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The Study of Extractable and Soluble Phosphorus on an Agricultural Watershed in Quebec

by Ali A. Nur

A thesis submitted to the Faculty of Graduate

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of the requirement for the degree of

Master of Science

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ABSTRACT

The purpose of this study was to determine how much phosphorus could be lost from soils in Quebec. Samples of four soil series and 3 sediment samples from the St. Esprit watershed, Quebec, Canada were treated with KH₂PO₄ solutions of 0, 50,100, and 500 mg kg¹ of soil. The relationship between water - extractable phosphorus (soluble phosphorus) and Mehlich III available phosphorus was determined at water: soil ratios 100:1, 200:1, 500:1. Measurements were made on a LACHAT Quick Chem AE instrument (based on EPA method 365.3; USEPA, 1983) after 4 hours of shaking. More than 90% of the soluble phosphorus was released after 3 hours of shaking for all the soil samples and the sediment sample. Therefore, the shaking time for release of soluble P was set at 4 hours for all soil groups of the watershed. Mehlich III extractable phosphorus was also determined for each soil and sediment sample. Using a modified form of a well-known equation, it was possible to show that, with appropriate values for the constants, linear relationships exist between the logarithm of soluble phosphorus and the logarithm of Mehlich III extractable phosphorus at different water: soil ratios. This was true for all soil groups and the sediment sample. Thus, given the soil type of a particular watershed, and using the linear relationship (isotherm) for that type, it becomes possible to predict the phosphorus yields from agricultural lands with reasonable confidence.

I

Résumé

Cette étude visait à déterminer la guantité de phosphore pouvant être perdue de certains sols au Quèbec. Des échantillons de quatre séries de sols et d'un échantillon de sédiment provenant du bassin versant St. Esprit, Québec, Canada, furent traités avec des solutions de KH₂PO₄ de 0, 50, 100, et 500 mg kg⁻¹ sol. Le rapport entre le phosphore extractable à l'eau (phosphore soluble) et le phosphore disponible Mehlich III fut déterminé a des rapports eau:sol de 100:1, 200:1, et 500:1. Ces quantités furent mesurées sur un instrument LACHAT Quick Chem AE (selon la méthode de l'EPA 365.3; USEPA, 1983), après 4 heures d'agitation. Pour tous les échantillons de sol et de sédiment, plus de 90% du phosphore soluble fut libéré après 3 heures d'agitation. La durée de l'agitation pour la libération du phosphore soluble fut fixée à 4 heures pour les sols du bassin versant. De même, le phosphore extractable Mehlich III fut déterminé pour tous les échantillons de sol et de sédiments. Pour tous les séries de sols ainsi que pour les sédiments, une relation plus ou moins linéaire exista entre le logarithme du phosphore soluble et le logarithme du phosphore extractable Mehlich III a différents rapports sol:eau. Pour tous les séries de sols ainsi que pour les sédiments, les équations de ces isothermes furent donc utilisées pour relier mathématiquement le rapport sol:eau et le phosphore extractable ou phosphore disponible Mehlich III. Avec de bonnes mesures du phosphore total Mehlich III, et les isothermes de désorbtion du phosphore pour les soils d'un bassin versant en particulier, il est possible de prédire le niveau de phosphore provenant des terres agricoles.

II

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List of Symbols and Abbreviations Used

α,β,γ,	constants related to soil type
δ,	Exponent of Mehlich III phosphorus in the desorbed phosphorus
	equation
λ	Exponent of water: soil ratio in the desorbed phosphorus isotherm
Р	Phosphorus
BP	extractable phosphorus Bray P1 mg P/ kg soil
BP1	Bray P1 available phosphorus of the soil surface, μg /g of soil
F	a conversion factor
EP	initial amount of extractable P present in the soil
k 1	Intercept in the desorbed phosphorus equation
PE	mass flow rate of sediment-bound phosphorus transported from the
	surface, kg/sec
PER	sediment-bound phosphorus enrichment ratio
٩ _s	Desorbed soluble phosphorus in an element, µg /g of soil
SED	mass flow rate of sediment, transported kg/sec
TOTAL P	total phosphorus of the surface soil of the element, μg /g of soil
WEP	amount of desorbed, P mg P/ kg (ie.NaHCO ₃ -extractable P mg P/ kg
	soil)
t	shaking time
W:S	Water:soil ratios

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1.0 INTRODUCTION

In agriculture, chemical and organic P fertilizers are added to the soil to increase production. Unfortunately, in spite of the obvious success of these methods the natural processes of overland flow and runoff from these treated soils transport significant amounts of P, leading to pollution of surface waters Sharpley and Halvorson (1994). Angle (1986) stated that one-half of all water pollution is traceable to nonpoint sources, and that agriculture is one of the most pervasive and important source.

Searing and Shirmohammadi (1993) reported that 67% of the nitrogen and 39% of the P pollution that reaches Chesapeake Bay is contributed by NPS. In recent years, increasing attention has been paid to the problem of P enrichment of surface waters. Algae and aquatic weeds require a number of elements for their normal growth, amongst which is P. Under normal conditions, the amount of nutrients entering into lakes is sufficient for algae needs, except for P, whose concentration is generally low, to the point of being a limiting factor to expansive growth (Kotak et al., 1993). For these reasons, high levels of P are considered to be a determining condition in the development of eutrophication. A major objective of pollution control is to protect water quality from the adverse effects of agricultural activity. Clearly, any program that attempts to deal with surface water pollution must find ways of limiting NPS pollution in runoff (Mannion, 1995).

The present research was undertaken as part of a larger project under the Canada-Quebec Green Plan to examine the effects of agricultural production on

environmental pollution at the St. Esprit basin, to develop strategies for pollution control (Enright et al., 1995). McGill University was the scientific partner in the project. Several research teams from the Department of Agricultural and Biosystems Engineering (Enright et al., 1995; Lapp, 1996; Enright et al., 1997; Perrone et al., 1997; Papineau and Enright, 1997; and Enright et al., 1998) and the Department of Agricultural Economics (Dissart, 1998) were involved in the project. Four tasks were assigned to McGill University, namely:

- Define and characterize the environmental problems related to agriculture activities on the watershed, and based on the initial findings, suggest remedial actions;
- 2. Monitor discharge and water quality at the outlet of the two watersheds and analyze the data as a function of the agricultural activities;
- Develop a methodology and associated tools for targeting conservation activities and assessing the potential impacts of conservation practices;
- 4. Assess the economic impacts of the soil and water conservation projects implemented at the farm and watershed scales.

Although not directly a part of the project, the work in this thesis can be considered the first task above.

1.1 Objectives

The objectives of this research were to:

- 1. Use the Mehlich III method to determine how much P is removed from each soil and sediment under simulated runoff conditions.
- 2. Determine the relationship between soluble P and available P at different water: soil ratios.
- Determine the relationship between water extractable P and total available
 P as measured using Mehlich III.

1.2 Scope

The scope of this study is to examine the extractable P and available P from agricultural lands in the St Esprit basin, and to observe the rate of release of soil P after various shaking times. It also seeks to quantify the degree to which various soils are likely to lose P to surface waters. Observations were made on samples taken 50mm from the soil surface from different areas on the watershed. The samples were collected during May 1998. The results of this study were used to develop a functional relationship between the water- extractable phosphorus (WEP) and Mehlich III P at different water : soil ratios.

2.0 LITERATURE REVIEW

In areas of intensive agricultural production, continuing inputs of phosphorus (P) from commercial fertilizers and manures to the landscape often exceed the natural depletion of P by assimilation in crops and animal products (Sims, 1997). Studies have shown that the number of soils with plant-available or soil test P exceeding levels required for optimum crop yields have increased greatly in recent years (Alley, 1991; Sims, 1992, Simard et al., 1992). This excess of P in agricultural soil, when carried off by overland flow or runoff, is an important contribution to surface water pollution, frequently leading to eutrophication of fresh water receiving bodies. In extreme cases, these activities can lead to losses in production, economic losses and losses of livestock. Kotak et al. (1993) suggested that algal toxins can kill cattle and other animals after they consume contaminated water. These toxins also pose a health hazard to humans. Largely due to the easy identification and the successful control of point source inputs of P, less attention has been given to management strategies aimed at minimizing NPS- P losses. These losses now account for a larger share of the nation's water quality problems than was the case a decade ago (Crowder and Young, 1988). The emphasis is now changing due to recent recognition of the direct human and animal health risks associated with eutrophication.

Clearly, the development of effective management of P is of great concern to both agronomists and environmentalists. The contribution of agriculture to NPS pollution in the USA has been estimated at 64% of total suspended sediment and

76% of total phosphorus (Duda and Johnson, 1985). The United States Environmental Protection Agency (USEPA,1990), similarly noted that routine agricultural activities were responsible for more than 60% of surface water contamination.

The amount of P lost to the landscape depends on such management factors as the timing and method of applying fertilizer, tilling systems, and climatic factors such as the distribution and intensity of rainfalls. For example, judicious use of fertilizer can reduce erosion and runoff potential by increasing vegetative cover (Simard et, al., 1992). Not the least of the difficulties of designing good management practices is the incomplete understanding of the nature of release of P from soils to surface runoff waters (Young, 1989).

2.1 Global Phosphorus

It has been estimated that there is $19,705 \times 10^6$ Mg (as P) of world phosphate reserve and $87,810 \times 10^6$ Mg (as P) of world phosphate resources (Cathacart, 1980) Although these estimates may vary somewhat, with world consumption of P fertilize at 12×10^6 Mg P/yr the resources will be eventually exhausted (FAO, 1979) However, It is well known that the P in fertilizer is inefficiently used, and that in general, crops take up only 10 -15 % of added fertilizer P (Tisdale et al., 1993), while the remainder accumulates in the soil increasing the potential for P in runoff. Consequently long - term land application of P fertilizer and animal wastes has resulted in elevated levels of soil P in many locations in the United States and Canada (Edwards and Daniel, 1992; McFarland and Hauck, 1995; Sharpley et al., 1996b; Sims, 1997), and has greatly increased the potential for P loss in runoff.

Since much of the P that enters ecosystems is exported from agricultural watersheds, the management of activities within these watersheds must be directed at minimizing P export. Increasing chemical utilization under intensive agricultural production has been recognized as a serious contributor to the degradation of water resources in Canada and the United States (Castle, 1993).

Many factors play a role in P export in water, including hydrology, natural land form, geology, soils, and land use (Dillon and Kirchner, 1975; Omernik, 1977; Clesceri et al., 1986). Additional factors are industrial activity, population, and technologies used to manage waste flows and land use. P exports from watersheds can vary widely over individual storm events (Verhoff et al., 1982, Meals 1996), over annual cycles, and over longer periods.

During runoff events, P is transferred from watershed areas in many ways. Methods of pollution control call for an understanding of the processes affecting P transport in watersheds and basins.

The International Joint Commission between the USA and Canada recommended controlling P inputs to surface waters as a means of managing nonpoint source pollution in the Great Lakes Basin (Rohlich and O'Connor, 1980). Different analyses of the processes involved in the release, transport, and biological availability of soil P exist (Logan et al., 1982 ; Sonzogni et al., 1982).

2.1.1 Inorganic forms of phosphorus

The major sinks for P in soil solution are generally adsorption to soil particle surfaces and conversion to secondary P minerals. These reactions of P in soil follow two rather distinct patterns: an initial rapid reaction involving exchange of P for anions (such as OH⁻) on the surface of Fe- and Al-oxide (Hingston et al; 1967; Kuo and Lotse, 1972), followed by much slower reactions.

Slower reactions are considered to involve1, slow sorption (Ryan et al., 1985; Hooker et al; 1980) and 2, precipitation (Low and Black, 1950; Lindsay, 1979). The distinction between sorption and precipitation was pointed out by Ryden and Pratt (1980). Sorption requires the structure of the sorbent to remain essentially unchanged throughout the process even though its surface activity decreases.

This leads to higher concentrations being maintained in solution at a greater surface-saturation than that at a lower saturation. In the precipitation process, the surface activity remains constant. However, precipitates are heterogeneous solids, with one component restricted to a thin outer layer because of poor diffusion (Sposito, 1984). It is difficult to distinguish between the two processes of slow sorption and precipitation.

According to Bear (1964) and Brady (1974), inorganic P in soils occurs in two forms, those containing Ca, and those containing Fe and Al. In calcareous soils, the dominant form of P is in combination with Ca. Usually less than 0.1 percent of the total P in soil is in the water soluble form (PO₄ -P) (USEPA, 1977). Low solubility and high susceptibility to adsorption result in low availability of P in soils. However,

the availability to the plant of the P in soil depends mainly on the pH (Brady, 1974; USEPA, 1977). When the pH of the soil is between 5.5 and 7.5, the HPO₄⁻² ion form is more available, while for a pH less than 5.5, the H₂ PO₄⁻ ion form is more available. Some of the P is adsorbed on the surface of Fe and Al in soil particles, resulting in precipitated, dissolved or adsorbed forms (USEPA, 1977) If soluble P is added or removed, the immediate reaction is with adsorbed P, but, at equilibrium, the precipitated forms control P in solution

2.1.2 Organic Phosphorus

Agricultural crops commonly contain 0.05 to 0.50 dry weight basis (dwb) percent P in their tissues (Alexander, 1977). Soluble organic forms of P are not available for plants since they must first become mineralized to be used by plants. Alexander (1977) identifies the organic P in soils as phytin, phospholipids, nucleic acids, phosphorylated sugars, coenzymes, and related compounds. Phytic acid is synonymous with inositol hexaphosphate.

Inositol phosphate may have one, two, three, four, five or six P atoms per inositol unit (Alexander, 1977). Inositol forms (isomers) make up 10-80 percent of the soil organic P. Nucleic acids make up 5-10 percent, while other forms make up the final 1-2 percent (Ryden et al., 1973). Ratios of organic Ca to organic P of 100:1 to 300:1 are common in mineral soils(Alexander, 1977).

2.2 Forms of Phosphorus in water

There are several reasons why P is of particular significance in freshwater ecology. It is commonly thought that P is the limiting to the production of biomass. 'Limiting' here means that P is the resource in shortest supply, so that increases or decreases in P have a direct effect on the phytoplankton biomass. There have been numerous studies to this effect, (Sakamoto , 1966; Dillon and Rigler, 1974; Straskraba, 1980; Smith, 1982; Ahlgren et al, 1988, Prairei et al., 1989).

Phosphorus is found in natural water systems in a wide variety of forms. The soluble forms vary in most cases between 5% and 40% (Ryden et al., 1973). Some inorganic polyphosphate species in water include $P_2O^{4-}_{,7}$, $CaP_2O^{2-}_{,7}$, $P_3O^{5-}_{,10}$, $CaP_3O^{3-}_{,10}$, $P_3O^{3-}_{,9}$ and $CaP_3O^{3-}_{,9}$ (Sundstorm and Klei, 1979). They also concluded that 80 percent of P in wastewater effluents are in the form of orthophosphate (PO³⁻₄) and HPO²⁻₄, H₂PO²⁻₄.

Organic P in water is the product of biological growth and occurs in a wide array of compounds. Orthophosphates are available for biological metabolism without further breakdown (Metcalf and Eddy, 1972). Logan (1980) reported that the ratio of soluble P in runoff water to total P (soluble plus sediment-bound) was mainly dependent on the crop coverage. Ratios of 4, 13, 15, 28 and 92 percent crop were given for idle crop land, row crops, orchards and vineyards, close grown crops, and pastures and meadows, respectively. However, the majority of researchers refer to PO_4^3 as the dissolved form of P in runoff and of natural waters bodies.

2.2.1 Phosphorus movement to water

Phosphorus usually shows limited mobility in soils, and its contribution to accelerated water eutrophication is mainly attributed to surface rather than subsurface flow (Sharpley et al., 1993). However, P leaching is an important source of water contamination in heavily fertilized organic soils and in sandy soils with low P sorption capacities (Sharpley and Halvorson, 1994). In an intensively cultivated watershed composed of sandy, P-saturated soils, Breeuwsma and Silva (1992) estimated that 87% of the water P contamination was due to leaching.

Until the 1980s, the problem of P leaching from soil to water was generally not considered as an important source of pollution. Cooke (1976) found Ρ concentrations in polluted water to be small (up to about 1 mg P/L) and not related to fertilizer use, pH of the soil parent material, and to weather conditions, i.e. factors that the farmer cannot control. He quoted others who reported average concentration of molybdate-reactive P in dammed water in the Netherlands of less than 0.1 mg P/L from marine clay soils and 0.04 mg P/L from river clay soils. Similarly, Zwerman et al. (1972) reported P concentrations of less than 0.01 mg molybdate P L⁻¹ in drainage water and that these levels were significantly influenced by fertilizer or management variables, e.g. presence of absence of cover crops or crop-residue incorporation. Baker (1975) showed that annual P losses in drainage water were negligible, because subsoils fix much of the P leached from the plough layer. Sharpley and Menzel (1987) also considered that losses of P in subsurface drainage water were small. The P in subsurface drainage waters from unfertilized and P-fertilized arable and grassland soils in North America range from

undetectable to 0.064 mg P/L, excluding particular soils where it averaged around

0.2 mg P/ L.

2.2.2 Loss of Phosphorus to surface waters

The major factors affecting the loads of P in surface runoff from agricultural lands(Ryden et al., 1977) include:

time amount of rainfall intensity of rainfall rates of infiltration and percolation slope soil texture nature and distribution of native P P fertilization history cropping practice crop type crop cover density

The control of water pollution from agricultural nonpoint sources includes both an estimation of their magnitudes and an evaluation of potential controls. However, monitoring cannot be applied to every site because of the time and cost involved. The difficulties in measuring nonpoint sources in a watershed and extrapolating the results to other watersheds usually call for modeling techniques. Modeling of watershed systems is an inexpensive and quick technique that has developed very rapidly, in the last decade. To model nutrient transport, e.g. P, both the background of nutrients in the watershed soils and the model type must be considered.

2.3 Forms of Phosphorus in Soil

The amount of P in different soils ranges from 0.01 to 0.20 percent by weight (Bear, 1964; Brady, 1974). According to Brady (1974), the following forms of P are found in mineral soils:

Group 1: Complex and less active forms.

Apatite, an original source;

secondary Ca, Fe, Al phosphate; or

organic forms such as phytin, nucleic acids

and other organic forms.

Group 2: Simple and more available forms.

HPO₄² and H₂PO₄ as phosphate of

Ca, K, Mg, etc. or soluble organic forms.

The P in soil occurs in both, inorganic and organic forms. There are no specific evaluations for the percentages of inorganic and organic P in soils; The quantity of each form of P depends on the physical and chemical characteristics of a soil (Alexandre 1977).

2.3.1 Phosphorus Movement in the Soil

The potential loss of P from agricultural land is dependent on several factors, including the relative importance of surface and subsurface runoff in a watershed area, land management, and the amount, form and availability of P in soil. Annual

runoff is usually generated only from limited source areas within a watershed. These source areas vary rapidly in time, expanding and contracting rapidly during a storm as a function of rainfall intensity and duration, antecedent soil moisture conditions, water storage, temperature, soils, topography, groundwater and moisture status over a watershed (Gburek and Sharpley, 1998).

For P, the most important soluble forms are orthophosphate and soluble organic P. The relative abundance of these forms is dependent on runoff, soil properties, vegetation, climate and fertilization (Metcalf and Eddy, 1972).

2.3.2 Mobility of Phosphorus in soil

Phosphorus is generally thought to be held sufficiently by soil particulate matter so that movement out of the soil profile in percolating water is minimal (Ryden et al., 1973; Taylor and Kunishi, 1971).

Johnston et al., (1964) showed that phosphates are readily removed through adsorption and precipitation processes in all soils except those in which the phosphate removal capacity has been exceeded. Brady (1974), showed that only trace amounts of P were lost by percolation, Taylor (1967) monitored experiments in well drained, poorly drained, manure fertilized, and unfertilized soils. He showed that with an application rate of 50 kg/ ha of P fertilizer, 95 to 97 percent of the total amount added was found in the top 0.175 m of the soil. As the soil solution moved downward through subsoil layers that had not received P fertilization, adsorption reduced the concentrations to negligible levels. The downward movement of P in crop land is usually a very slow process; (US EPA, 1977; Shah et al., 1975; Taylor, 1967; Sawhney 1978). Under normal fertilizer practices on agricultural lands, the net leaching of P is usually very small. Goodrich and Monke (1971) showed that some P might be leached into 3-foot deep drains in a sandy loam soil if the soil was heavily irrigated with wastewater.

2.4 Losses in surface runoff

Hydrologic processes of rainfall and runoff are the major driving forces for soil detachment, transport and deposition. The major factors involved in the hydrologic response of a watershed to single storms are precipitation, interception, surface retention, surface detention, infiltration, drainage, interflow, overland flow, and channel flow (Romkens and Nelson (1974).

In many models, sheet flow is considered as the mechanism for soil detachment and transport of the soil particles. This would be true for the interills area of an element, except that flow generally concentrates quickly into rills. However, the complexity of the overland flow process is such that it cannot easily be modeled, and so, within a specified small area (elements), flow is considered to have a uniform depth. Rainfall detachment and overland flow detachment both influence P transport. Many investigators have shown that, as long as there is a significant level of sediment in runoff, P will occur in both sediment-bound and dissolved forms. Furthermore, an equilibrium condition occurs between soluble sediment P and soluble forms of phosphorous in runoff (Logan, 1980).

From experimental field plot studies, it was shown that the relation between

P added to selected soils and the available P in sediment was linear (Nelson and Romkens, 1970). The same data also show a linear relationship between available P in sediment and soluble PO_{4}^{3} in runoff water. The linear relationship between soluble P in runoff and extractable P from surface soil has been reported by Sharpley et al (1978).

Soluble forms of P in runoff and the ratio of sediment-bound to soluble forms of P depend on many factors such as soil fertility, crop coverage and soil texture. Ahuja et al.,(1981), and Sharpley et al., (1981) showed that the equilibrium between soluble and extractable P depends on the ratio of water: soil in solution. Sharpley et al, (1981) also showed that the slope of the isotherms will remain the same at different water: soil ratios but that the isotherms will shift higher and higher corresponding to the dilution factor. However, their experiments did not cover high water: soil ratios and they did not suggest an upper limit for this ratio. Their approach was time dependent and the form of the derived equilibrium equation was governed by diffusion phenomena. Romkens and Nelson (1974) and later Oloya and Logan (1980) showed experimentally that desorbed P was a function of (BP1) Bray-P1 at equilibrium.

In the present study, Mehlich III was considered the most appropriate and economic procedure to be used for soil P testing in the laboratory for different kinds of soil because of its capacity to extract simultaneously other soil nutrients. The Al content in the Mehlich III extract also gives an estimate of P-sorption capacity.

2.5 Erosion

Erosion is a function of rainfall amounts and intensities, and soil texture, topography and management. Management practices designed to minimize erosion must take account of these factors. Of prime importance is the reduction of erosion due to detachment and transport. Often detachment control (e.g. more crop or residue cover) is reported to be more effective than transport control (e.g. vegetative filter strips), (Simard et, al., 1992). As soil P content increases, the potential for particulate P and dissolved P transport in runoff increases.

Sources of particulate P in streams include eroding surface soil, stream banks and channel beds. So, processes determining soil erosion also control particulate P transport. In general, the P content and adsorption capacity of eroded particulate material is greater than that of source soil, due to preferential transport of clay-sized material. The transport of dissolved P in runoff is initiated by the desorption dissolution and extraction of P from soil and plant material. These processes occur when rainfall interacts with a thin layer of surface soil (1-50 mm) before leaving the field as runoff (Sharpley,1985b). Although the proportion of rainfall and depth of soil involved are difficult to quantify in the field, they will be highly variable, due to variations in rainfall intensity, soil tillage and vegetative cover.

Various workers have reported that the loss of dissolved P in runoff is dependant on the soil P content of surface soil. For example, a highly significant linear relationship was obtained between the dissolved concentration of runoff and soil P content Mehlich III P of surface soil (50 mm) from cropped and grassed catchments in Arkansas, Oklahoma and Texas (Sharpley and Menzel 1987).

A similar dependance of the dissolved concentration of runoff on Bray-1 was found by Romkens and Nelson (1974),for a Russell silt loam in Illinois ($r^2 = 0.81$) and on water-extractable soil P ($r^2 = 0.61$) of 17 Mississippi catchments and 11 Oklahoma catchments ($r^2 = 0.88$) by Schreiber (1988).

On a silt loam and a sandy loam, but not on a clay loam, large rainfall events caused much soil to be eroded and therefore large losses of total P with conventional tillage systems. However, with conservation tillage and no tillage with surface mulching these losses were diminished. Losses of dissolved P ranged between 0.3 and 2% of the total P lost. Erosion losses can be reduced by sowing alternated strips of different crops, by establishment of plant cover to protect soil against the impact of raindrops, by planting strips of woodland, by leaving areas at fields edges under green cover, and by other appropriate cultivation practices. In certain cases, drainage reduces erosion losses; however it may carry the risk of increasing leaching.

2.6 Slow P sorption

Sorption rates of P by soil components decrease with time, but reactions can continue for a long period. Peña (1990), found that slow sorption, i.e., between 6 and 126 days after P addition, averaged only about 5% of the rapid, initial 6-day sorption. It is often doubtful whether the reaction reaches equilibrium. These slow reactions may not be useful for indexes of labile P and may affect P bioavailability (Barekzai and Mengel, 1985). Characteristics and consequences of soil P sorption *in situ* need to be evaluated after long-term additions of fertilizer P.

At low P concentrations (10 to 100 µg), where precipitation processes do not take place, continuous loss of P in soil solution has been attributed to diffusive penetration into soil particles, diffusion into surface defects and pores and adsorption in inter-particle pores (Parfitt, 1989). Changes of a mono to a binuclear surface complex can occur (Kafkafi et al., 1967). Slow P sorption due to the presence of surface pores has been reported for synthetic Fe oxides (Madrid and Arambarri, 1985). In general, the slow sorption processes involve formation of covalent Fe-P or AI-P bonds on Fe and AI oxide surfaces (Willett et al. 1988).

Slow reactions are mainly a function of Fe- and Al-oxide contents (Ryan et al. 1985), calcium carbonate content (Solis and Torrent, 1989), temperature and time (Barrow, 1980). Kinetics of slow reactions were found to be insensitive to soil moisture content or soil type, such that reactions in solution may not be the rate-limiting processes (Parfitt, 1989), and slow reactions perhaps occur at the original sorption site (Ryden et al., 1977).

Water discharge into streams and lakes may transport significant amounts of dissolved P. The desorption is usually simulated with the equation presented by Sharpley and Ahuja, (1981), and Sichani et al., (1993). These equations assume that a thin layer of surface soil interacts with runoff water (Storm et al., 1988; Lee et al., 1989; Ashraf and Borah, 1992; Daniel et al. 1993), and that desorption from the soil surface depends on the amount of desorbable P available P) in the soil, and contact time. The equation of Sharpley and Ahuja (1981) was developed for rainfall and runoff characteristics in the United States, where most runoff occurs during heavy rain storms falling on a relatively dry soil.

A few physical and chemical factors controlling desorption of P from soil were also investigated to simulate the effects of dilution by runoff water on the dissolved P concentration and total P load. Desorption tests were carried out at various water: soil ratios. Moreover, the liability of soil P and the buffering of soil were investigated by a sorption-desorption isotherm. The information obtained from this study can be used when simulation models are used to estimate the transport and temporal variation in dissolved P and to calculate the annual P load from cultivated land.

2.7 Eutrophication

Orthophosphate is the only form of P that autotrophs can assimilate. Extracellular enzymes hydrolyze organic forms of P to phosphate. Eutrophication is the over enrichment of receiving waters with mineral nutrients, which engenders excessive production of autotrophs, especially algae and cyanobacteria. This high productivity leads to high bacterial populations and high respiration rates, which, in turn, produce hypoxia or anoxia in poorly mixed bottom waters or, in surface waters under calm, warm conditions at night. Low levels of dissolved oxygen kill many forms of aquatic biota, releasing many materials normally bound to bottom sediments, including various forms of P. This release of P reinforces eutrophication.

Excessive concentration of P is the most common cause of eutrophication in freshwater, lakes, reservoirs, streams, and headwaters of estuary systems, whereas in the ocean, N becomes the primary mineral nutrient controlling production. Estuaries and continental shelf waters are a transition zone, where excessive P and N both create problems. Obviously it is best to measure and regulate total P inputs to whole aquatic ecosystems; however, an alternative, effective method is to assay total P concentration, including particulate P in surface waters, or N / P atomic ratios in phytoplankton.

2.7.1 Biovailable Phosphorus

Bioavailble P in dissolved and particulate forms in agricultural runoff can promote freshwater eutrophication (Sharpley et al., 1994b). While soluble P is immediately available for uptake by aquatic biota, the available portion of particulate P represents a secondary and long - term source of P in lakes (Sharpley,1993). Dissolved P in runoff originates from the release of P from a thin zone of surface soil (about 0 to 50 mm) and vegetative material (Sharpley,1985). Relationships between P in runoff and surface P can be used as the basis to establish critical soil - test P levels, above which P enrichment of runoff becomes unacceptable. The first step in formulating P-based management recommendations is to establish an acceptable P concentration in runoff for a given physiographic region.

Once this is done, soil-test P values in excess of critical values may indicate a need to change the management of fertilizer and manure P inputs. Changes may include conservation measures to reduce erosion and runoff, removal of harvested crop P from the management system, and a possible reduction in fertilizer and manure application rates.

Although soil- test P is related broadly to P concentrations in runoff, different amounts of P can be lost from sites with similar surface soil - test P contents (Sharpley, 1996). In fact, variability in runoff volume and erosion as a result of climatic, topographic, and agronomic factors plays a larger role than soil- test P in determining P loss. Thus, a more comprehensive approach is needed for reliable yet flexible recommendations of fertilizer and manure P management. Such an approach must integrate soil - test P with estimates of potential runoff and erosion losses.

2.8 Phosphorus and Sediment

With low P loadings sediments generally contain less than 1 mg P/ g dry sediment, but as P loading increases both the degradable carbon (C) and P contents of the surface sediment increases. The increased C input creates a greater oxygen demand, which generally promotes chemically reducing conditions in the sediment. This, combined with the greater P content, causes a progressive tendency for more P to be released from the sediment. A large number of lakes, in which P inputs have been decreased, have shown a tolerance of approximately 1 mg P/ g dry sediment, below which sediments tended not to release P back to in the water column. Much of the feedback mechanism between sediment and water P is chemically driven either by the oxidation-reduction status of the iron-P complexes or in calcareous sediments by the pH / calcium / P reaction.

Disturbance of the bottom by animals can also be an important feedback mechanism by way of turning over sediment and resuspending it in the water

column or by irrigating deeper layers with water currents. Gallepp, (1979) suggested that bottom-feeding fish feeding on chironomid midge larvae can be significant factors in this regard. In addition, the growth of rooted macrophytes (`pondweed`) may act as a nutrient pump, taking up P from the sediment and releasing it to the water column when the plants die back in the autumn (Granéli and Solander, 1988). In a shallow Norfolk Broad (Moss et al., 1986) isolation of the lake from its inflows at first restricted the nutrient input and the sediment P release. However, greater water clarity due to smaller phytoplankton crops allowed rooted macrophytes to become re-established and P release began again, perhaps due to the input of organic matter from the plant remains. This illustrates the importance of the hydrological cycle, a lake with little hydrological flushing is likely to accumulate nutrients. Such a regime promotes closed nutrient cycles in which sediment-water fluxes dominate the annual budget. The loading of sediment-bound P can be expressed as follows:

$$PE = SED \times TOTAL P \times PER1 \times F$$
(2.1)

where,

- PE = mass flow rate of sediment-bound P transported from the surface of an element, kg/sec
- SED = mass flow rate of sediment, transported from the element, kg/sec TOTAL P = total P of the surface soil of the
 - element, µg /g of soil
- PER1 = sediment-bound P enrichment ratio
- F = a conversion factor
2.9 Summary of Literature review

The importance of P originating from agricultural sources to the NPS pollution of the surface watershed has been a serious environmental issue because of the well-known role of P in eutrophication. Although the loss of agricultural P in runoff is normally not of economic importance to a farmer, off- site it can lead to significant economic impacts, frequently many miles from the P source. By the time these impacts are manifest, remedial strategies are often difficult and expensive to implement. Thus, a greater knowledge is needed of what land systems are primary sources of P, how much P in soil and water is too much, how and where we can reduce P inputs and losses, and what will be the required efficiency of remedial action in order to develop agricultural systems that sustain production as well as a healthy environment. These challenges will require innovative interdisciplinary cooperation and applied research that is directed toward existing problems.

The present study required a soil testing laboratory for better understanding of the P dynamics in the dominant soils of the St Esprit watershed, and a quick chemical method that can be used to formulate the P fertilizer recommendation for all dominant soils. The available P can be determined by six different chemical methods (Mehlich - III, Bray - II, Bray-I, Mehlich-I, Mehlich-II,Olsen). Compared to the other chemical methods for determination of available P in the St. Esprit watershed, the Mehlich III method was found to be most reliable and most accurate in estimating available P in these soils. Furthermore, Mehlich- III has the advantage of permitting the simultaneous determination of available K, Ca, Mg, Na, Al and micro-nutrients contents.

3.0 MATERIALS AND METHODS

3.1 St. Esprit Watershed Description

The soils and sediment used in this study were obtained from the St. Esprit watershed (26.1 km²) located approximately 50km northeast of Montreal in the St Esprit river basin which forms part of the larger L'Assomption river basin. Figure 3.1 shows the location of the watershed with respect to the island of Montreal. There are approximately 27 commercial farms within the study watershed. Of the total area, 64 % is under crop production (Table 3.1).

Сгор	Area (%)	Area (km ²)					
Corn	23.9	6.29					
Cereals	13.3	3.47					
Hay	11.2	2.97					
Soybeans	3.3	0.86					
Vegetables	3.1	0.82					

Table 3.1 Agricultural land use on the St. Esprit watershed [‡].

*- Enright et al., (1995).

Forest accounts for 25.2% of the total area and consists largely of sugar maple (*Acer saccharum* L.) bush. The remaining land coverage is residential area (4.97%) and 6.1 % of unused area. The population in this area is approximately 800 people (Enright et. al., 1997).



Figure 3.1 Location of the St. Esprit and Desrochers Watersheds and Watercourses

3.2 Soil Texture

Basically, 12 different soil series can be found on the watershed (Table 3. 2) covering the entire basin. They originate from four types of deposits : glacial till, out wash plain, marine sediment, and alluvial deposits (Lajoie, 1965). The lower portion of the basin is mostly composed of clays and clay loams, including the Ste. Rosalie and St. Laurent series Figure 3.2. The upper region of the watershed is composed of loamy and sandy soils including Belle River Soulanges, Perrot, St. Bernard, Chicot, Peningue, Aston, and St. Benoit lists the percent of land use and soil texture in the Saint Esprit sub watersheds.

Soil texture	Area (%)	Area (km ²)
clay	17.5	4.57
clay loam	14.1	3.67
clay to clay loam	9.1	2.37
fine loamy sand to sand	0.1	0.03
fine sandy loam	3.2	0.84
loam	3.4	0.88
loam sand	5.6	1.46
loam to sand loam	2.1	0.54
sand	8.4	2.14
sand clay	1.0	0.26
silty clay loam	2.3	0.6
sand loam	33.4	8.71

Table 3.2 Soil Texture in the St. Esprit watershed[‡].

+ Enright et. al., (1997).

The topography on the watershed can be described as flat to rolling. The slope of cultivated land generally ranges between 0 and 3%. The length of the main channel to the outlet, is approximately 9 km. The watershed has a 40 m drop in elevation from its highest point to the outlet. The top of ridges, land with slopes more than 5%, and stony areas tend to be under forest, or managed sugar maple bush (Lapp, 1996).



Figure 3.2 Soil series map

St- Esprit Watershed Soil Texture map



Climatologically, the watershed is temperate. The period of frost varies between 122 and 138 days. Average annual precipitation varies between 860 and 1050 mm, with 20 to 25% appearing as snow. Average annual potential evapotranspiration is between 400 and 560 mm (MAPAQ,1983). Heavy rainstorms are most likely to occur in mid -summer or in early fall. The average annual temperature is 5.2 °C. July temperatures vary between 18 and 21 °C (MEF,1995). The stream gauging station at the outlet of the watershed and the meteorological station on the watershed were established in the winter of 1993-94 by staff of the Department of Agricultural Engineering of McGill University.

3.3 Soil sampling

Based on the soil series (Figure3.4) of the St. Esprit watershed, four major soil groups were considered for composite soil sampling. In the fall of 1994, the administration committee gave priority to development of fertilizer management plans for each farm. It soon became clear that there was a general lack of soil fertility data to develop these plans; therefore the committee supported a soil sampling program for about 30% of the St. Esprit agricultural fields.

Figure. 3.5 shows the distribution of soil P. About 270 ha of the basin had a high level of soil P of more than 400 kg/ha. Most of the area had soil P within the range of 100 - 200 kg/ha. Almost 27% of the agricultural lands received P fertilizer applications of between 25 to 75 kg/ha per year. More than 100 kg/ha of P were applied on 7% of the land. Figure 3.6 shows P fertilizer applied in 1996.

The four soil groups (Figure 3.4) were loam (soils with more than 400 kg/ha

P), clay (soils with 300-400 kg/ha P), silt (soils with 300 to 400 kg/ha P), and sandy loam (soils with more than 400 kg/ha P) (Mousavizadeh, 1998). There are 27 farms, of which 18 are participating in the project. The participating producers account for approximately 67% of the agricultural land of the watershed. Data was collected for about 40% of the basin. Taking into account that 36% of the basin is non-agricultural, the data collected covered a good portion of the watershed. From each soil group, samples were taken at regular distances from each other to guarantee complete coverage of the area of a soil group. Four randomly selected soils and sediment samples per hectare (from 0 to 50 mm depth) were obtained for each soil group. For comparison of the behavior of the watershed. To prepare the soil and sediment samples for laboratory analysis, samples were air-dried and passed through a 2 mm sieve after removing visible root and crop residues. Particle-size distribution was determined by the hydrometer method (Day, 1965)

3.4 Available Phosphorus

For each soil group sample, 100g of dry of soil were wetted with a KH_2PO_4 solution at a P application rate of 50 µg P/g of soil, 100 µg P/g of soil, and 500 µg P/g of soil at 30%. The samples were incubated at room temperature (25 °C) for 7 days. After incubation, two replicate 2.5 g soil samples from each soil group and sediment samples were transferred into plastic Dixie cups 155.5g (SWEETHEART plastic. ING 5F Wilmington. MAO1887) and 25 ml of MehlichIII extractant (Mehlich, 1984) were added. This extractant is composed of 0.2 MCH_3 COOH, 0.25 MNH_4 NO₃, 0.015 MNH_4 F.

0.013 *M* HNO₃, and 0.001 Methylene diamine tetra acetic acid (EDTA). In the Mehlich III procedure, P is extracted by reaction with the acetic acid and fluoride compounds. The extractant - soil mixture was shaken for 5 min, then filtered through Whatman No 42 filter paper. The filtrates were collected in culture tubes. Soluble P was measured using an automated colorimetric method on a LACHAT Quick Chem AE 1992 instrument (based on EPA method 365.3, USEPA 1983). This gave a measure of available P.

3.4.1 Soluble Phosphorus

The determination of available P was followed by the release of soluble P at different water/soil ratios with replicated soil samples (2 g in each of 15 jars with 200 ml of water). These were shaken for 4 h, then 40 ml from each jar was collected, flocculated, and centrifuged at 2000 rpm for 15 min (using a Sorvall RC-2B high speed refrigerated centrifuge) at 25 °C. To determine the appropriate shaking time, soil and sediment samples were used in a separate experiment in which, at P rates of 0 and 100 mg P/ kg soil, water extractable P (WEP) was determined at shaking times of 0.1, 0.2, 0.3, 0.5,0.7,1.0,2.0, and 3.0 hours. Approximately 45 ml of each suspension were centrifuged at 2000 rpm for 15 min until a clear supernatant was obtained, the supernatant were filtered using Whatman No 42 filter paper.

The amount of WEP in the filtrates was determined by automated flow injection analysis based on, U.S. Environmental Protection Agency USEPA, Methods for Chemical Analysis of Water and Wastes, EPA -600 / 4 - 79 - 020, Revised March 1983, EPA Method 365.3 (1983).



Legend

0-100 kg/ha and sand loam 100-200 kg/ha and sand loar 300-400 kg/ha and sand loar >400 kg/ha and sand loam 0-100 kg/ha and loam 100-200 kg/ha and loam 300-400 kg/ha and loam > 400 kg/ha and loam 0-100 kg/ha and silt $\approx 100-200$ kg/ha and silt 300-400 kg/ha and silt >400 kg/ha and silt 0-100 kg/ha and clay 300-400 kg/ha and clay > 400 kg/ha and clay

2 km





3.5. Data Analysis Methods

To quantify the functional relationship (R^2) between WEP and Mehlich III P, multiple linear regression analysis was performed for different water: soil ratios of four soils and sediment samples taken in 1998. Two-way factorial analysis of variance (ANOVA) was used to investigate the combined effect of w:s ratio (factor A) and P level (factor B) on Mehlich III. In the absence of significant interaction,

the main effect of individual factors was investigated. To estimate appropriate shaking time for the soluble P, repeated measures analyses were used with time being the repetition factor. With the modified ANOVA, total interactions (soil type X shaking time X treatment) were not setup as there were insufficient degrees of freedom. To separate the means within each factor, protected least significant difference (I s d) was used. All statistical analyses were done using proc GLM (General Linear Model procedure) available in SAS for Windows, version 6.12.(SAS, institute, 1989-1996, NC).

3.6 Empirical Relationship between WEP and P

An empirical relationship can be developed between dissolved P in runoff and extractable P in surface soil (Nelson and Logan, 1982). Soil texture and soil chemical properties are among the parameters affecting such a relationship. Römkens and Nelson (1974) showed that there was a more or less linear log-log relationship between NaHCO₃ extractable P in soil, and water extractable P at a water: soil ratio of 50 : 1. The relationship deviated from linearity in some soils.

On the addition of up to 100 mg P/kg soil, Oloya and Logan. (1980) found

that the amount of P desorbed from soil and sediment was highly correlated with

Bray-P1 extractable P.

Sharpley and Ahuja (1981) investigated the kinetics of P desorption for several soils

at different water: soil ratios for short time periods.

Their kinetic equation for P release was:

$$WEP = k(EP)t^{\gamma}(W_{s})^{\alpha}$$
(3.1)

where

WEP= amount of desorbed P, mg P/ kg k = desorbed P, mg P/kg soil at the axis intercept EP=initial amount of extractable P present in the soil (i.e., NaHCO₃ - extractable P, mg P/kg soil) t=shaking time γ , α =constants related to soil type W_s=water: soil ratio Sichani (1982) used the ANSWERS model (Beasley, 1977) to study the

forms of P(dissolved and total P) that were transported in surface runoff from agricultural watersheds. He proposed the following modification to Eq. (3.1).

$$WEP = K (W_s)^{\alpha} (BP1)^{\beta}$$
(3.2)

where

٧

BP1 = extractable P Bray P1 mg P/ kg soil K, α , β = constants related to soil type

He concluded that soluble P loss could be predicted by Eq 3.2 using the ANSWERS model, and that results of the model output were close to the observed values.

In the present study, we suggested a modification of Eq 3.2 by replacing BP1 phosphorus with Mehlich III phosphorus. This modified equation, Eq 4.1 on page 52, was used to study the dynamics of P from the St. Esprit watershed.

4.0 RESULTS AND DISCUSSION

4.1 Effect of Shaking Time

Over the range of soils treated with 100 µg P/g of soil and in untreated samples, P released from the four soil groups and sediment particles was found to increase with time Figures 4.1 and 4.2 However, different soils showed different amounts of P released. There are consistent patterns between different soil samples in the treated and untreated cases. The amount of P released at any given shaking time was lower in sediment samples untreated with P than in the case of treated sediment Figure 4.1 However, for those samples treated with P, loam soil released the lowest P Figure 4.2 Among the soil groups, the clay soil groups showed greater P release than the loam, silt, sand, and sediment, in both treated and untreated cases. Low levels of suspended solids occur only as a result of low erosion or sediment transport rates. Generally in such cases, only small particles (clays) are delivered to a watercourse. In statistical analysis, shaking time showed significant effect on the amount of P released (Table 4.1).

Source	df	Pr > F	Pr > F (H-F)
Soil Type	4	0.845	NA
Treatment	1	0.004	NA
Sh. Time ‡	6	0.0001	0.0028
Soil Type x Sh. Time	24	0.068	0.149

Table 4.1 Repeated measures analysis of variance for soluble

*Significant at P = 0.05 *Significant at P = 0.01

NA not Applicable

(H-F) Huynh-Feldt Test

The effect was highly quadratically significant (P<0.0004 and 0.007) before and after modification of ANOVA. This means the functional relationship between desorbed P and shaking time was most pronounced at first hour, and stabilized thereafter Figure 4.1 and 4.2. The results of this research show that soil properties influence the reaction of P in soil as a function of shaking time for the different soil groups and sediment used in this study. This, in turn, will have a great influence on P enrichment of P desorbtion in soils. This finding is in agreement with results obtained under similar experimental conditions (Sharpley al. et., 1981 and Sichani et. al., 1993).

For particles of approximately the same density, the ratio of surface area to mass varies inversely as the size of the particle. Therefore, for a given mass, the smaller the constituent particle the greater is the surface area available for P ad sorption. Consequently, P is adsorbed more readily to a given mass of small clay or organic matter particles than to the same mass of larger silt or sand particles. Finer-textured soils usually contain lime and, the lime being more finely divided, is more effective in causing the formation of calcium phosphates. It is noteworthy that, whereas the total surface area of soil lime initially increases with increasing lime content, a point is reached where the specific surface area of lime drops dramatically causing the total surface area of soil lime to decrease, even though the percent lime content continues to increase.

Figures 4.1 shows desorbed soluble P as a function of shaking time for different untreated soil groups and sediment samples. At a shaking time of 0.1h, desorbed soluble PO_4^3 was 0.12 mg/L for clay, 0.11 mg/L for silt, 0.10 mg/L for

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sand, 0.04 mg/L for loam, and 0.02 mg/L for sediment. This increased to 0.33,0.25,0.22,0.17 and 0.07 mg/L, respectively; for a 3h incubation.

Desorbed soluble P as a function of shaking time for different treated soil groups and sediment samples (100 μ g added P/g of soil) is shown in (Figure 4.2). Shaking times of 0, 1 and 3h for treated clay samples resulted in values of desorbed soluble PO₄³⁻ greater than those of untreated clay samples by 0.52 mg/L. Similarly the increase in desorbed soluble PO₄³⁻ for silt soils is 0.4 mg/L, for sand soils 0.15 mg/L, for loam soils 0.2 mg/L, and for sediment 0.39 mg/L, for a shaking time of 3h.

Water-extractable P (WEP) increased sharply with increased shaking time up to 42 min (Figures 4.1 and 4.2) for both treated and untreated cases. Since about 90 % of WEP was released in less than 2 h, a 4-h shaking time was chosen to ensure complete P release for clay soil groups and sediment samples.

4.2 Effect of Water : Soil Ratio

The relationship between water-extractable P (soluble P) and Mehlich III available P was determined for water: soil ratios of 100, 200, and 500. Soluble P was measured after 4h of shaking.

All data were corrected for the amount of surface- P initially present on the soils. Soil groups and sediment had different initial P concentrations which altered the rate of the initial or 'adsorption' reaction and the secondary 'fixation' phenomenon. The released soluble P for different soil groups and sediment at



Figure 4.1 Desorbed Soluble P as a function of shaking time for different soil groups and sediment sample for 0 µg added P/g of soil.

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Figure 4.2 Desorbed Soluble P as a function of shaking time for different soil groups and sediment sample for100 µg added P/g of soil.

different levels of available P for a water: soil ratio of 100 is shown in Figure 4.3. The soluble P released from clay samples was measured to be 0.22 μ g P/g to 1.10 μ g P/g at added available P of 50 μ g P/g, 100 μ g P/g and 500 μ g P/g of soil . For sediment samples, the soluble P released ranged between 0.08 μ g P/g and 0.80 μ g P/g of soil for added available P of 50 μ g P/g, 100 μ g P/g and 500 μ g /g soil. Comparing the maximum release of soluble P measured at an added available P of 500 μ g/g, the clay samples were the highest, while the lowest was observed in the loam samples. Figure 4.4 shows the released soluble P for different soil groups and sediment. Considering the added available P (50, 100, 500 μ g /g of soil) in clay samples, the values of soluble P released for a water: soil ratio of 200 increased only slightly compared to the values for a water: soil ratio of 100. For clay soil the increase was from 0.22 to 1.20 μ g P/g, for silt soil from 0.14 to 0.92 μ g P/g, for sand soil from 0.22 to 0.87 μ g P/g, for loam soil from 0.08 to 0.84 μ g P/g , and for sediment from 0.08 to 0.90 μ g P/g.

After subjecting the data to a 3 X 3 factorial ANOVA, Mehlich III P concentration was found to be significantly affected by the level of P added in all soils and sediment except sandy loam soil (Table 4.2). For the sandy loam soil, the adding of 500 μ g P/g produced the highest P adsorption capacity followed by 100 μ g P/g and 50 μ g P/g. This relationship was linear over the range of Mehlich III extractable P content of surface soil (50mm) and was related (P<0.0001) to the desorbed soluble PO³⁻₄ of surface soil. This trend was consistent, at least numerically, but not significant statistically at the different levels of P (Table 4.2).

Previous studies clearly showed that there are some situations where sandy loam can show less P release in the most common agricultural land and a similar linear relationship between soluble orthophosphate P in w:s ratio and available P (extractable P) content of soils and sediment (Breeuwsma and Silva ,1992; and Sharpley and Halvorson, 1994). In fact, silt was the only soil showing significant differences between 50 μ g P/g and 100 μ g P/g, while the rest were unaffected by the application of 50 and 100 μ g P. It is worth mentioning that P concentrations in this study were little affected by the w:s ratio (Table 4.2).

ªW: S	Soil Texture	Intercept	[⊳] Sterr (±)	Slope	[▶] Sterr (±)
100	Loam	0.04	7.0x10 ⁻³	2x10 ⁻³	2.7x10 ⁻⁵
100	Clay	-0.14	2.9x10 ⁻⁴	2x10 ⁻³	8.2x10 ⁻⁷
100	Silt	-0.02	0.9x10 ⁻³	2x10 ⁻³	2.8x10 ⁻⁵
100	Sand loam	0.1	2.2x10 ⁻²	1x10 ⁻³	7.6x10 ⁻⁵
100	Sediment	0.07	9.7x10 ⁻⁴	2x10 ⁻³	3.8x10 ⁻⁶
200	Loam	-0.046	1.3x10 ⁻²	2x10 ⁻³	5x10 ⁻⁵
200	Clay	-0.17	6.0x10 ⁻³	2x10 ⁻³	1.8x10 ⁻⁵
200	Silt	0.05	2.6x10 ⁻²	2x10 ⁻³	8.4x10 ⁻⁵
200	Sand loam	0.09	1.9x10 ⁻²	2x10 ⁻³	6.6x10 ⁻⁵
200	Sediment	-0.06	1.2x10 ⁻²	3x10 ⁻³	4.8x10 ⁻⁵
500	Loam	-0.025	3.8x10 ⁻²	3x10 ⁻³	1.5x10 ⁻⁴
500	Clay	-0.28	7.8x10 ⁻²	4x10 ⁻³	2.2x10 ⁻⁴
500	Silt	0.1	3.0x10 ⁻²	2x10 ⁻³	1x10 ⁻⁴
500	Sand loam	0.11	3.5x10 ⁻³	2x10 ⁻³	9.1x10 ⁻⁵
500	Sediment	-0.026	5.3x10 ⁻²	3x10 ⁻³	2.1x10⁴

Table 4.2 Slope and intercept values for the regression linear coefficients of four soil groups and sediment

* W:S = Water And Soil Ratio * Standard error of the means

For available P up to 500 μ g /g of soil, the released soluble P for different soil groups and sediment at different levels of available P is shown in Figure 4.5. There was a significant increase in the measured values of soluble P released in clay samples (Table 4.2), compared with the corresponding for values for added available P of 100 μ g /g soil in Figure 4.3. For clay soil this increase was (0.29 to 1.80. μ g P/g), for silt soil (0.23 to 1.32 μ g P/g), for sand soil (0.26 to 1.00 μ g P/g), for loam soil (0.13 to 1.10 μ g P/g), and for sediment (0.13 to 1.42 μ g P/g).







Figure 4.4 Released soluble P for different soil groups and sediment at different levels of available P for water: soil ratio of 200.



Figure 4.5 Released soluble P for different soil groups and sediment at different levels of available P for water: soil ratio of 500.

The above results were plotted on log-log scale to show the relationship between water-extractable P and added available P at different water :soil ratios for all the soil groups and the sediment samples Figures 4.3 to 4.5. The relationship was linear for all samples for the different water :soil ratios. Soluble P released from different soil groups and the sediment sample tended to increase with an increase in water: soil ratio. In all the cases, P released is a power function of the water: soil ratio due to an increase in P diffusion/desorption from the soil and sediment particles to overlying water during the shaking period. This is in response to a reduction (by dilution) in soluble P concentration in the water: soil suspension as a result of an increase in the amount of water in the suspension.

Treatments	Loam	clay	Silty	S. loam	Sediment
Phosphorus					
50	0.096 b ^{§§}	0.243 b	0.203 c	0.168 a	0.099b
100	0.190 b	0.403 b	0.315 b	0.276 a	0.233 b
500	0.867 a	1.353 a	0.863 a	0.656 a	1.046 a
W:S Ratio					
100	0.287 a	0.530 a	0.358 c	0.365 a	0.358 a
200	0.365 a	0.590 a	0. 463 b	0.443 a	0.389 a
500	0.500 a	0.880 a	0.560 a	0.293 a	0.631 a
			Significance		
P level	**	**	**	ns	**
W:S Ratio	ns	ns	**	ns	ns
PXW:S	ns	ns	ns	ns	ns

Table.4.3 Concentration (μ g g⁻¹ soil)and significance of Mehlich III P and w:s from different soils at different rates of P.

 significant at 5%
 significant at 1%
 ns not significant at 5%
 ¹¹ Column values of the same factor followed by same letter are not significantly different from each other at 5 % probability level

The measured values of water-extractable P and added available P for clay soil were greater than those for sediment and the other soils. This was related to the higher clay content in this soil group. By comparison to the trend of the plotted lines, one can observe that the slope remains fairly similar in all soil groups, with highly significant correlation coefficients(Table 4.3). Small differences in the slope of the log-log relationship between P released and the water: soil ratio Figures 4.3 to 4.5 implies that there is a consistent pattern between different soil groups of the watershed in the increase of P release as a result of an increase in water: soil ratios. Therefore, the effect of water: soil ratio on P released from the soil and sediment particles can be helpful in evaluating net P released from the surface soils of the St. Esprit watershed and other areas.

4.3 Effect of Mehlich III available P

The quantity of available P (Mehlich III) released from the soils and sediment particles depends on the soil groups and sediment, and on the water: soil ratio. The relationship between desorbed P and available P at different water: soil ratios was studied mathematically. The linear relationships determined using log-log scale Figures 4.6 to 4.10 are called isotherms. The figures demonstrate that the position of the isotherms shifted up as the water/soil ratio increased, whereas the slope of lines were reasonably similar. Therefore, the following equation was obtained, which expresses the relationship between WEP and Mehlich III P, (M III).

$$WEP = k_1 (W_s)^{\delta} (M \text{ III})^{\lambda}$$

(4.1)

where.

WEP= amount of desorbed P, mg P/kg

 k_1 =desorbed P, mg P/kg soil, at the axis intercept

 λ,δ =constants related to soil type

M III =Mehlich III P

W_s=water: soil ratio

To determine the values of k_1 , δ , and λ , the relationships between desorbed soluble P and water :soil ratios for different soil groups and sediment were plotted in Figures 4.11 to 4.15. The values of these constants were obtained using log-log paper and the corresponding values of soluble P released at a constant available P (i.e. 100 mg P/kg soil) at different water: soil ratios. The results indicate that for every water: soil ratio, there exists a linear isotherm for each soil group of the St. Esprit watershed. Table 4.3 presents the values of k_1 , δ , and λ for the different soil groups and sediment of the watershed.

Soil type		к,	δ		λ		R²	n	Reg SD	P
	Value	SD	Value	SD	Value	SD				
Clay	0.0018	0.0005	0.3539	0.0308	0.7519	0.0345	0.99	9	0.0495	<0.0001
Sand	0.0010	0.0002	0.3640	0.0200	0.7909	0.0237	0.99	9	0.0233	<0.0001
Loam	0.0004	0.0001	0.3193	0.0150	0.9375	0.0229	0.99	9	0.0151	<0.0001
Silt	0.0055	0.0014	0.2246	0.0328	0.6177	0.0313	0.99	9	0.0353	<0.0001
Sed	0.0003	0.0002	0.3836	0.0426	0.9565	0.0654	0.99	9	0.0510	<0.0001

Table4.4values of K_{τ} δ,λ , in the equation of WEP =K₁(Ws) ^{δ} (M III)^{λ} for the soil and sediment

Sed = Sediment

Reg SD= Regression Standard error

For each type of soil, the relationship between desorbed soluble P and Mehlich III available P at different water :soil ratios is presented in Figures 4.6 to



Figure 4.6 Relationship between desorbed soluble P and available P at different water : soil ratios for <u>loam</u> soil groups



Figure 4.7 Relationship between desorbed soluble P and available P at different water : soil ratios for clay soil groups







Mehlich III available P, ug/g of soil

Figure 4.9 Relationship beetween desorbed soluble P and available P at different water : soil ratio forsandyloam soil groups



Figure 4.10 Relationship between desorbed soluble P and available P at

different water : soil ratio for sediment groups

In loam soil (Figure 4.6) the relationship was illustrated using water :soil ratios: of 100, 200 and 500. For example, the desorbed soluble P measured for the loam soil groups was 0.06 μ g /g to 0.07 μ g /g at water: soil ratio of 100, 0.08 μ g /g to 0.84 μ g /g at water: soil ratio of 200; and 0.13 μ g /g to 1.11 μ g /g at water: soil ratio of 500. So using different soil :water ratios of 100, 200 and 500, the values of desorbed soluble P were measured to be 0.5 μ g /g, 0.20 μ g /g and 0.50 μ g /g at an available P of 100 μ g /g. Following a similar trend, the soil samples of loam, clay, silt, sand, sediment are shown in (Figures 4.6, 4.7, 4.8, 4.9 and 4.10) respectively. The trend of the relationship between desorbed soluble P and available P was found to increase with an increase in the water: soil ratio. In (Figures 4.6 to 4.10) there are only 3 data points. We recognize that more values of desorbed soluble P and Mehlich III available P in order to verify the straight line relationship.

The different values of the k, δ , and λ constants for the four soils and sediment are given in Table 4.4. Values were constant for each soil group and sediment and corresponded to the soil characteristics (for example clay, organic matter, etc). The maximum desorption and corresponding final P concentrations for the four soils indicate that the equilibrium concentration of P in a soil suspension closely reflects the degree of P saturation on the adsorbing surface of the soil colloids.

The results for the zero level of P are thus not strictly comparable to those for the $100\mu g$ added P/g levels of P. This appears to be more important for loam soil than for others soils. For loam soil, the variation in size of the soil aggregates, and



Desorbed Soluble Phosphorus µg/g of soil

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Figure 4.12 Relationship between desorbed soluble phosphorus and water:soil ratios for cilay soil groups.



Figure 4.13 Relationship between desorbed soluble phosphorus and water:soil ratios for silt soil groups.







Figure 4.15 Relationship between desorbed soluble phosphorus and water:soil ratios for sediment sample.

the ease with which they break down when wetted can influence the rate of desorption with time. These characteristics would cause some of the differences observed in the results for different water: soil ratios, this factor would cause some differences between the results for the water: soil ratio 100:1 and those for the higher ratio, as we observed in some cases Table 4.3. Acceptable concordance between soil and sediment data and the isotherm equation as a straight line correlation was obtained for the four soils and sediment Figures 4.6 to 4.10. However, the regressions may be critiqued for the few number of data and for closeness of the lower data point, which may be considered as one diffuse point. Nevertheless, Sharpley et al., (1981) and Schicani (1982) showed that this relationship between desorbed soluble P and Mehlich III available P is linear. Based on these study results from literature, we concluded that our data could also fitted to linear relationships.

The maximum desorption for the soils are shown in Figure 4.2. The relationship between sediment and loam soil after treatment with 100µg P shows that the sediment curve lies above the loam curve in contrast to their juxtaposition when untreated Figures 4.1 and 4.2. After a shaking time of 1h there was little increase in desorption and all curves levelled off parallel to the x axis. The relationship between soluble P release and added available P at different water/soil ratios for all the soil classes and the sediment sample are shown on a log-log scale in Figures 4.3 to 4.7.

Figures 4.11 to 4.15 show the relationship between desorbed P and available P at different water: soil ratios and for all soil groups and sediment sample.

The low extraction of the added P from loam soils is due to the low amount of P adsorbed from solution, whereas the reverse is true for the clay soils. The intermediate slopes of the silt and sandy soils can be explained in a similar manner. The relationship between desorbed soluble P and available P for different water: soil ratios is given in Figures 4.6 to 4.10. There is a linear relationship between the two variables for each soil but with different slopes. However, where extractable P is corrected for the amount of water extractable P present in the soil initially, the separate straight lines of each soil (Figures 4.6 to 4.10) converge to form a reasonably common relationship between adsorbed P and MehlichIII extractable P.

5.0 SUMMARY AND CONCLUSIONS

A study was conducted of the rate of soil P released from the soils found in the St. Esprit watershed. Four soil groups and a sediment sample were selected for the study. The amount of P released at different shaking times at different water: soil ratios was measured. Based on work conducted in this study, the following conclusions were drawn:

- 1- Phosphorous released from four soil groups and sediment sample increased with an increase in time over a range of soil samples both untreated and treated with 100 µg P /g of soil. However, different soil samples showed different amounts of P released. The amount of P released at any given shaking time was lowest in sediment samples when untreated by P. In the case of treated sediment the amount of P released was more than the loam soil group. After 3 hours shaking time the dominant clay soil group had a higher P released than for the loam, silt, sand, and sediment samples for both treated and untreated cases.
- Water-extractable P (WEP) increased sharply with increased shaking time, up to 42 minutes for both the treated and untreated cases.
 Thereafter, there was little increase in WEP with respect to shaking time. About 90% of WEP was released in less than 2 hours. A shaking time of 4 hours was therefore chosen to ensure complete P release

for soil groups and sediment samples.

- 3- The relationship between WEP and Mehlich III available P at different water: soil ratios for the soil groups and sediment samples were investigated mathematically using equation (4.1). These relationships were linear for all samples at different water: soil ratios.
- 4- Soluble P released from all soil groups and sediment sample increased with an increase of water: soil ratio. In all cases, P released was a strong function of water: soil ratio due to an increase in P diffusion/desorption from the soil and sediment sample into overlying water during the shaking period. This is in response to a reduction (by dilution) in the concentration of soluble P in water as a result of an increase in the amount of water.
- 5- The measured values of WEP and Mehlich III P for the clay soil group were greater than those for sediment and the other soil groups. This was due to the greater content of clay in the clay soil group. The small difference in the slope values of the log-

log relationship between P released and water: soil ratios reveals a consistent pattern between the different soil groups of the watershed in the increase in P release as a result of an increase in water: soil ratios.

6- The amount of P released from the soil and sediment samples depended on the shaking time, the soil groups, the amount of available P and the water: soil ratio. This study investigated mathematically the relationship between desorbed P and available P at different water: soil ratios. The graphic presentation demonstrated that the position of the isotherms shifted up as the water: soil increased. It has been shown that the equation: WEP = k₁ (W_s)⁵ (M III)^λ expresses well the relationship between WEP and Mehlich III P. The values of the constants K₁,δ, and λ for the four soil groups and sediment sample, are given in Table 4.4.

6.0 RECOMMENDATIONS FOR FUTURE RESEARCH

- The linear relationship between soluble P and extractable P from surface soil, reported in this study, has demonstrated that equation
 (3) is a good mathematical represent of variables involved. This equation could be usefully applied to soils of different characteristics relationships between these parameters.
- 2) In this study, the desorption of soluble P was considered to be a function of the Mehlich III available P at the soil surface for different water soil ratios. The upper limit of the water soil ratio was considered as 500. This was a practical necessity because otherwise the soluble P level might exceed the Mehlich III levels in the soils. More work is needed to better define the basic relationships in the procedure for the determination of soluble P transport.
- The isotherm equations depict results from laboratory investigations under precisely controlled conditions and precise shaking times. These equations can perhaps be inserted into mathematical models for the St. Esprit watershed.

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