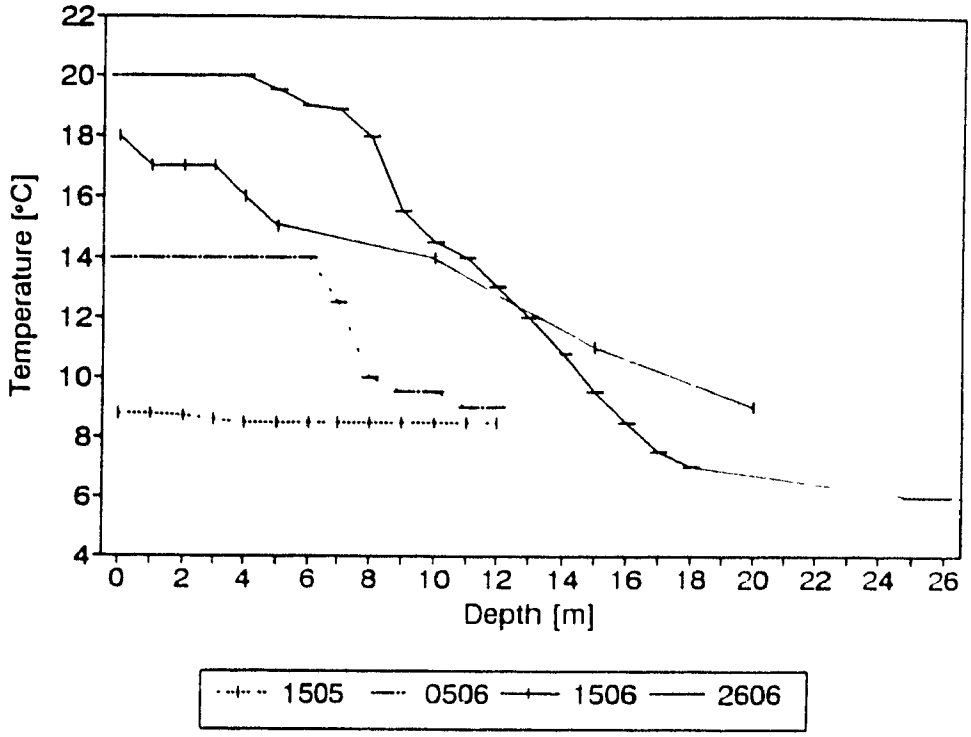

Figure 68. Temperature profiles for May-June 1991 at Central site

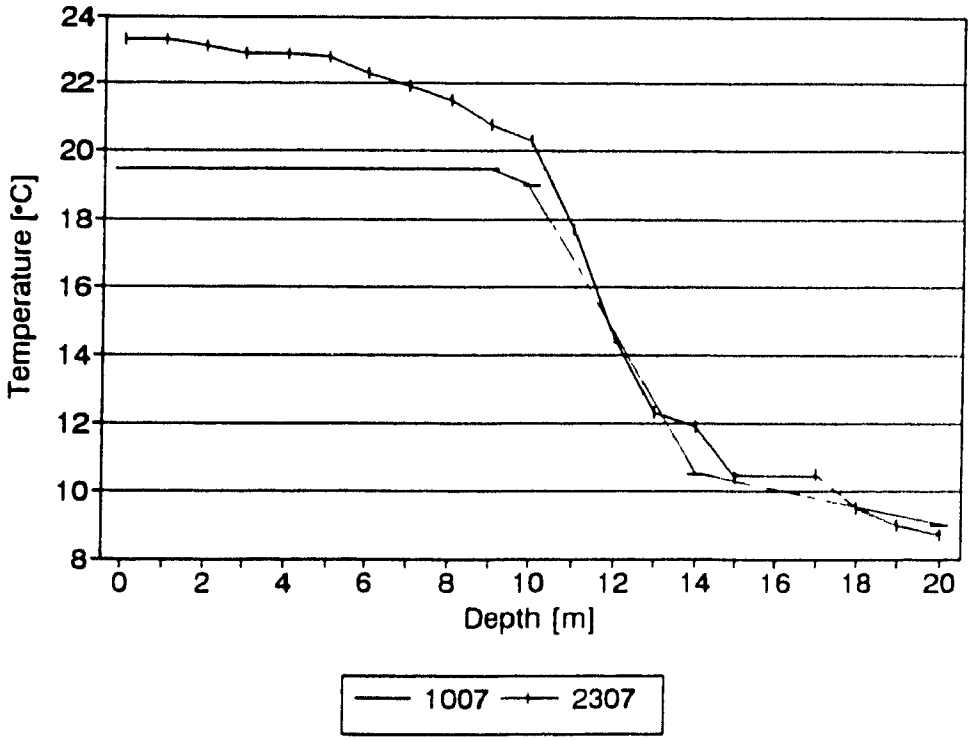

Figure 69. Temperature profiles for July 1991 at Central site

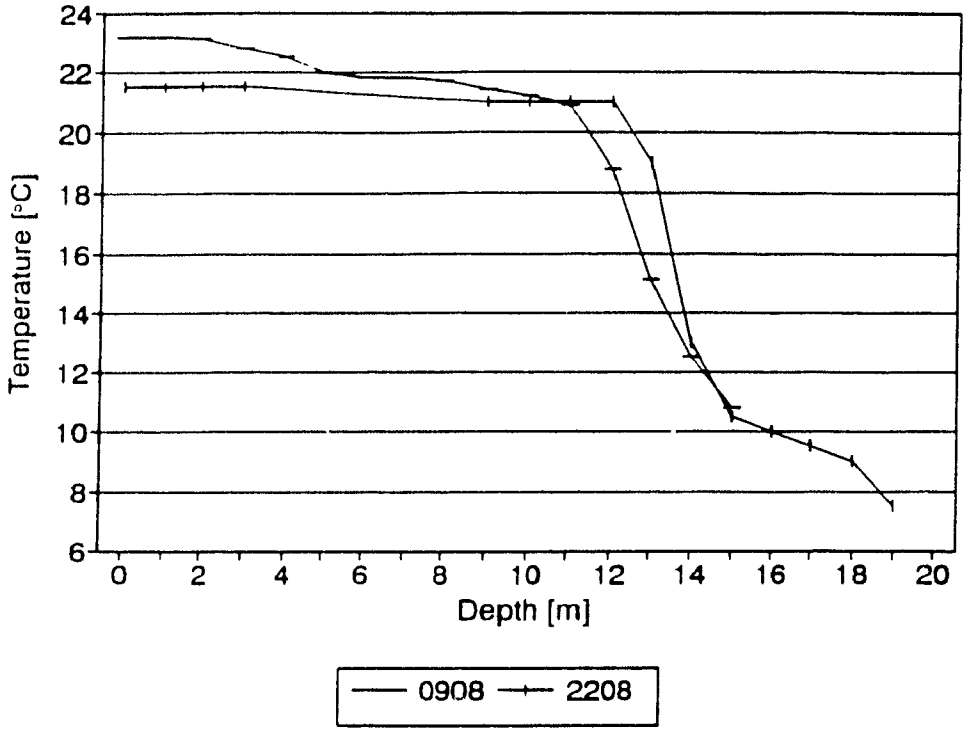

Figure 70. Temperature profiles for August 1991 at Central site

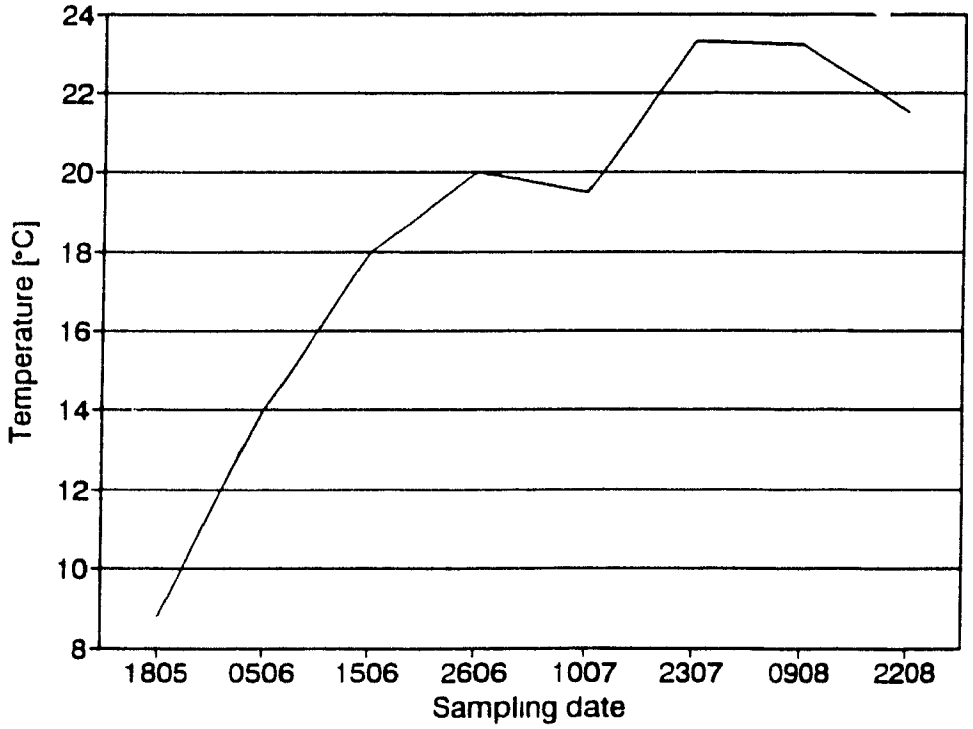

Figure 71. Surface temperature profile over 1991 sampling season at Central site

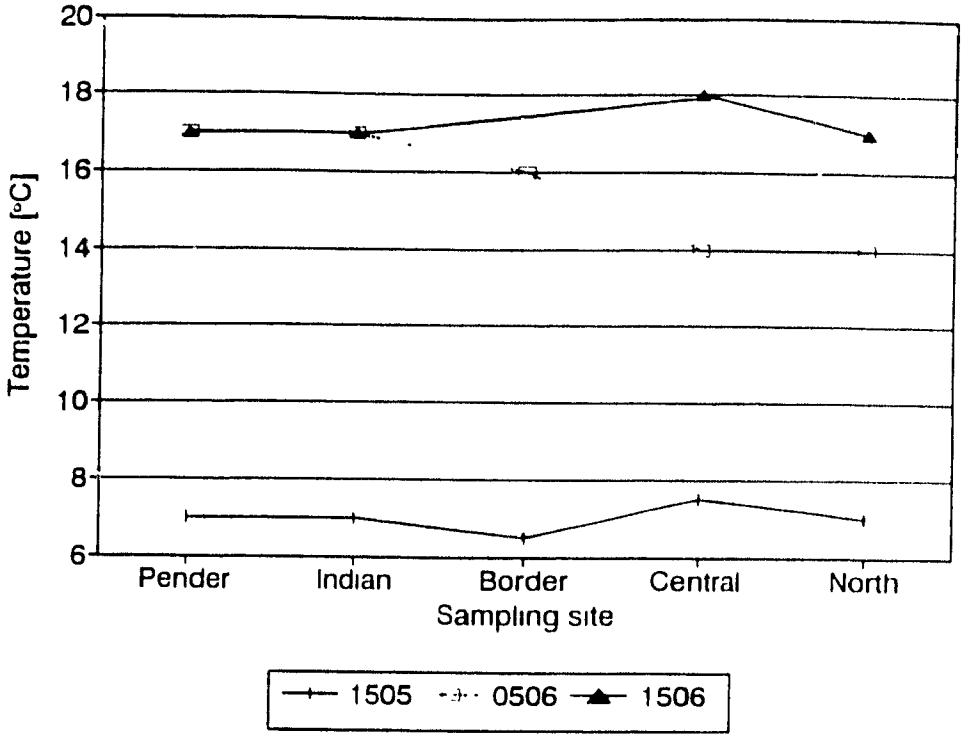

Figure 72. Surface temperature variation between sites (1991)

APPENDIX K

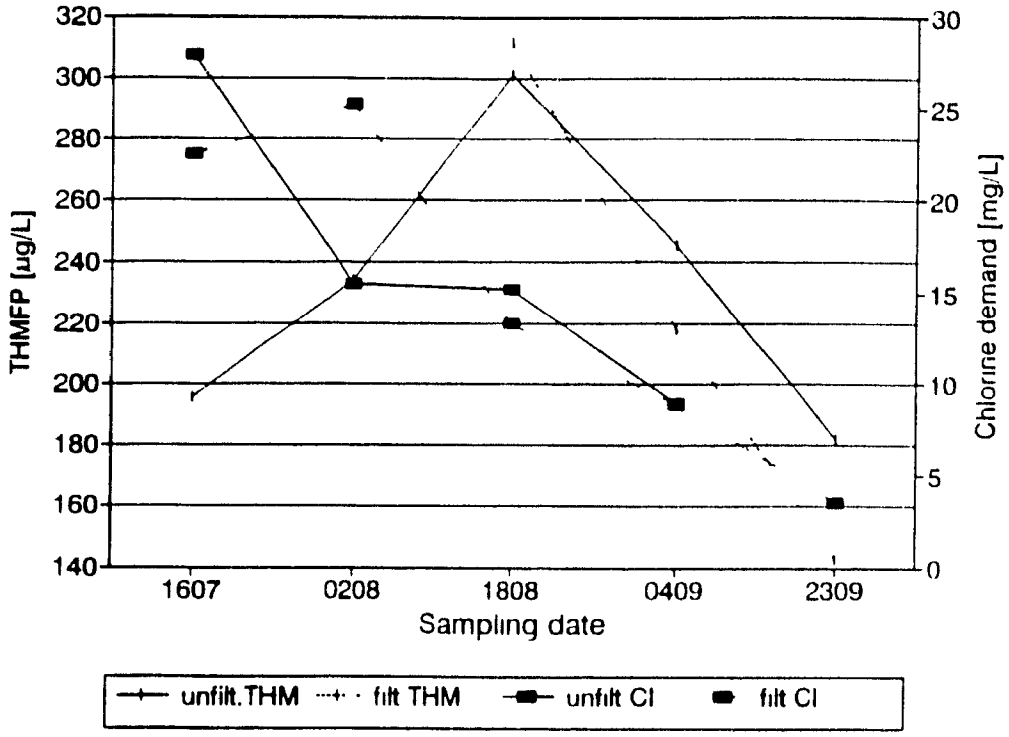

Figure 73. Seasonal variation of THMFP and chlorine demand at Pender site (1990 only)

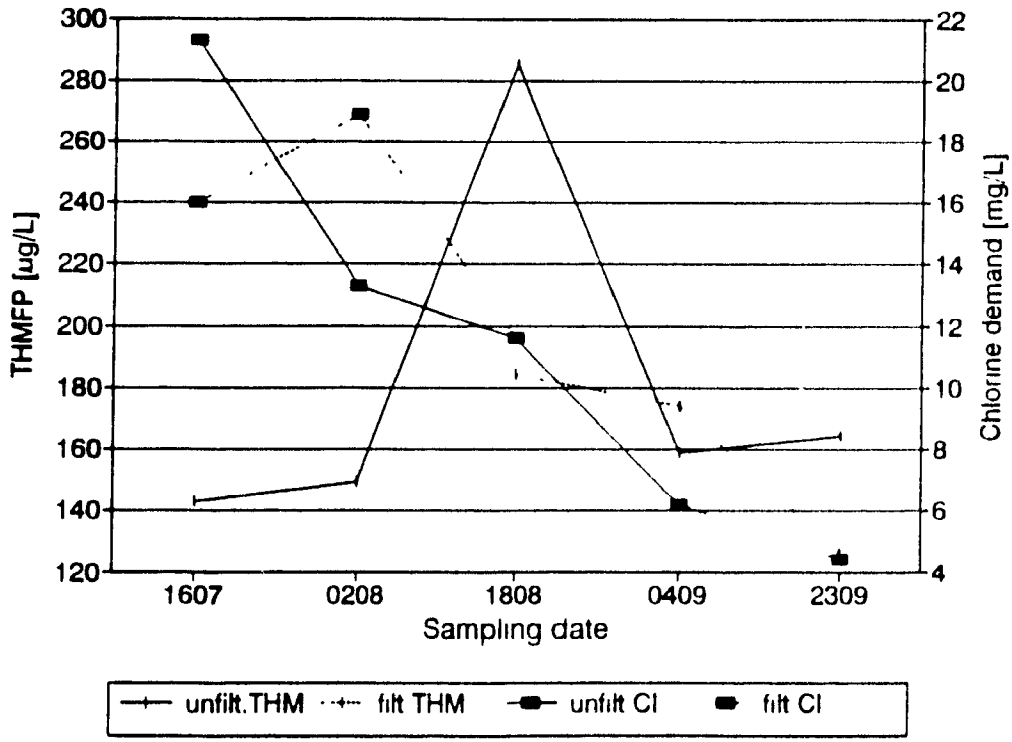

Figure 74. Seasonal variation of THMFP and chlorine demand at Indian site (1990 only)

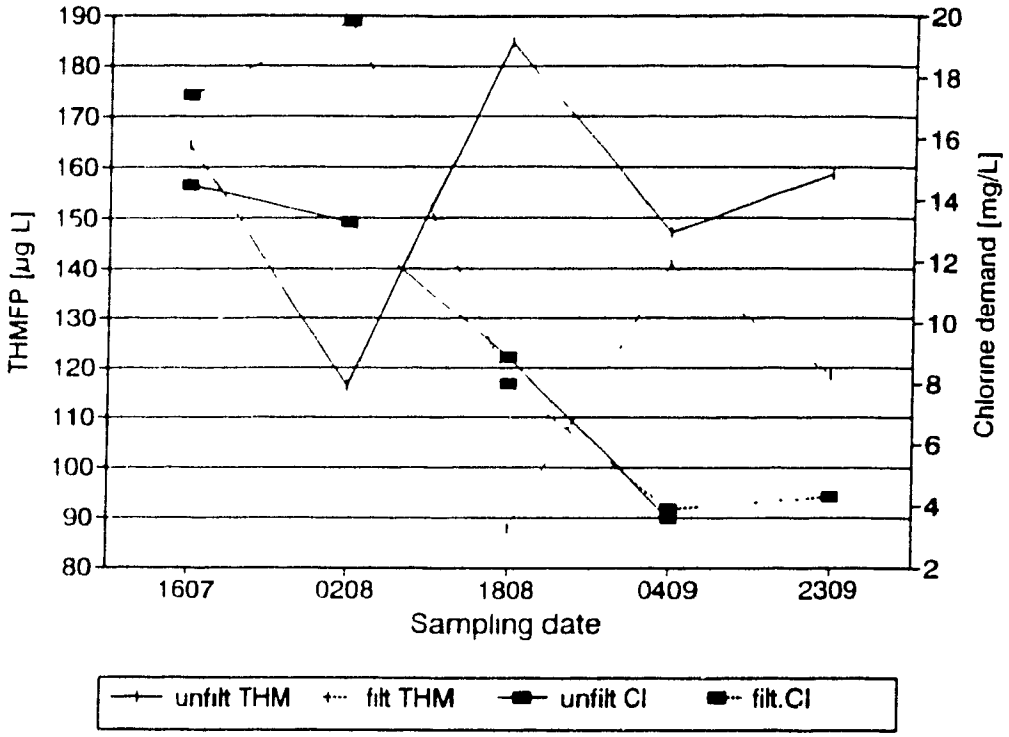

Figure 75 Seasonal variation of THMFP and chlorine demand at Border site (1990 only)

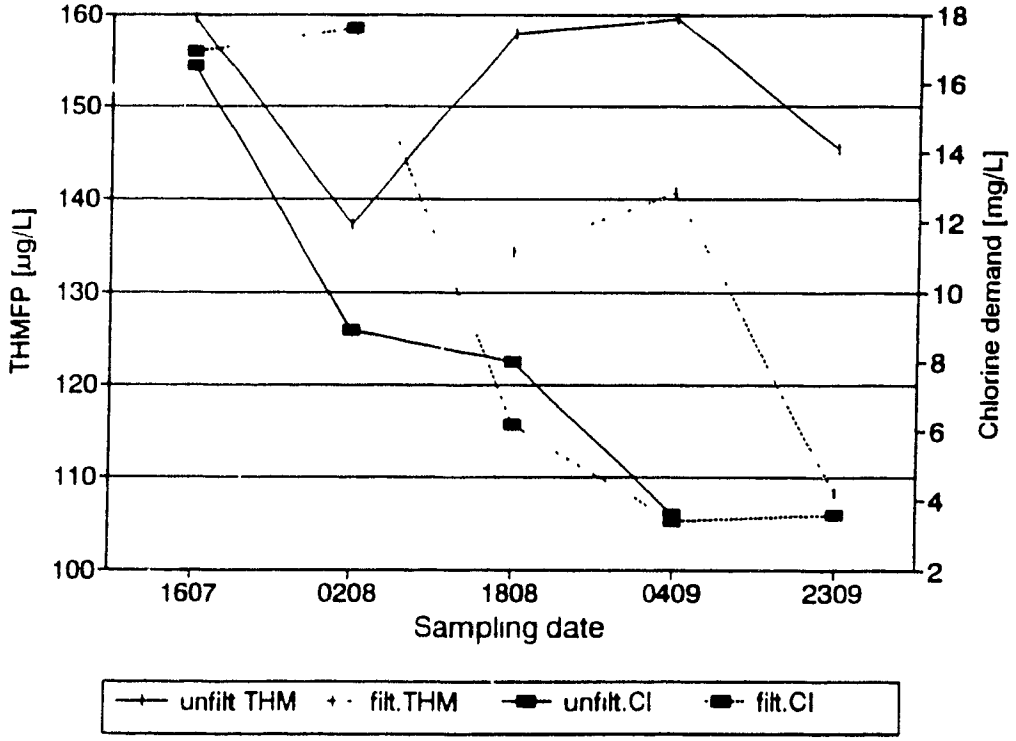

Figure 76 Seasonal variation of THMFP and chlorine demand at Central site (1990 only)

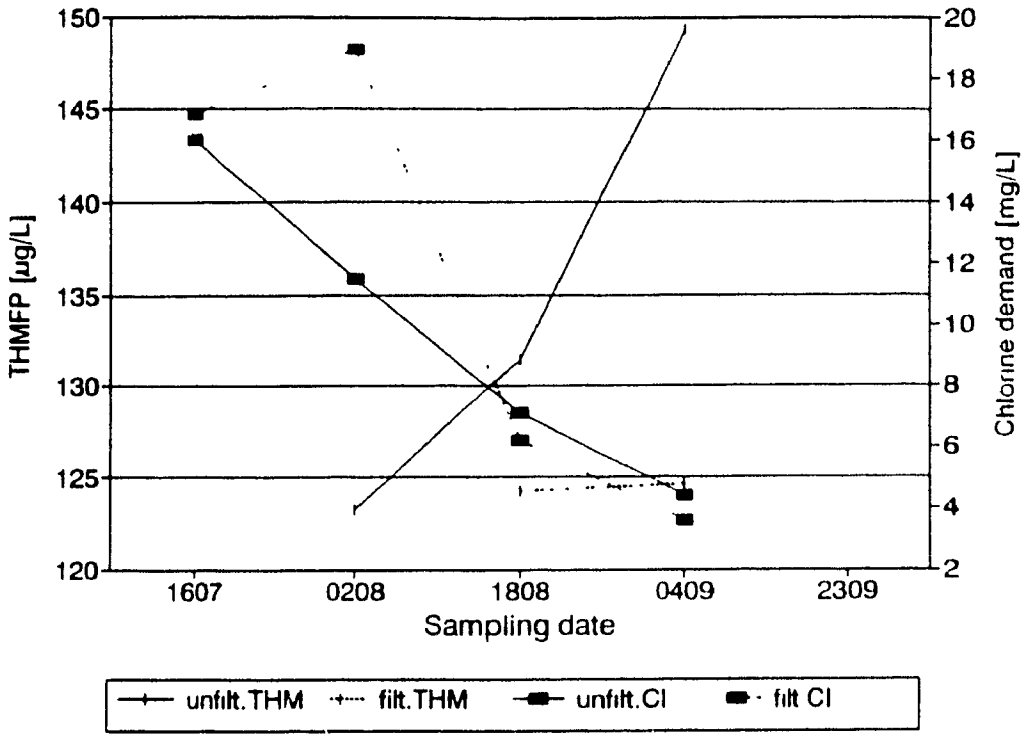

Figure 77. Seasonal variation of THMFP and chlorine demand at North site (1990 only)

APPENDIX L

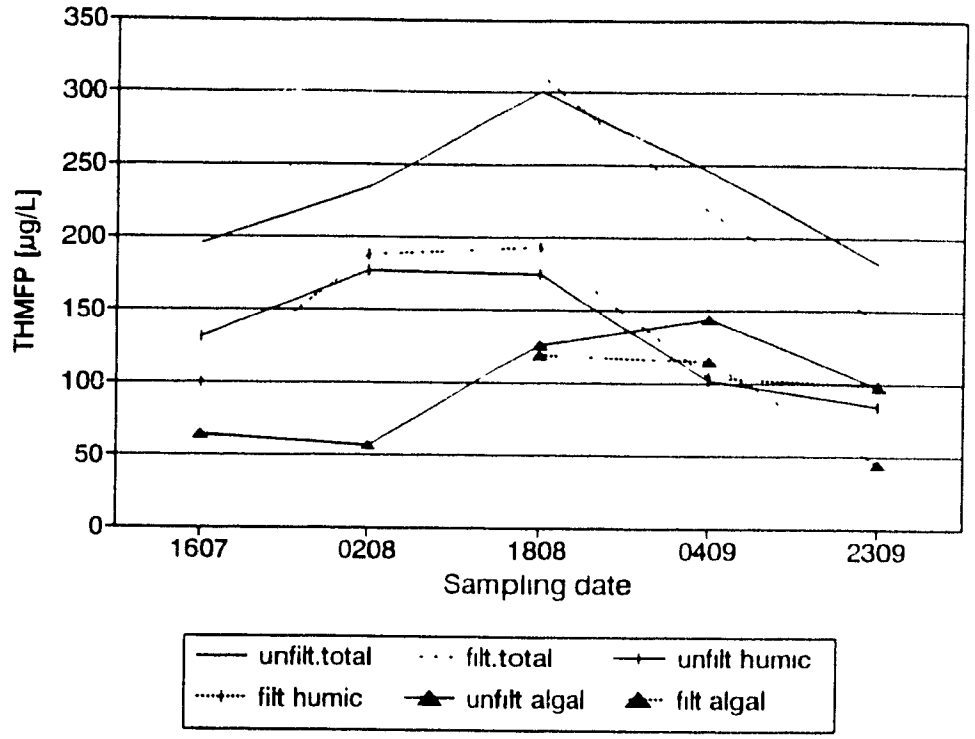

Figure 78. Predicted humic and algal components of THMFP at Pender (1990 only)

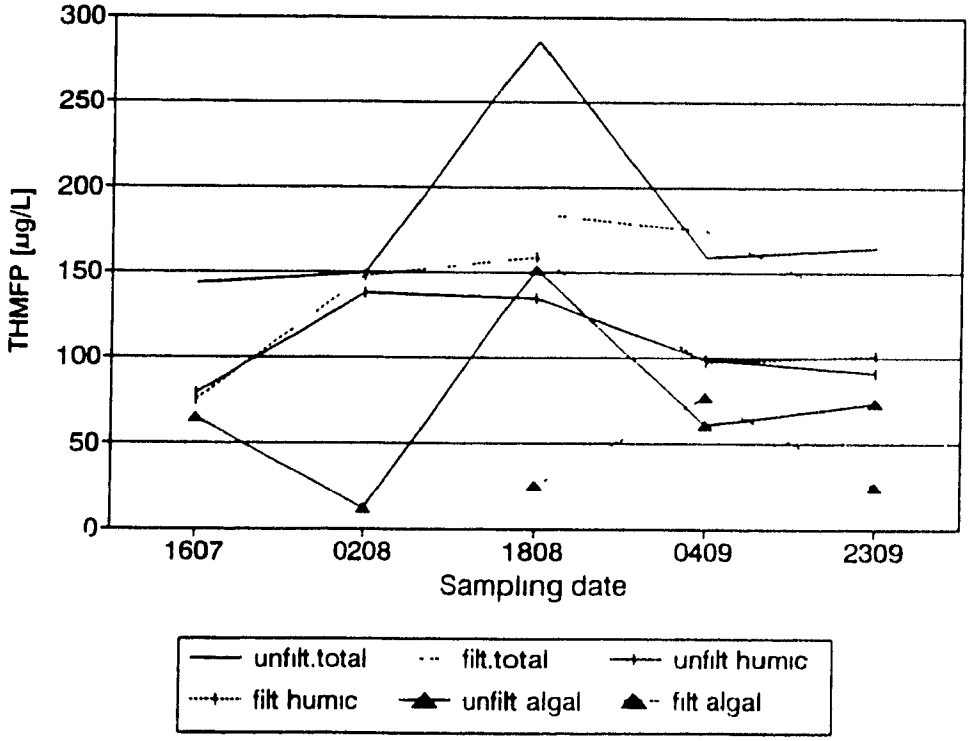

Figure 79. Predicted humic and algal components of THMFP at Indian (1990 only)

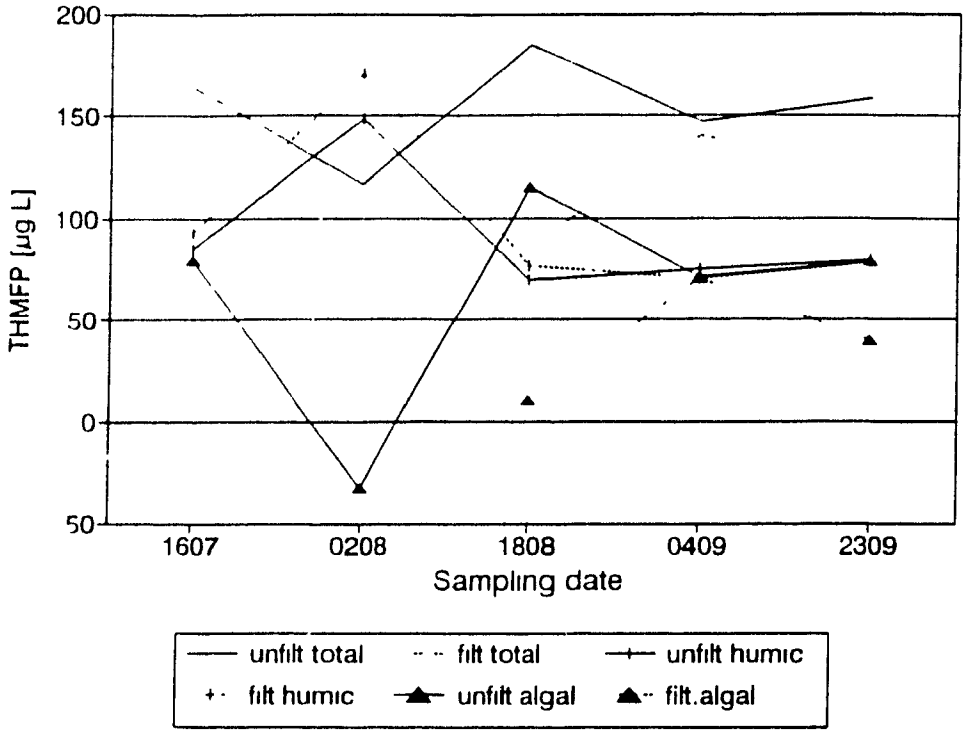

Figure 80. Predicted humic and algal components of THMFP at Border (1990 only)

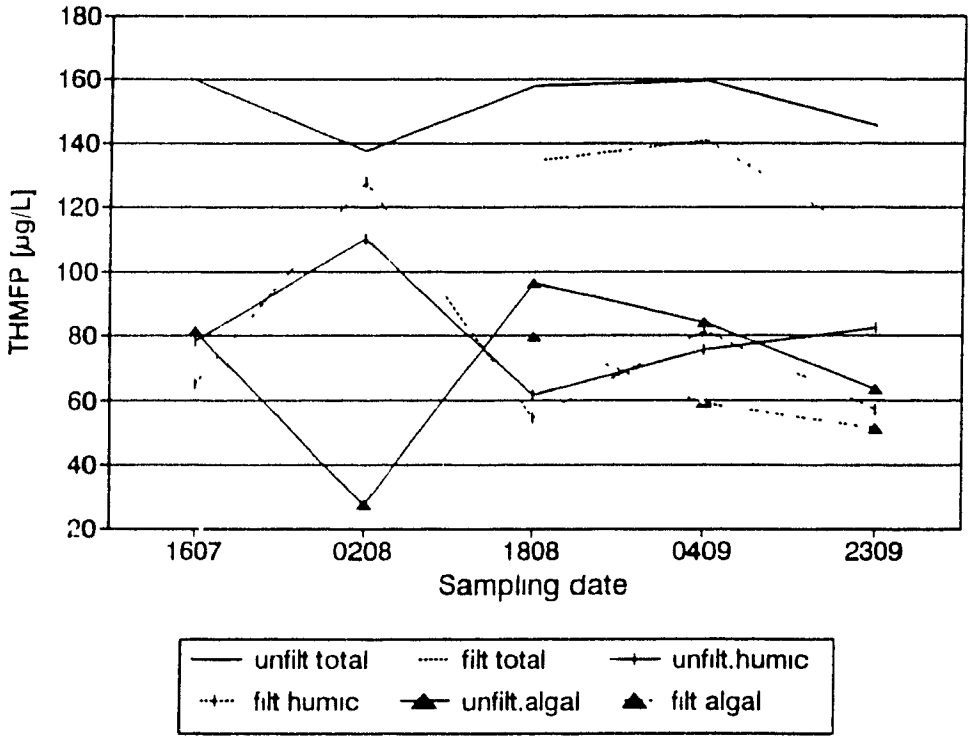

Figure 81. Predicted humic and algal components of THMFP at Central (1990 only)

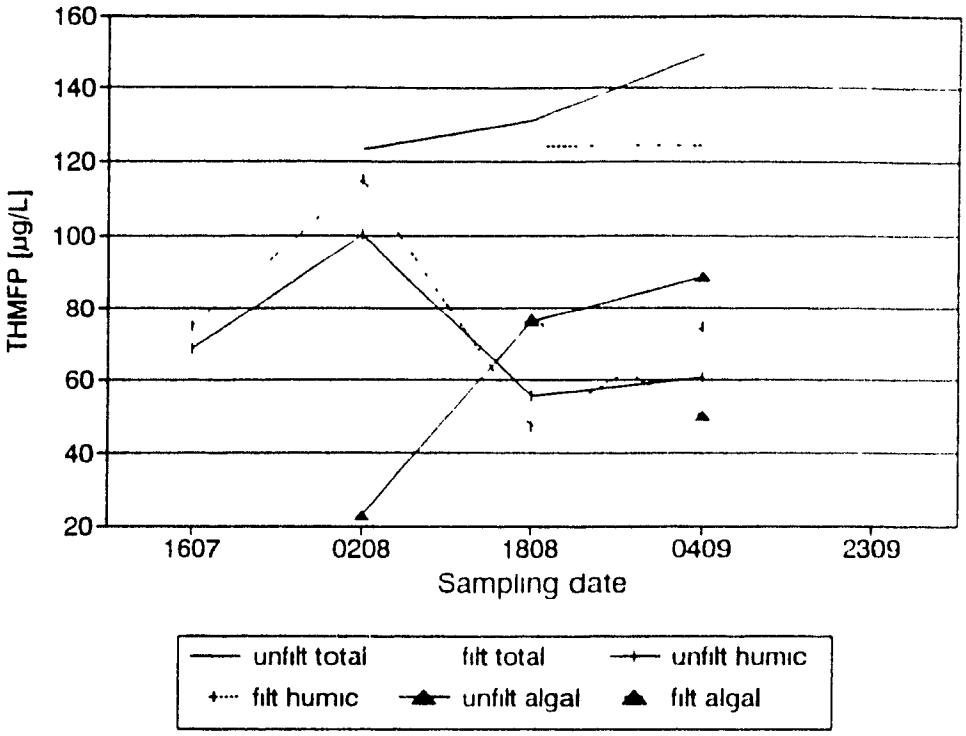

Figure 82. Predicted humic and algal components of THMFP at North (1990 only)

APPENDIX M

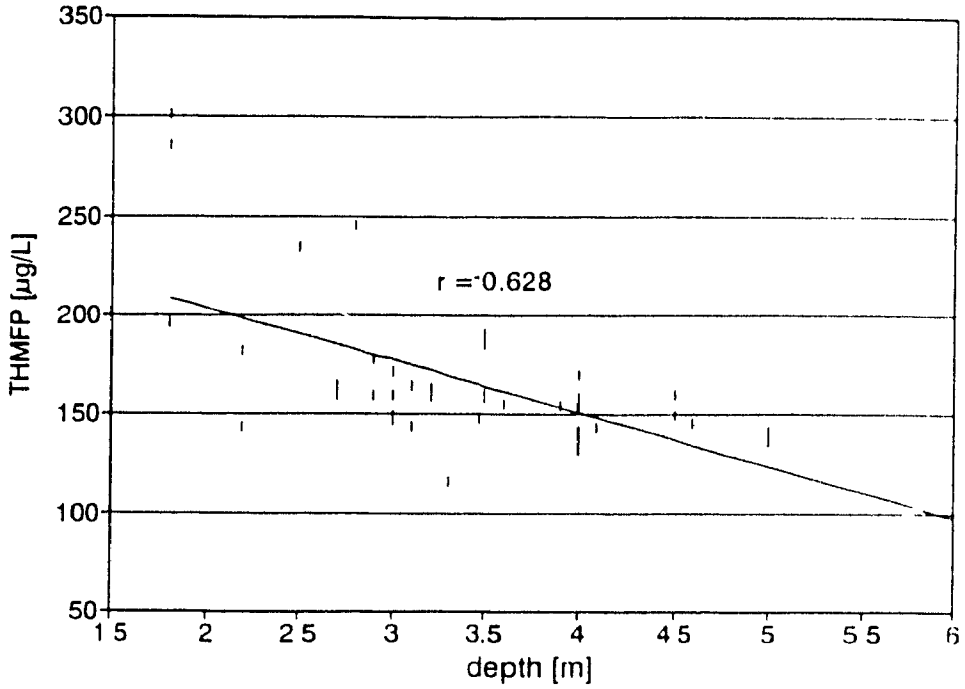

Figure 83. Correlation between unfiltered THMFP and secchi depth

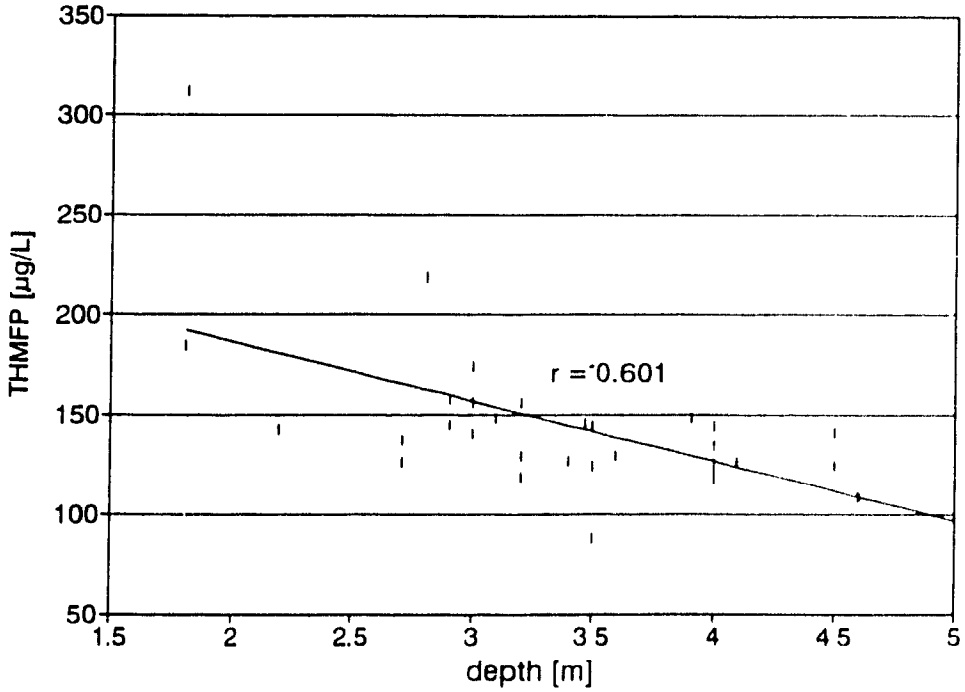

Figure 84. Correlation between filtered THMFP and secchi depth

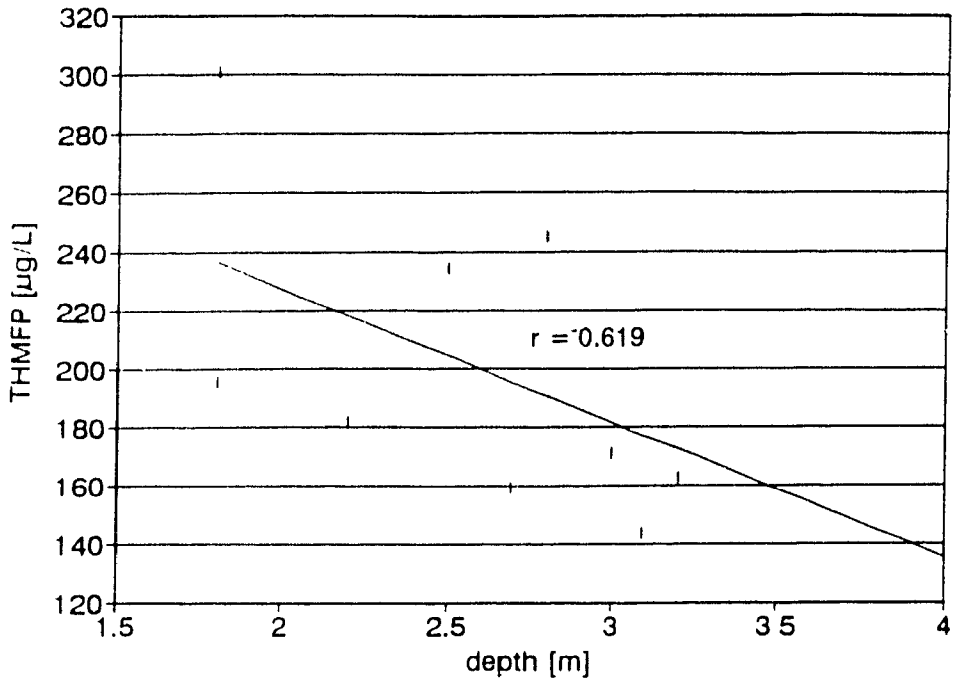

Figure 85. Correlation between unfiltered THMFP and secchi depth at Pender site

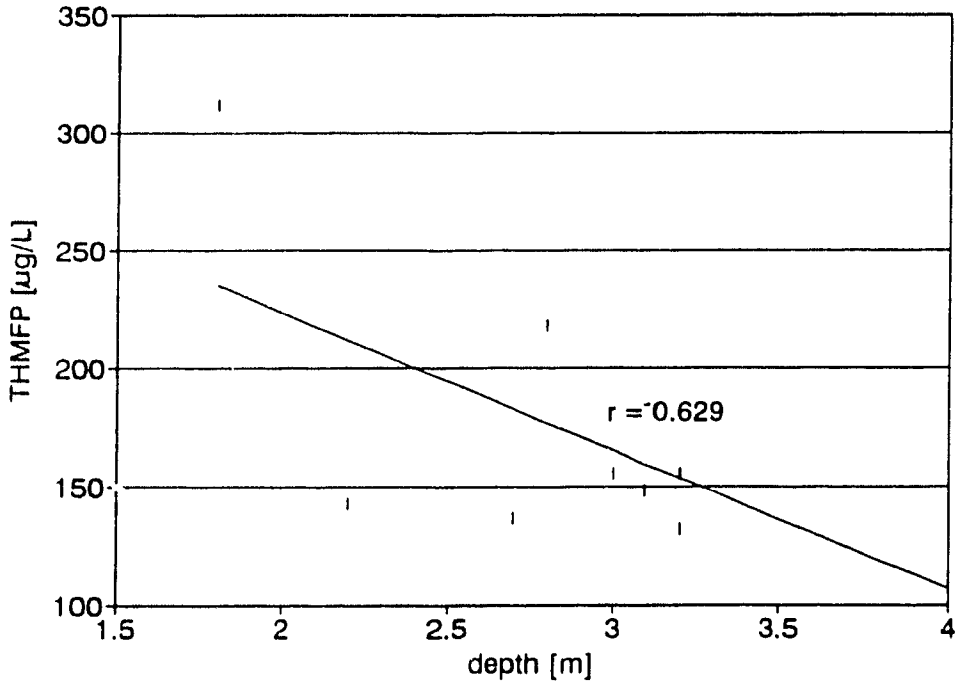

Figure 86. Correlation between filtered THMFP and secchi depth at Pender site

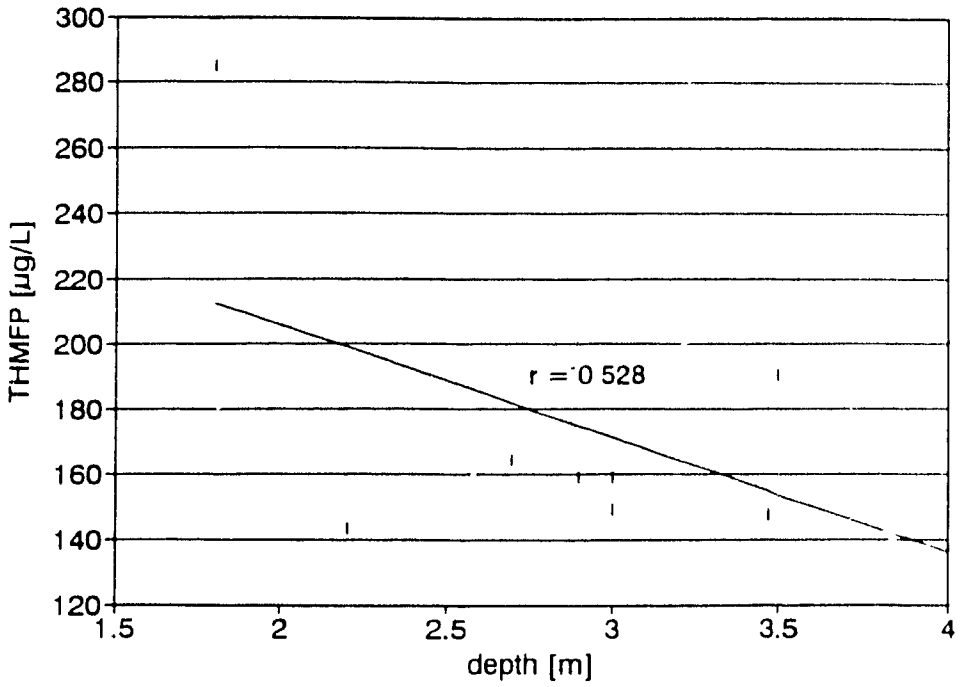

Figure 87. Correlation between unfiltered THMFP and secchi depth at Indian site

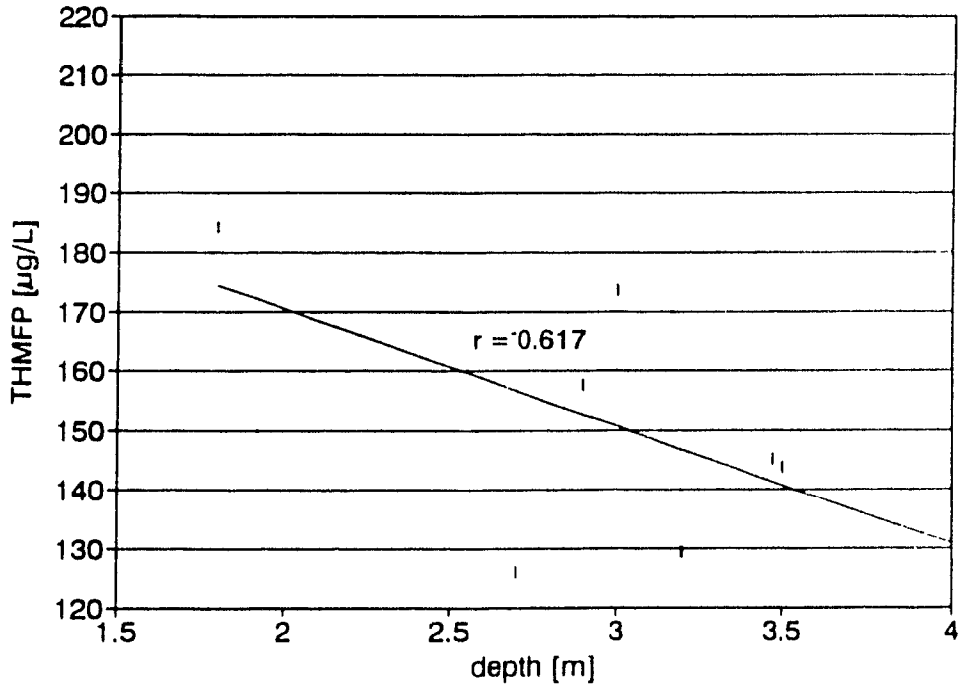

Figure 88. Correlation between filtered THMFP and secchi depth at Indian site

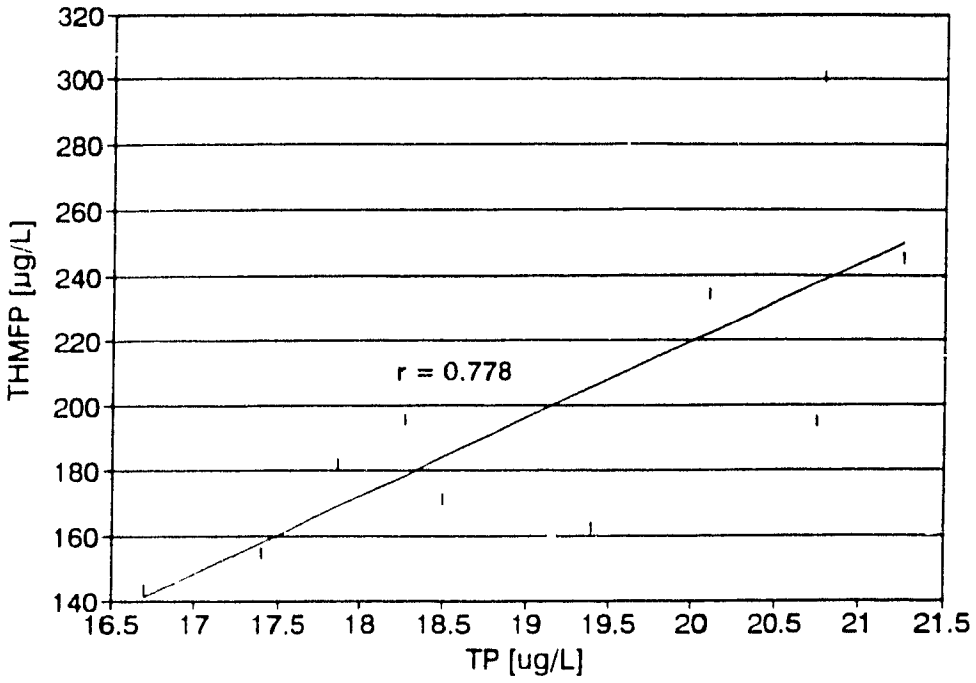

Figure 89. Correlation between unfiltered THMFP and TP at Pender site

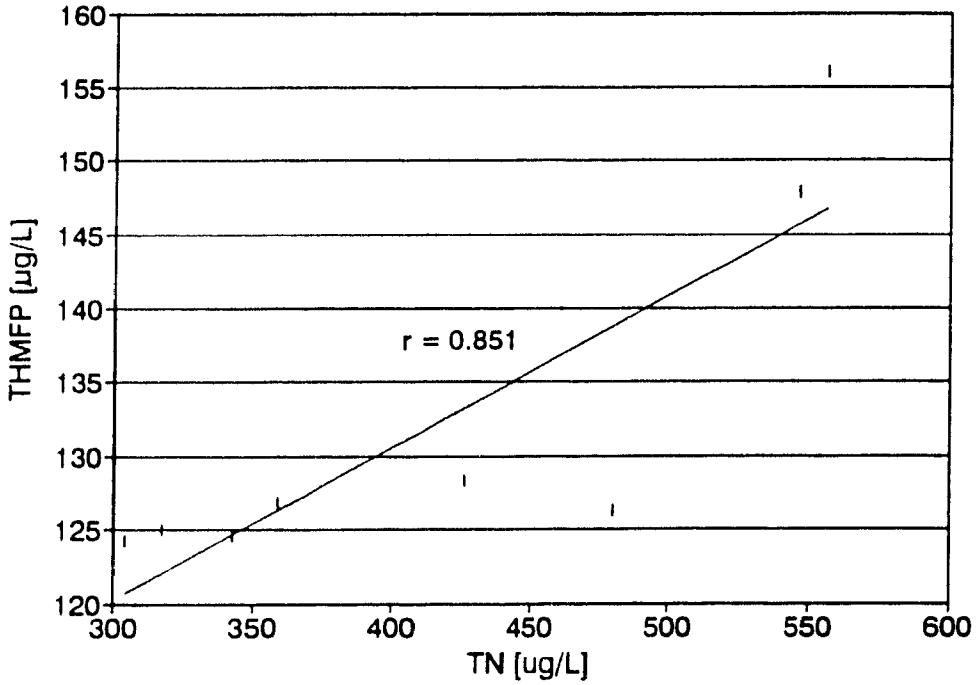

Figure 90. Correlation between filtered THMFP and TN at North site

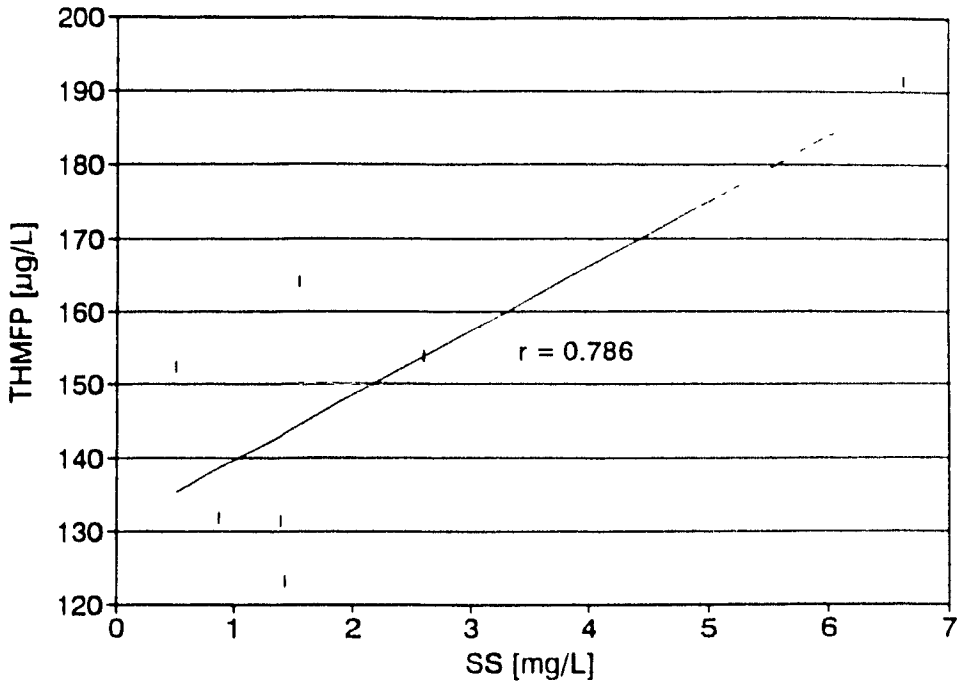

Figure 91. Correlation between unfiltered THMFP and Solids at North site

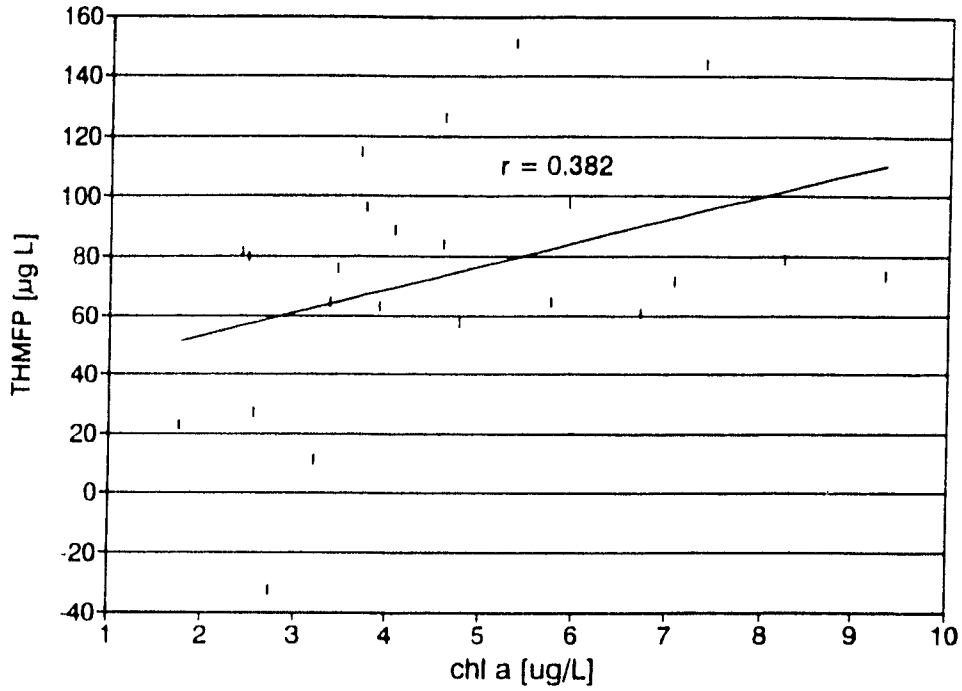

Figure 92. Correlation between predicted algal THMFP and chl a (unflitered 1990)

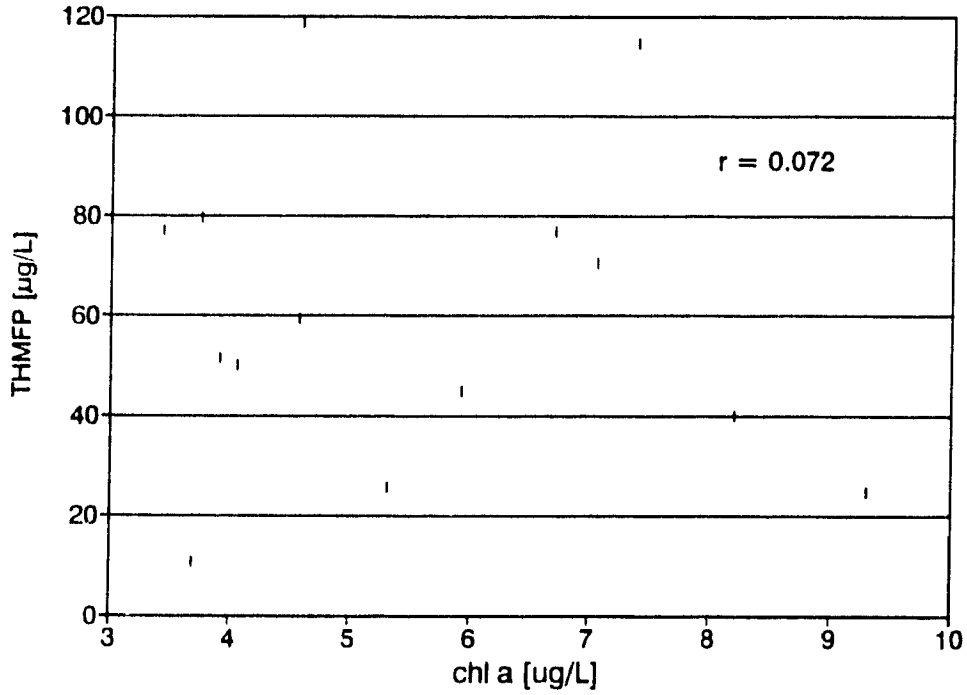

Figure 93. Correlation between predicted algal THMFP and chl a (filtered 1990)

APPENDIX N

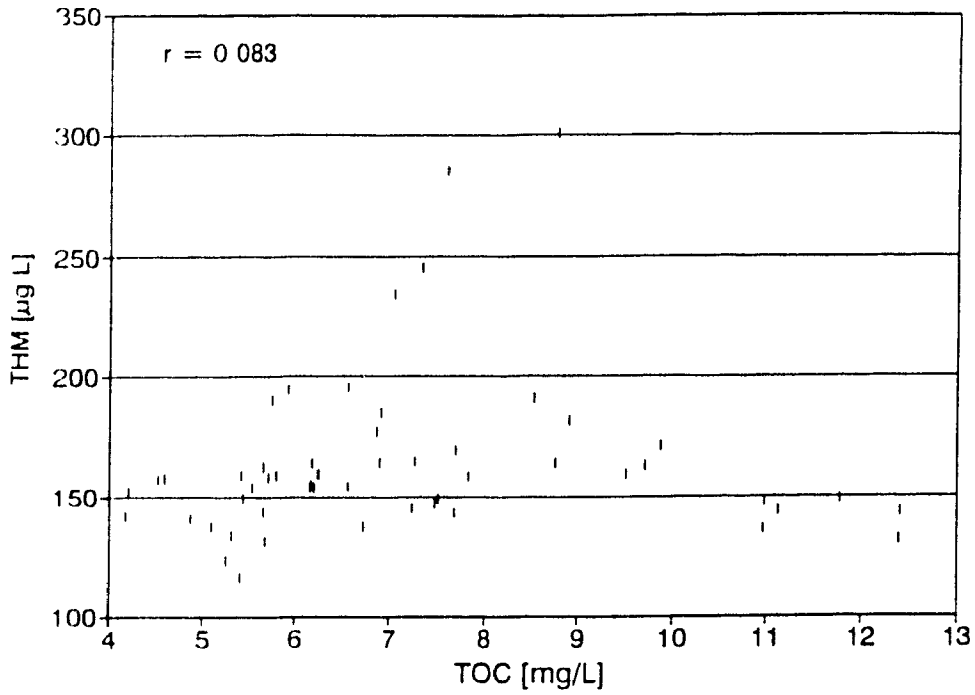

Figure 94. Unfiltered THMFP versus total organic carbon

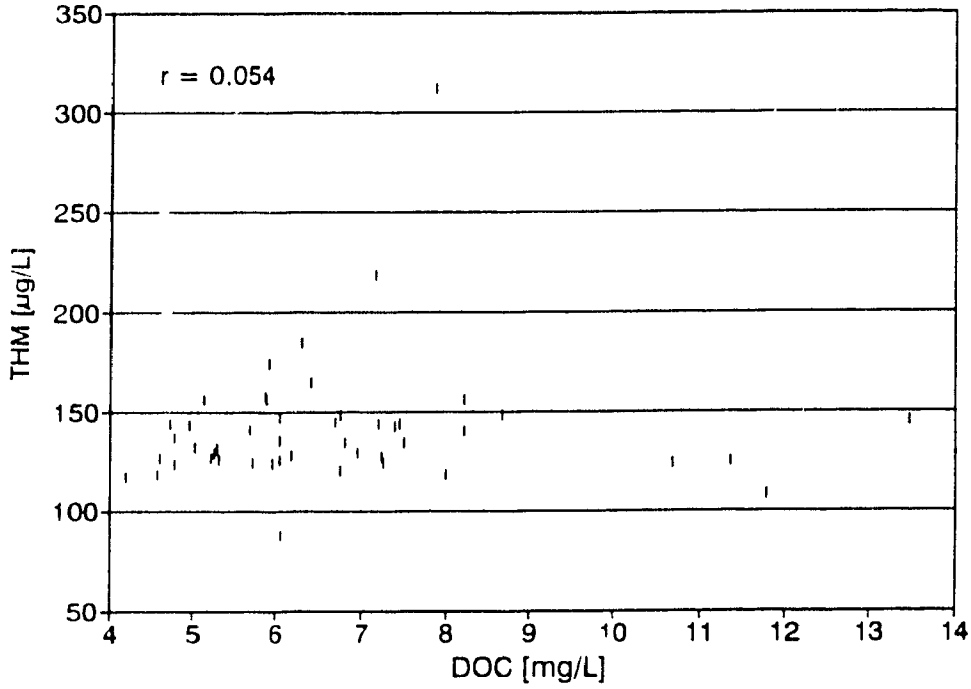

Figure 95. Filtered THMFP versus dissolved organic carbon

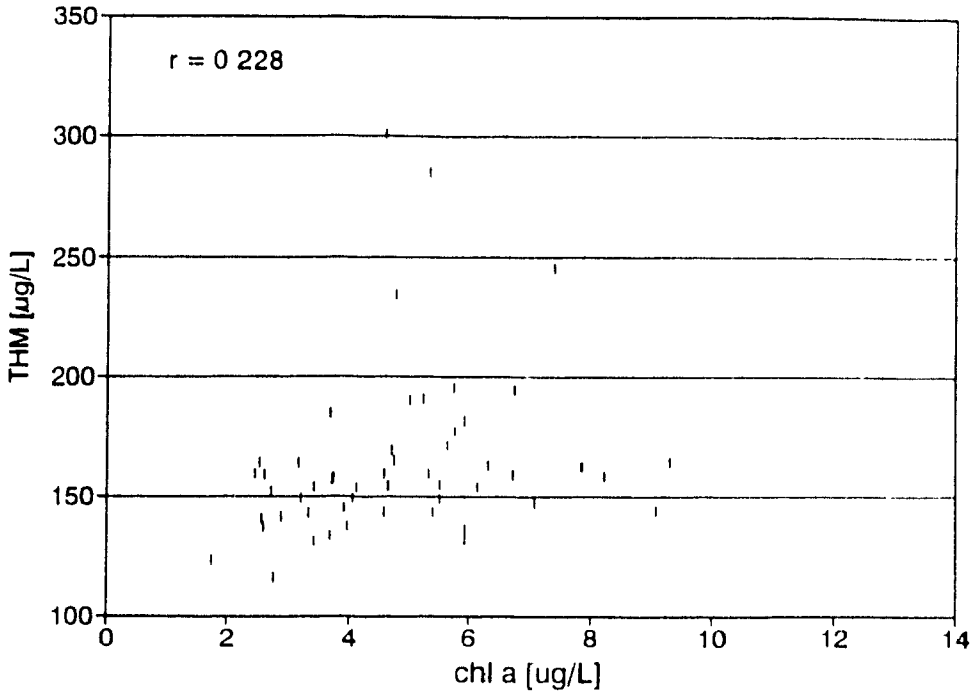

Figure 96. Unfiltered THMFP versus chlorophyll a

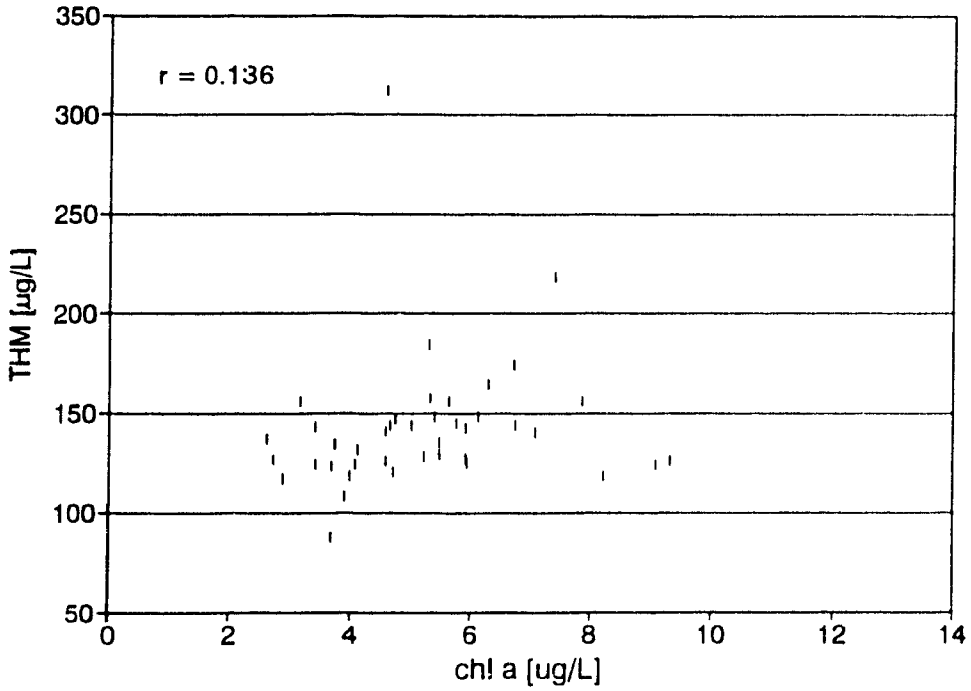

Figure 97. Filtered THMFP versus chlorophyll a

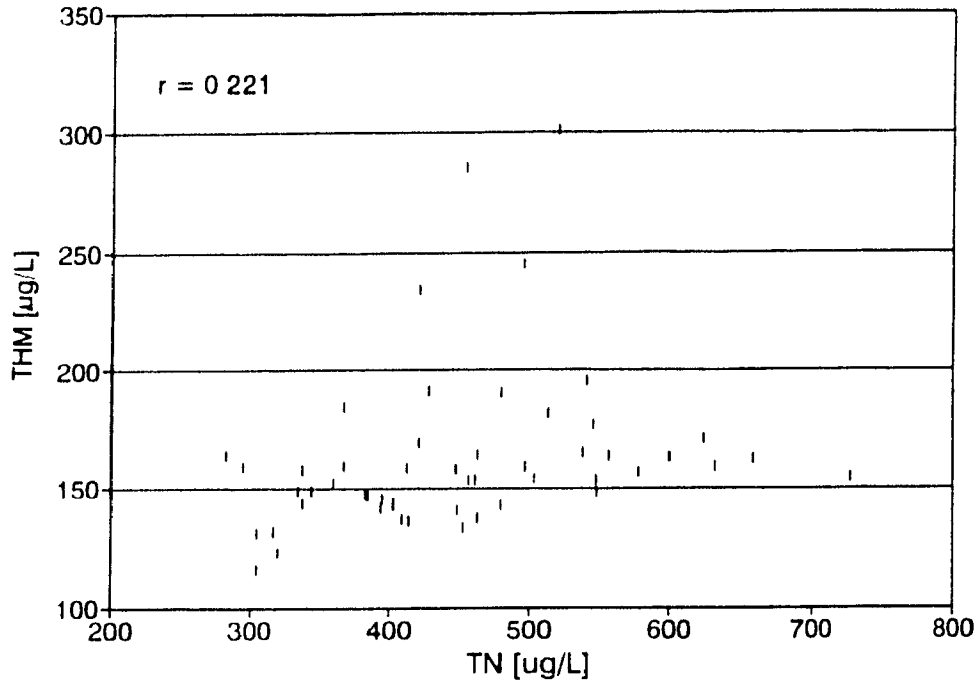

Figure 98. Unfiltered THMFP versus total nitrogen

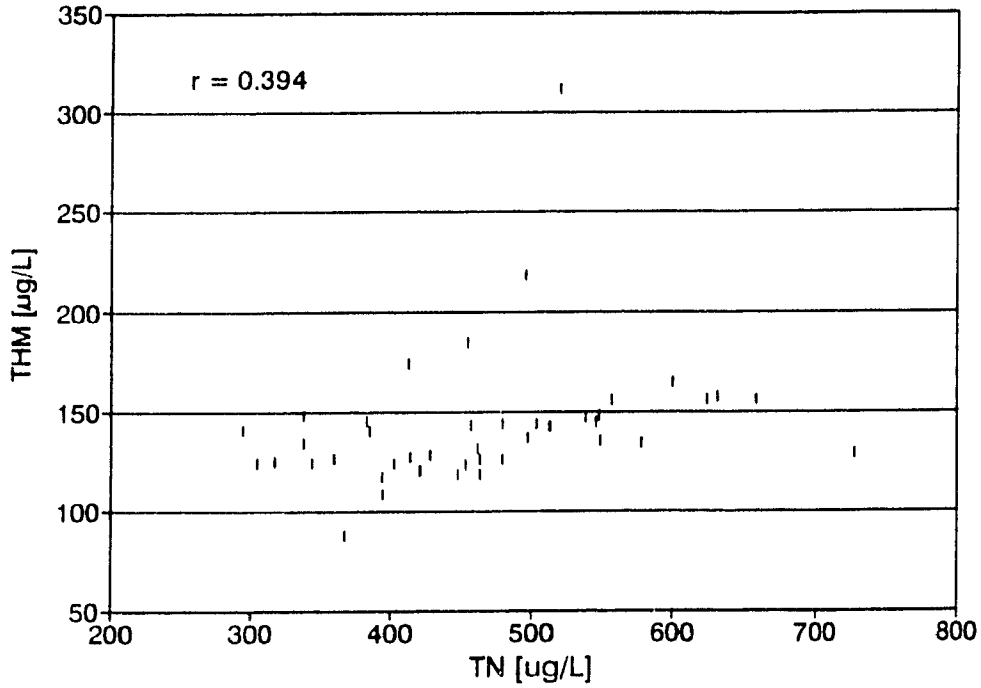

Figure 99. Filtered THMFP versus total nitrogen

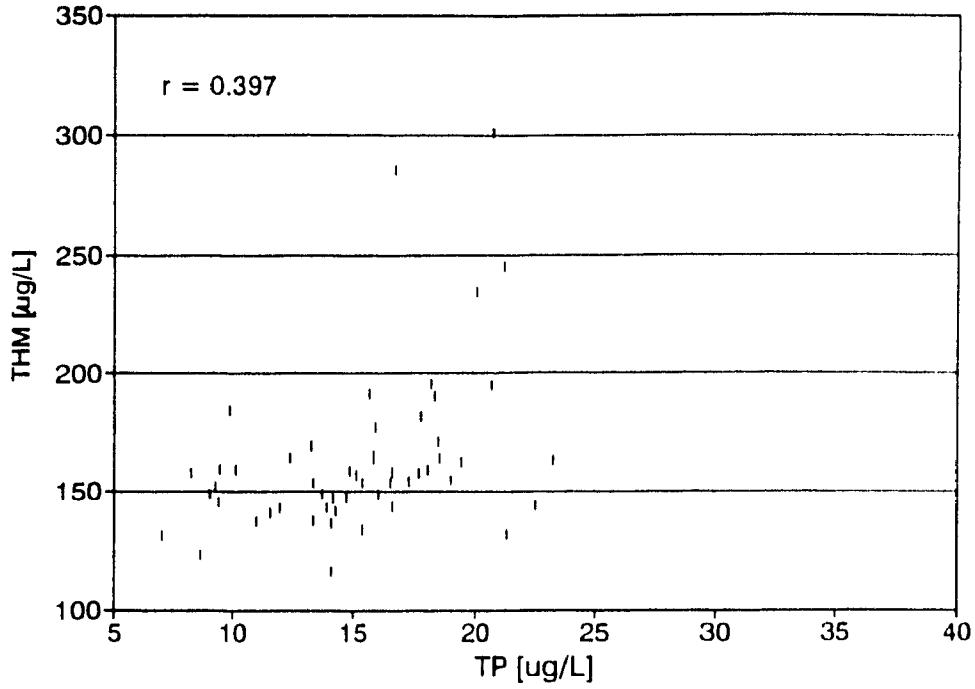

Figure 100. Unfiltered THMFP versus total phosphorous

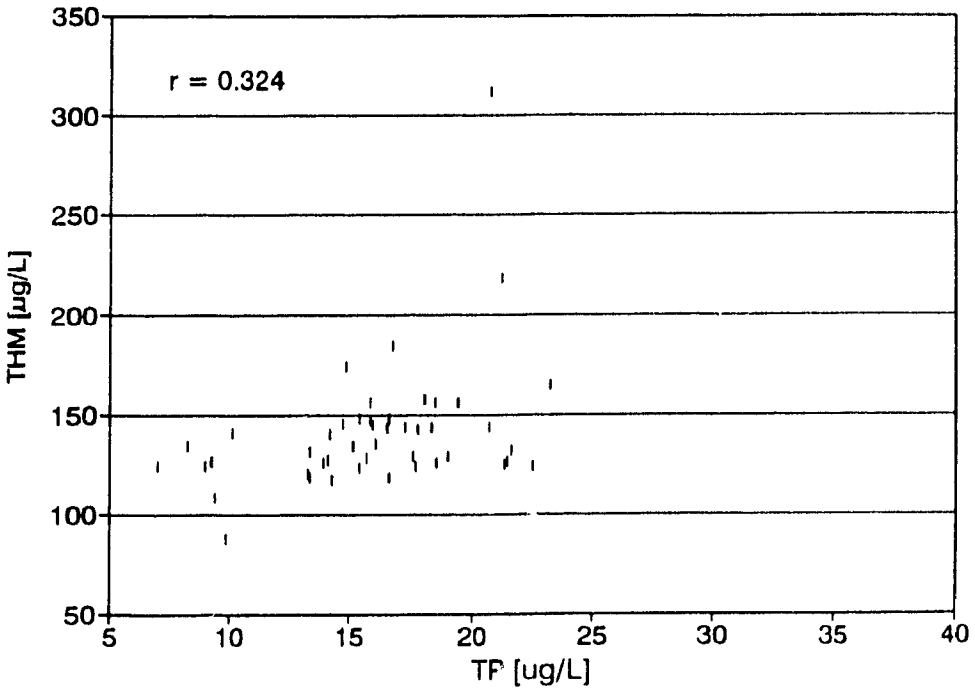

Figure 101. Filtered THMFP versus total phosphorous

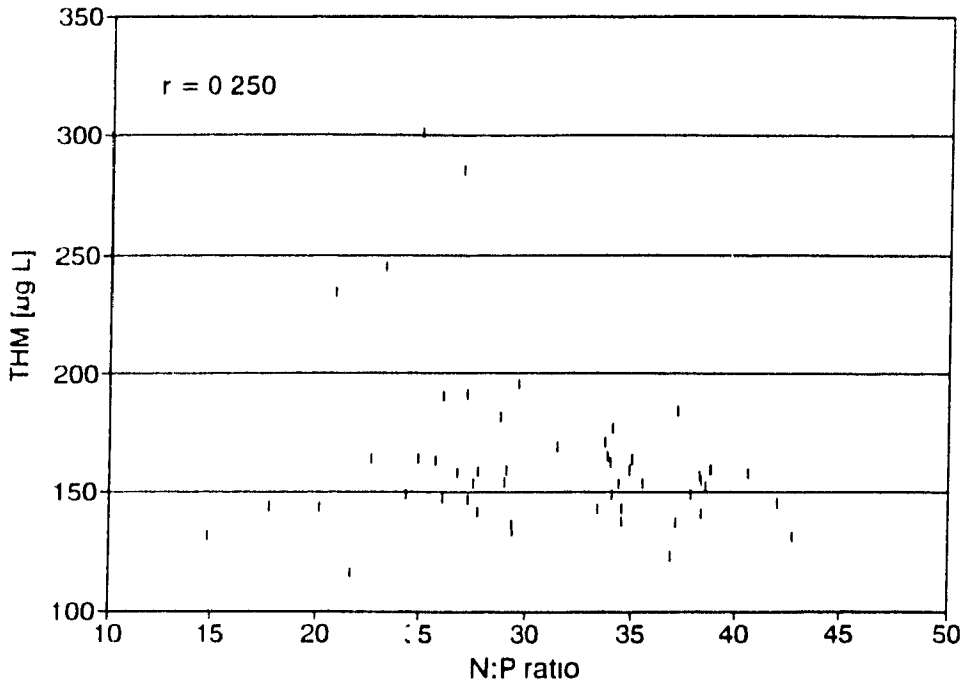

Figure 102. Unfiltered THMFP versus N:P ratio

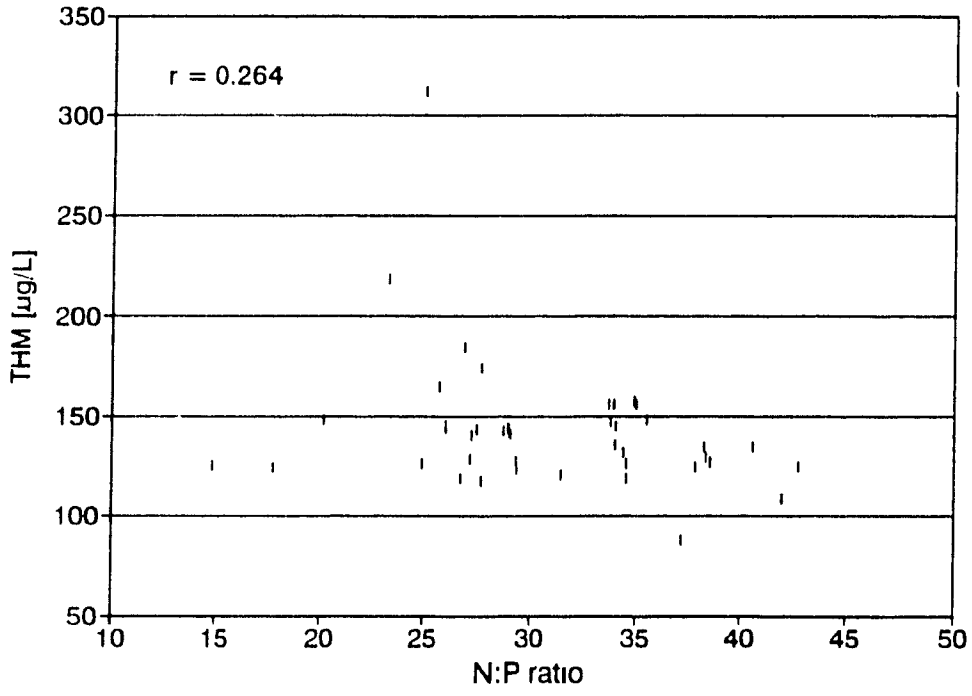

Figure 103. Filtered THMFP versus N:P ratio

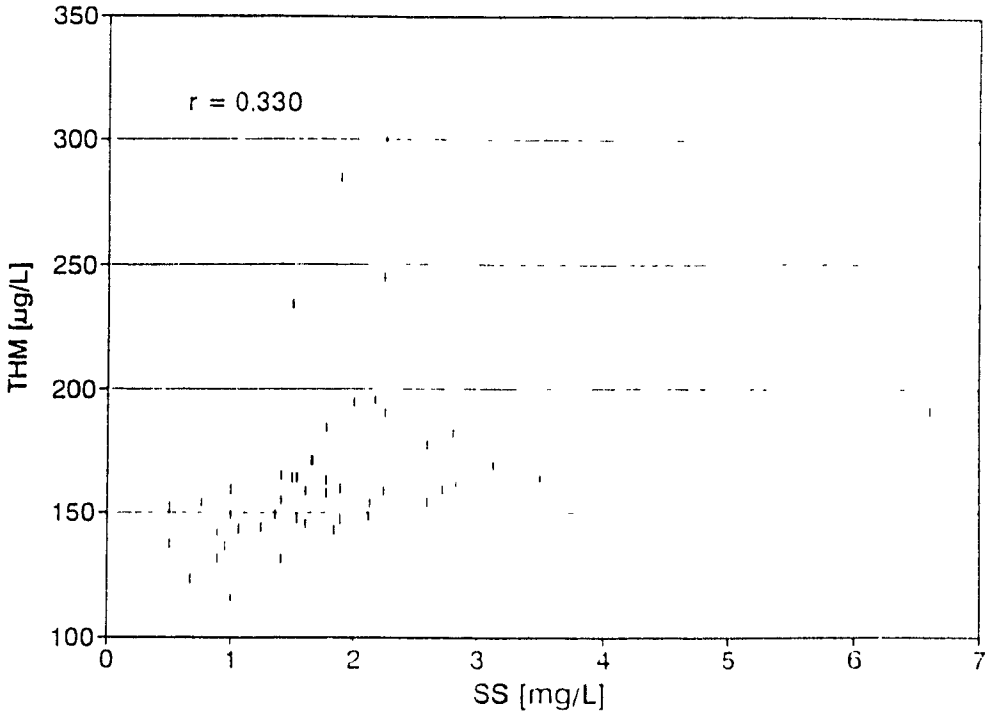

Figure 104. Unfiltered THMFP versus suspended solids

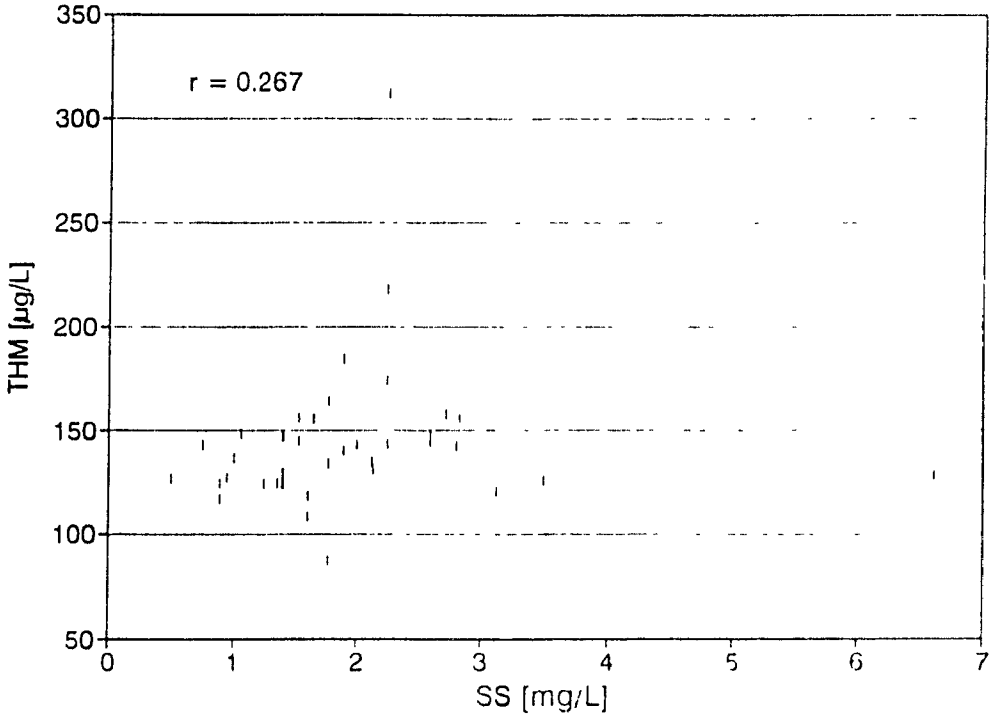

Figure 105. Filtered THMFP versus suspended solids

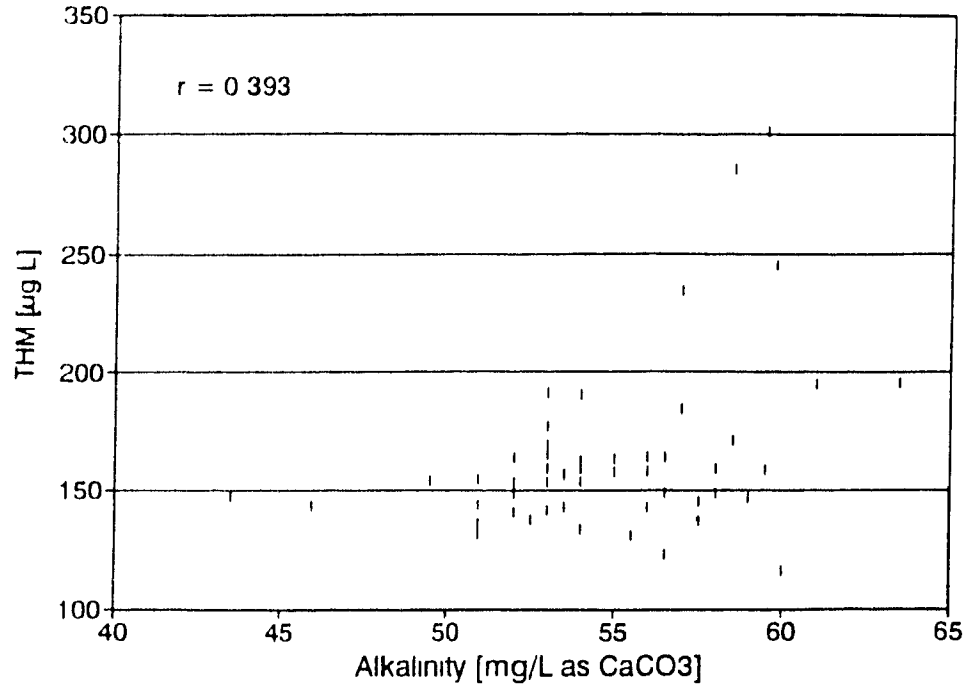

Figure 106. Unfiltered THMFP versus alkalinity

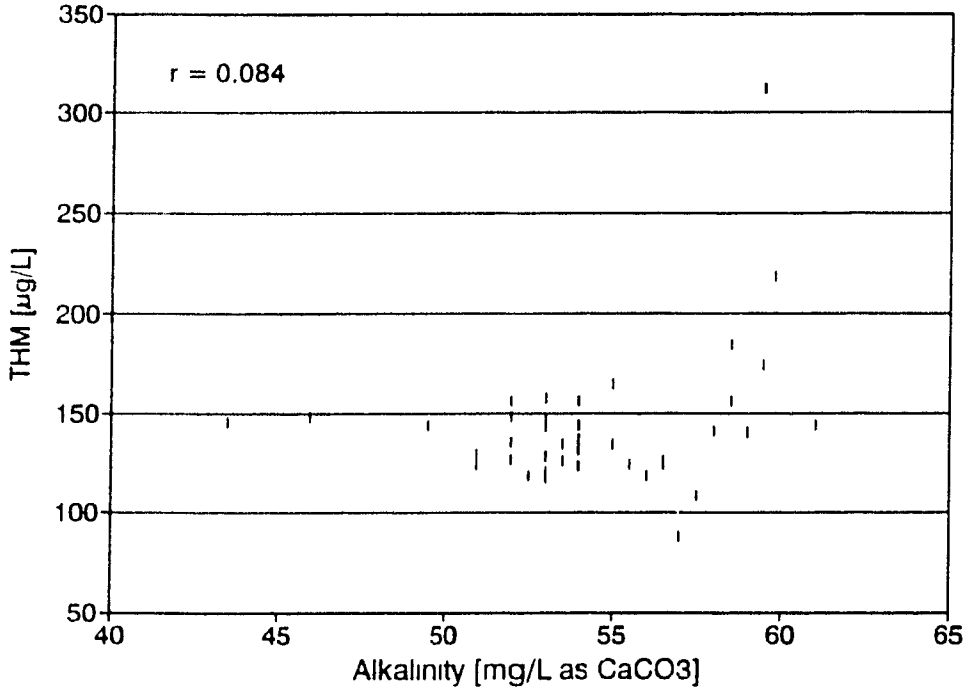

Figure 107. Filtered THMFP versus alkalinity

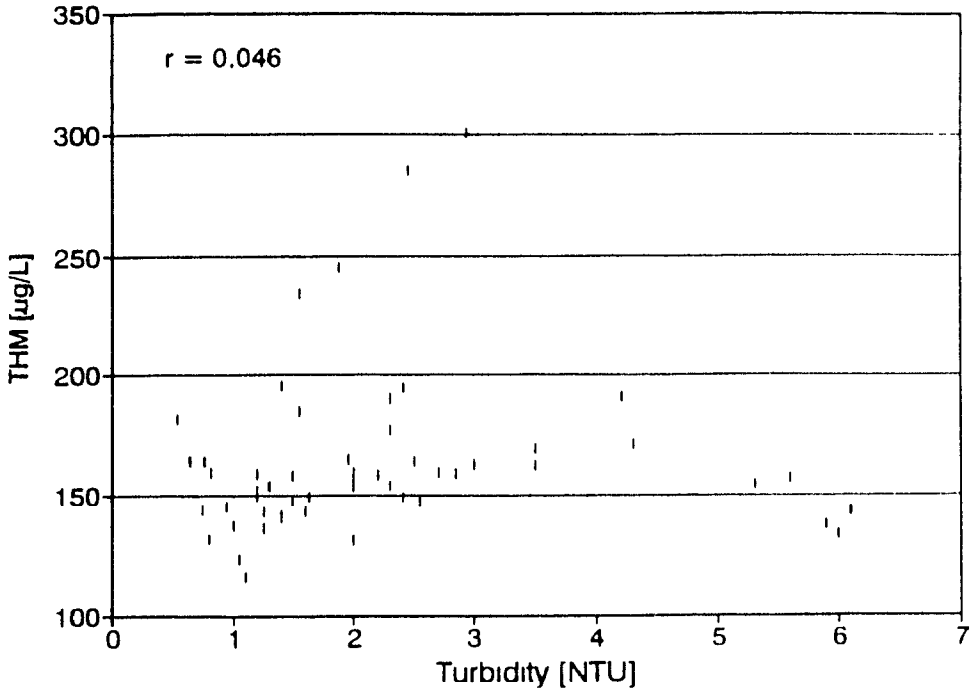

Figure 108. Unfiltered THMFP versus turbidity

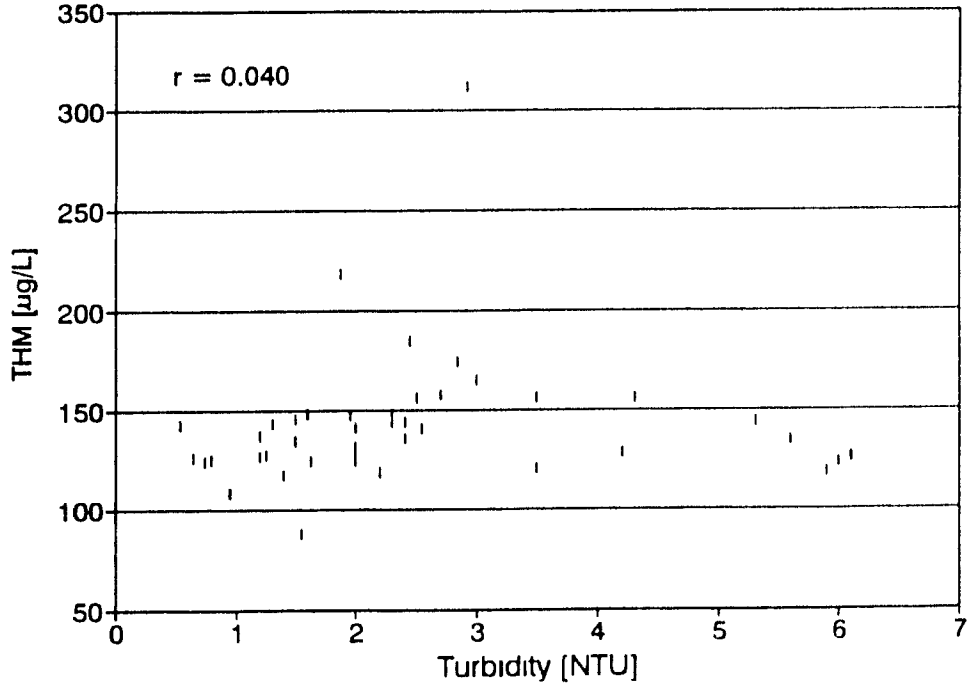

Figure 109. Filtered THMFP versus turbidity