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Sediment - Related Fluvial Transmission of Contaminants: Some Advances by 1979

R.J. Allan



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SCIENTIFIC SERIES NO. 107
(Résumé en français)

INLAND WATERS DIRECTORATE
WESTERN AND NORTHERN REGION
REGINA, SASKATCHEWAN, 1979



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This document was prepared as a presentation for the Water Survey of Canada Sedimentation Seminar held in Calgary, Alberta, February 1979. The fact that much of the information used came from Europe and eastern Canada emphasized the deficient data base in this area of research in western Canada.

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**INLAND WATERS DIRECTORATE
WESTERN AND NORTHERN REGION
REGINA, SASKATCHEWAN, 1979**

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Cat. No. En 36-502/107

ISBN 0-662-10675-X

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Abstract

Suspended sediment can be a major transport mechanism for nutrients and contaminants in drainage systems. Bottom sediment pollution has been extensively studied, but until recently suspended sediment has seldom been chemically analyzed. Sufficient suspended sediment could not be collected for detailed nutrient and contaminant analysis until the advent of land-based continuous flow centrifuges. This report describes the evolution of this area of investigation and the stage of development reached in Canada as of 1979. Problems of sampling and analytical requirements are discussed. Examples are included of the types of results being obtained by the main Canadian investigators. Relationships between suspended and bottom sediment chemistry are described. Interaction between those involved in sediment surveys for engineering purposes, water quality monitoring, and research into drainage system contaminant transmission is advocated. Such interaction could rapidly extend existing knowledge in this area, critical to pollution control and environmental basin management.

Résumé

Un des principaux mécanismes de transport des substances nutritives et des contaminants dans les systèmes de drainage peut être leur transport sous forme de sédiments en suspension. La pollution des sédiments de fond a fait l'objet de nombreuses études, mais ce n'est que récemment que les sédiments en suspension ont pu être vraiment soumis à des analyses chimiques. Il était auparavant impossible de recueillir suffisamment de sédiments en suspension pour étudier en détail leur teneur en substances nutritives et en contaminants, ce qui n'est plus le cas depuis qu'il existe en laboratoire des centrifugeuses à écoulement continu. La présente étude décrit l'évolution de ce domaine de recherche et les réalisations canadiennes jusqu'en 1979. Elle traite des problèmes d'échantillonnage et des exigences des analyses, fournit des exemples de résultats obtenus par les principaux chercheurs canadiens, et décrit les rapports de nature chimique qui existent entre les sédiments en suspension et les sédiments de fond. On y insiste également sur la collaboration des différents groupes chargés des études techniques des sédiments, du contrôle de la qualité des eaux et des recherches sur le transport des contaminants dans les systèmes de drainage. Une telle collaboration permettrait d'élargir rapidement le champ des connaissances actuelles dans un domaine qui est critique pour le contrôle de la pollution et la gestion environnementale des bassins.

Sediment - Related Fluvial Transmission of Contaminants: Some Advances by 1979

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INTRODUCTION

Bottom materials have been used extensively to assess riverborne and airborne heavy metal pollution of rivers, lakes and reservoirs. Reviews of the Canadian (Allan, 1975) and West European (Förstner and Müller, 1976) experience are available. Numerous references to bottom sediment contamination in lakes, reservoirs, estuaries, bays and oceans are quoted. Early study of bottom sediment contamination was based on one or two types of established chemical extraction. Today the field of bottom sediment chemistry, for which sample size is no problem, emphasizes study of forms of metals and their biogeochemical, regeneration pathways (Williams and Mayer, 1972; Förstner, 1976; Golterman, 1976; Förstner *et al.*, 1978; Jackson, 1978). Bottom materials permit differentiation of degree of pollution far better than water analyses (Förstner and Müller, 1976) and provide chemical data on the bed load at rest. By sampling at widely spaced intervals (years), knowledge of bed load transmission can also be obtained (Thomas *et al.*, 1975). In contrast with the well-developed literature on bottom sediment pollution, knowledge of suspended sediment pollution chemistry is very limited.

Contaminants transported primarily in or sorbed onto the sediment phase fall into three categories: (1) nutrients, mainly phosphorus and carbon and to a lesser extent nitrogen; (2) heavy metals, including some of the more toxic such as Hg, As, Se, Cu and Zn; and (3) organochlorine residues. In spite of this suspected significance of suspended sediment chemistry to pollutant transport and thus to basin management, however, no texts cover the subject exclusively. Even the best textbooks on sediment transport in alluvial systems (Bogárdi, 1974), sedimentation engineering (Vavoni, 1975), and sediment transport technology (Simons and Sentürk, 1977) do not include sections on sediment chemistry. A major yet limited source of information is provided by a workshop organized by the International Joint Commission (IJC) to review the state of the art in the area of fluvial transport of sediment-associated nutrients and contaminants (Shear and Watson, 1977). The workshop was held in Kitchener, Ontario, in October, 1976. Only a few of the 18 presentations directly concerned the chemistry of suspended sediment loads. The attendees concluded that there were large gaps in the existing knowledge and emphasized the need for study of

transport processes, sediment-water interactions, and bio-availability and storage of nutrients and contaminants after they enter the drainage system.

The role and significance of suspended sediment for nutrient and contaminant transport in rivers are partly under-researched because of historical disciplinary divisions. Suspended sediment is mainly studied by engineers, sedimentologists and geomorphologists who are primarily concerned with engineering and physical aspects such as the lifetime and power capacity of reservoirs, shoreline erosion, downstream erosion or sedimentation, siltation of deltas and waterways, effect of sediment loads on bridges and turbines, and theoretical studies of sediment transport and stream bed topography. Suspended sediment chemistry is only now entering the field of interest of these professionals who are becoming more directly involved with environmental impact. A second group of professionals peripherally associated with suspended loads are water quality chemists. In water quality monitoring, the water analyzed is often a filtrate that has passed through a 0.45- μ m filter or an acidified nonfiltered sample. These measurements provide useful comparisons within and between rivers but only limited knowledge of geochemical transmission mechanisms. Water quality staff are usually chemists rather than geochemists, and thus they are concerned with the solution phase rather than the total biogeochemical mixture of water, which includes mineral sediment, organic acids, organic material and amorphous oxides. Also, a water chemist focuses on water chemistry from an industrial, urban and agricultural resource viewpoint, and in many cases, these uses are governed by solution chemistry, since the suspended sediment is removed before use by settling and filters. Water chemists today, however, are involved with environmental management and protection and thus with contamination of rivers, pathways of contaminant transport, and finally, the chemistry of the suspended sediment phase.

In the last two years, this vacuum has begun to be filled in response to requirements about key controls of river transmission of chemicals as an input to realistic drainage basin and lake or reservoir loading models. For example, recent information, unlike earlier International Joint Commission statements drawn from inadequate data, indicates that the bulk of phosphorus flux to the lower

Great Lakes is from non-point sources and is largely associated with fluvial suspended sediment (Baker and Kramer, 1975; Ongley, 1976; U.S. Army Corps of Engineers, 1975; Ongley, 1978; Thomas and McMillan, 1978; Thomas, 1979). European data indicate that most heavy metal transport is also associated with sediment flux (DeGroot and Allersma, 1975; DeGroot, 1976). In Canada, although suspended sediment from major rivers such as the St. Lawrence (Anglejan and Smith, 1973) has been studied with respect to particle size, organic content and major element chemistry, attempts are only now being made to study temporal and spatial trends in the St. Lawrence suspended sediment contaminant chemistry (R.L. Thomas, Canada Centre for Inland Waters, personal communication). Some suspended sediment total nutrient (C, N, P) and total major and trace element chemistry is available for the Mackenzie and Porcupine River systems of the Northwest Territories and Yukon (Brunskill *et al.*, 1975; Wagemann *et al.*, 1977) and the mouth of the Mississippi River (Presley and Trefry, 1978).

Additions of nutrients and contaminants to rivers and thus to suspended sediment come mainly from: (1) agricultural point and non-point sources; (2) urban point and non-point sources; and (3) industrial point sources. Studies of the relation of suspended load chemistry to agricultural runoff (Schulte and Tokarz, 1977), urban runoff (Marsalek, 1978) and industrial runoff (Jackson, 1978) are rare. Because of lack of integrated land use and related suspended sediment chemistry studies, the links between the two in terms of nutrient and contaminant transmission are little understood. Furthermore, any realistic basin modeling of transmission of these substances requires both spatial and temporal data for calibration and long-term prediction purposes. Water management strategies for river basins releasing nutrients and contaminants to rivers, lakes, reservoirs and oceans will depend largely upon the availability of reliable data of this type.

THE PROBLEM OF SAMPLING

The prime reason why bottom material has been the most extensively studied to date is the relative simplicity with which it can be collected and the larger sample size, even with a coring device, which can be obtained for analysis. A variety of grab samplers such as Ekman, Ponar, Shipek and double-Shipek are in regular use. Coring devices such as single-Benthos, triple-Benthos and Mackereth are also extensively used. Recently, a very sophisticated corer has been developed at the National Water Research Institute (NWRI) (Williams and Pashley, 1978) for sampling extremely loose or flocculated bottom sediment. Sampling bed load directly is still a very questionable procedure, especially

for material of less than 100 μm . However, the bed material can be loosely taken as representing the bed load sediment at rest.

Suspended sediment chemistry is only now beginning to be appreciated in spite of sampling problems. Reliable analyses for nutrients and contaminants require a considerable volume of representative material. Not only must the quantity of material be relatively large but it must reliably represent the chemically active suspended sediment component, usually particle size less than 20 μm and thus part of the "wash load," a fraction not usually included in discharge-sediment-load predictive modelling (Culbertson, 1977).

The finest particle sizes are the most critical and coarse filtering techniques are not viable, as most of the active fraction is lost. The use of fine filters generally limits sample size, with concomitant clogging of filters and other problems. Often very large quantities of water must be filtered, precluding this technique for routine field use. Accordingly, the historic (pre-1975) situation has been the collection of a few samples as part of larger investigations of sediment load and particle size distribution. A limiting factor in most particle size distribution analysis (PSDA) is the considerable amount of sediment required. It follows that, using conventional collection techniques, an intensive research program such as that required for modelling purposes is severely handicapped by the inability to collect sediment information distributed in time and space.

Historically, suspended sediment has been collected in Canada and elsewhere to determine sediment load with a secondary objective of determining the particle size distribution. Textbooks provide detailed descriptions of samplers and sampling methods used (Bogárdi, 1974; Vavoni, 1975; Simons and Sentürk, 1977). Methodology tries to take into account the vertical and lateral distribution of suspended load. Vavoni, however, notes that silt and clay are generally uniformly distributed over the depth of the stream, and because these are the main active components of the sediment, vertical integration is apparently less critical than lateral changes. For lateral studies, concentration at each stream vertical is determined from depth- or point-integrated samples. Tributary streams can have particularly marked effects because of lack of mixing for some distance downstream from a confluence.

Up until 1940, sediment surveyors were still developing their own sample methods. There was little calibration and samples were taken under widely varying field conditions. Early on, an open bucket dipped samples from the stream. Then a bottle that could be opened or closed at

any depth was used. Later horizontal traps were employed. All of these devices collected small samples. Meanwhile, depth-integrating and point-integrating samplers were developed. The former fills as it is lowered and raised to the surface on a vertical transit. The latter fills while suspended at a selected depth. There are now a number of established criteria for design and use of sediment samplers, most of which rely on pint milk bottles as containers. All point-integrated samplers are similar in that they collect a fixed volume, they are not flow through, and the suspended sediment collected is often insufficient for PSDA and chemical analysis. The use of this type of sampler has simply precluded the study of suspended sediment chemistry. Pumping samplers have been developed and designed to obtain continuous records by sampling a fixed point at timed intervals. This removes the need for an operator, but the sediment quantity in each sample is still too small for serious chemical study. Another problem with automatic samplers is the time that elapses before collection of the sample, often days or longer, and sorption-desorption reactions or metal-humate precipitation (Jonasson, 1977) may complicate subsequent interpretation.

The solution is, as usual, obvious once it has been found. What is needed is the ability to operate at remote sample sites a continuous flow centrifuge of the type used on research vessels to obtain samples of the suspended material in oceans.

Such a procedure was first developed as a land-based operation by Dr. R.L. Thomas at Canada Centre for Inland Waters (CCIW). The International Joint Commission's interest in non-point source pollution of the Great Lakes from land use activities created the necessity to test and establish a viable technique (Shear and Watson, 1977). The system uses two Westphalia continuous flow separators mounted in a Ford LN 750 truck (Thomas and McMillan, 1978). Sampling of the river is carried out using a Dodge 3/4 ton vehicle; the containers are filled by direct pumping at the stream site, with subsequent transfer to the centrifugation system. Standard sample size is 600 L or multiples thereof. Recovery of suspended sediment, as determined by pre- and post-filtration, is 90% and 95% effective for the two centrifuges at a standard flow rate of 6 L/min. Particle size determination showed that as much as 70% of the total solids recovered were finer than 12ϕ ($0.2 \mu\text{m}$). This system is fairly expensive. The centrifuges alone are in the \$9000 range but the trucks, pumps and auxiliary equipment result in a total operational cost of some \$70 000. The only system of this configuration is at Canada Centre for Inland Waters; it was assembled there and used extensively in the PLUARG program.

A similar, but less expensive, unit has been developed at Queen's University, Ontario, by Dr. E.D. Ongley. This

unit, designed on the basis of the CCIW experience, uses Swedish MAB-102 industrial continuous flow clarifiers. The unit can be assembled on a trailer at a cost of some \$10 000 if only one centrifuge is used. This system removes $>0.45 \mu\text{m}$ material with 95% to 98% efficiency for mineral sediment with decreasing efficiency as organic content becomes predominant. Water can be transported to the centrifuges in 600-L containers or can be pumped directly to the centrifuges using an aqueous sample splitter. This unit has been used routinely in detailed, intensive studies of suspended sediment chemistry in two rural catchments in southeastern Ontario (Ongley, 1978). Presently, Dr. Ongley is designing a similar system¹ using a Swedish MAB-103 clarifier for use in a federal-provincial study of mercury transport in the Wabigoon-English River system of north-western Ontario.

To plan operations using these centrifuges, calculations are made with respect to the time required to centrifuge out sufficient suspended sediment at a site for particular analyses. For example, some 35 g of solids is required for PSDA, total and extractable heavy metals, organic content, mineralogical analyses and organo-chlorine scans. With a median suspended sediment load of 20 mg/L, some 5 h of centrifugation is required to obtain 35 g of sample, assuming 100% efficiency at a flow rate of 6 L/min.

Time of sampling is also critical, as will be discussed later. If one site is being studied in detail, most samples are collected on the rising hydrograph and in detail during peak spring flows. During low flow, sample intervals can be further apart. Sampling should often be event-related. If a large number of streams entering a large lake are to be sampled, such as in the PLUARG studies, only sites near their mouths are sampled during seasonal flow regimes. There are many combinations once the equipment is available. One valuable technique used by Ongley and Thomas (unpublished study) is to follow the same body of water down a river system, at least as far as is possible with storage features. Such serial time sampling is of great importance because it permits downstream monitoring of sorption-desorption and other biogeochemical interactions. In a set of hydrologically synoptic samples, serial sampling may be done in each of the major flow regimes: (1) spring runoff, (2) summer low flow and (3) fall rains. In the spring, suspended sediment is usually coarser and mainly mineral in composition. It may be expected to reflect the bedrock and soil geochemistry of the catchment area. The lower quantities of organics and active mineral fractions are still able to transport contaminant residues flushed from the drainage area. Contaminants in spring are usually non-point source in origin, although spring flood resuspen-

¹ Patent applications have been made for this recovery system.

sion of heavy metals such as mercury can occur in river systems, such as the Wabigoon of northwestern Ontario, which are already contaminated from point sources (Dr. T.A. Jackson, NWRI, Western and Northern Region, personal communication). The passage of organic-rich algal suspended loads can act as a sink and transport mechanism for point source inputs (Cahill, 1977), (e.g., during low-flow summer months when algal growth builds up the organic content of the suspended load). In the fall, the contaminants can then be returned to the bottom sediments or released into solution on the death and decay of the algal cells. It is then of critical importance to be able to fractionate the suspended load into mineral and organic components.

THE PROBLEM OF ANALYSIS

Detailed chemical analyses of sediments and interpretation of the results make up a broad field of applied research found predominantly in the geochemistry and soil chemistry literature. For many years, geochemists and soil chemists have developed partial dissolution or selective dissolution analysis (SDA) techniques to identify forms of nutrients, heavy metals, and pesticides in soils and sediments. In conjunction with these types of investigations, there is a need for knowledge of the organic biogeochemistry of sediment, sediment mineralogy, especially the layer silicate mineralogy, and the sediment exchange-sorption potential. The basic text used in laboratories engaged in such activities is *Soil Chemical Analysis—Advanced Course* (Jackson, 1967), although anyone seriously involved in such research must rely on a large literature base provided in soil science journals. Relevant information is not normally found in the pure geological, sedimentological or chemical literature. The analytical techniques that have evolved in the study of sediment chemistry are aimed at elucidating the forms and thus the transport pathways and biogeochemical cycles of nutrients and contaminants in drainage systems. Much of the nutrient work to date has focused on phosphorus, rather than carbon and nitrogen, and only phosphorus is used here as an example.

Soil phosphorus fractionation schemes, developed over many years by Jackson and his colleagues at the University of Wisconsin, have for some years been applied to lake sediments. There are few experts in this field. The scheme for fractionation of phosphorus into its three major forms (Fig. 1)² in lake bottom sediments has been best developed by Dr. J.D.H. Williams of the National Water

Research Institute. The fractionation technique separates phosphorus in sediment into apatite (A-P), organic (O-P) and non-apatite inorganic (NAI-P) fractions.

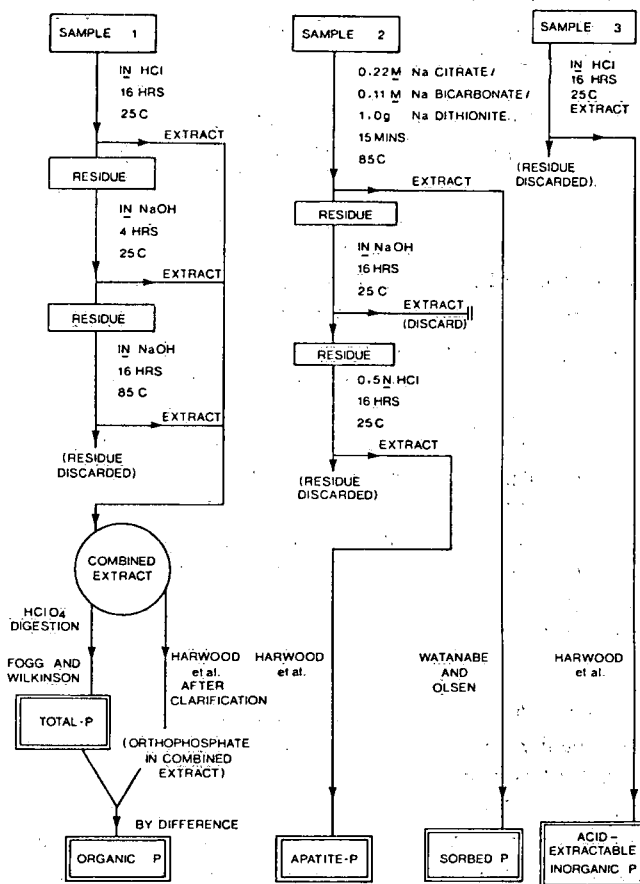


Figure 1. Flow sheet for phosphorus form fractionation in sediment (Williams, 1973).

The A-P is terrigenous in origin. It is not available for biotic growth, at least in the geochemical environment normally associated with rivers and lakes and not in the time periods during which it is associated with the water phase. The significance of A-P is in its proportion in the total particulate phosphorus in unfiltered river water. Because of historic modelling constraints, total P is often used to estimate total phosphorus loading by rivers to lakes and reservoirs. In some cases, what may be of equal significance is the loading of potentially non-bio-available or non-recyclable sediment-related phosphorus. A good example of the problem occurs in some of the fiord valley lakes of eastern British Columbia. Volcanic bedrock in the area can be rich in apatite. On erosion this forms a major portion of the particulate and probably $<0.45\text{-}\mu\text{m}$ particulate fraction of the rivers draining into lakes such as in the Okanagan Valley. Estimates of T-P loading can be erroneously used and interpreted unless one is aware that much

² Reference to data must be to the original publication given in parentheses for each figure or table. Permission to reference unpublished data should be obtained from the respective source.

of the phosphorus load is in the inert A-P form. Concern with measurement of the true bio-available loading of phosphorus led to the application through PLUARG of the phosphorus fractionation technique to suspended loads of rivers draining to the Great Lakes from the Canadian side (Thomas, 1979).

The O-P consists of all phosphorus in organic forms. In lakes and rivers the organics may be derived allochthonously from eroded and leached soils and other surficial deposits. In many cases, however, the organics are largely autochthonous or produced *in situ* by biotic growth. Usually this involves phytoplankton primary productivity (algal blooms). Soluble phosphorus, orthophosphorus, is built into algal body cells. In the filtration of river sediments, both dead and living algae are removed along with coarse allochthonous organics. On death of the algae, phosphorus may be released directly to the water or the algae can be bacterially degraded to orthophosphorus. The O-P, however, is not considered to be immediately available for biotic growth but is a pool of potentially available P and is often a fraction enhanced by cultural activities—sewage effluent and agricultural runoff—because of the effect of these on algal productivity.

The NAI-P or CBD-P (citrate-bicarbonate-dithionite P) is the readily bio-available phosphorus fraction. The CBD-P is slightly less than the NAI-P but this difference is usually insignificant. The NAI-P or CBD-P consists of orthophosphorus sorbed or occluded by and in clay-organic-amorphous iron/aluminum hydroxide complexes. It can be released under differing redox conditions. It is the fraction of phosphorus that algae can directly extract from sediment. The (CBD-P) (Fig. 1) is the best approximation by a quick chemical extraction method to the fraction that algae can extract if permitted to use sediment as a growth substrate. It should be noted here that details of the procedures in Figure 1 are continually changing. The commercial cost of fractionation of one sample according to this technique was quoted as \$75 in 1977. Alternatively, an experienced technician can process some 300 samples in about a year. Thus sediment phosphorus form analysis, although critical to phosphorus loading and cycle interpretations, remains a research activity carried out in Canada primarily by the National Water Research Institute and a few university staff.

Analyses of suspended sediments for heavy metals can be even more complicated than those outlined for phosphorus. In many river systems polluted by heavy metals, a suite of metals must often be analyzed. The forms in which these metals are held by the suspended and bottom load are very significant to processes of downstream transmission, eventual sedimentation, and release under changing

physico-biogeochemical conditions. Historically, toxic metals have been analyzed for total content by complete dissolution of the sediment sample with strong acids. This approach gives clues concerning total transport but is of limited value if the aim is to determine contaminant transmission pathways and biogeochemical cycles. The suspended sediment quantities collected by Thomas and Ongley are still such that following PSDA, phosphorus fractionation, and loss on ignition, metal analysis has to be limited to available and total acid extractable metals. Another procedure involves sediment-heavy metal extraction; it has been used by Dr. T.A. Jackson, National Water Research Institute, Winnipeg, to study mercury in the bottom sediments of the contaminated English-Wabigoon River system (Fig. 2). The seven extracts can of course be analyzed for a suite of heavy metals and for other parameters, although the study of a few dozen sediments would occupy a highly skilled technician for a full year. This sophistication of investigation can never become routine but is the level of study required to resolve the mechanisms of transmission in specific problem rivers.

At the Sediment Research Institute of the University of Heidelberg, extractions similar to those of Jackson are being used by Professors Förstner and Müller to study heavy metal forms in sediment of polluted European river systems including the Rhine, Ems and Elbe. Förstner uses eight extractions of the sediment to remove specific chemical fractions (Table 1). Before extraction, however, the sediment is usually separated by PSDA into six fractions from 0.2 μm to $>63 \mu\text{m}$ in size. Thus there is a total of 48 (8 x 6) extracts. These extracts are analyzed for a heavy metal suite such as Hg, As, Zn, Pb, Cd, Cu and Se, giving a total of 336 individual analyses from the original one-

Table 1. Extraction Techniques Used by Förstner at Heidelberg (Förstner *et al.*, 1978)

Extraction method	Extracted phase
H ₂ O	Easily soluble fraction
0.2 N BaCl ₂ -TEA pH 8.1	Exchangeable cations
0.1 N NaOH	Humates, fulvates
Acidic cation exchange	Carbonate fraction
0.1 N NH ₂ OH · HCl + 0.01 N HNO ₃	Easily reducible fraction (Mn-oxides, amorph. Fe-oxides)
30% H ₂ O ₂ + 1 N NH ₄ OAc	Organic residues + sulphides
1 N NH ₂ OH · HCl + 25% acetic acid	Moderately reducible fraction (hydrous Fe-oxides)
HF/HClO ₄ -digestion	Inorganic residues

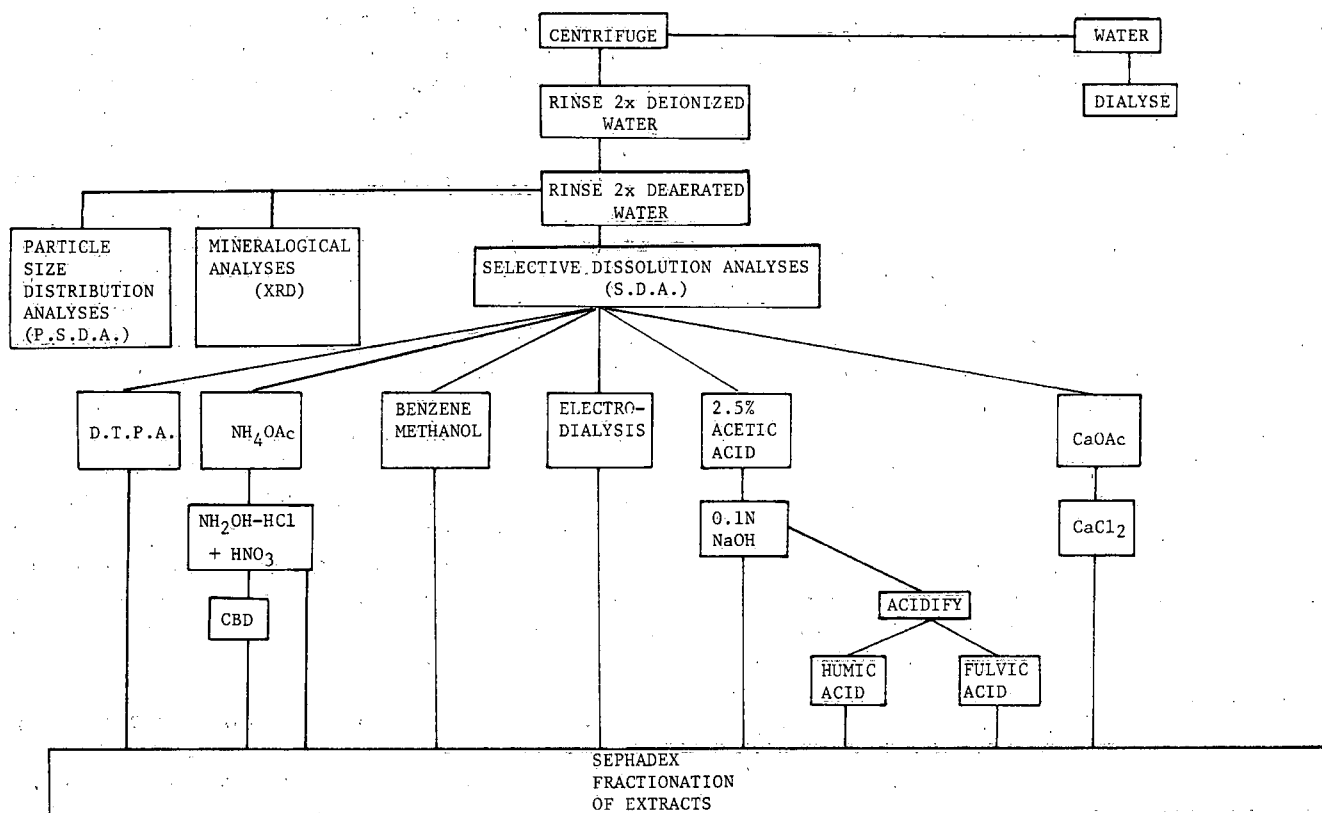


Figure 2. Flow sheet for mercury pathway analysis in sediments (provided by Dr. T.A. Jackson, National Water Research Institute, Western and Northern Region). D.T.P.A. = 0.005 M diethylenetriaminepentaacetic acid. CBD = citrate bicarbonate dithionite.

sediment sample. In Wilton Creek (Ongley, 1978), ten samples of suspended sediment were collected during the spring runoff peak. Analysis by Förstner's fractionation technique could generate 3360 individual metal determinations. This could keep a complete geochemical laboratory with several technicians busy for several months, which is exactly the case when such investigations are commenced.

The various extractants described remove heavy metals in different phases in the sediment. Förstner (Table 2) provides a summary of geochemical metal associations in sediments. Separation of these phases is important in the Rhine, where toxic metals of anthropogenic origin are found sorbed onto bottom sediments or as carbonate precipitates (Förstner, 1977) and are thus subject to recycling under changing chemical conditions.

The organo-chlorines are the third and perhaps the most insidious group of contaminants of drainage systems. The volume of sample required for analysis plus the expensive capital equipment needed usually limits the number of analyses. Thus, there are even fewer examples of comprehensive studies for these contaminants than for those mentioned earlier. Water analyses for organo-chlorine

residues are made routinely by water quality agencies but quantities determined are often beneath detection, which raises some doubt concerning whether they are present or not. Many of the most persistent non-ionic pesticides, however, are sediment-associated (Pionke and Chesters, 1973), and unless bottom and suspended sediments are collected and analyzed, water analyses alone are insufficient to explain transmission processes. Organo-chlorine residues associated with mineral and/or organic solids are those of pesticides with low solubility and high persistence; they include lindane, α -BHC, and DDT and its metabolites. Anionic acid herbicides such as 2,4-D are only sorbed by sediments in small amounts, are thought to readily desorb in aqueous systems, and are normally found in the water phase as opposed to the suspended sediment-bottom sediment phases (Pionke, 1977). Chacko and Gummer (1978) showed this to be the case for 2,4-D released to the Red River in Winnipeg sewage effluents. Of importance is the disappearance of pesticide residues as opposed to the persistence of heavy metals. For example, 2,4-D can be lost by biodegradation, photolysis, volatilization and hydrolysis. Thus, to be considered for transmission study in fluvial systems, a pesticide must be widely used and should be highly toxic and/or persistent (Pionke, 1977). Polychlorinated biphenyls

(PCB's) are a related type of contaminant in drainage systems; they are sediment-associated and readily detected in suspended sediment (Frank, 1977) and bottom sediment (Frank *et al.*, 1978) in the Great Lakes drainage basin.

Table 2. Metal Associations in Sediment (Förstner, 1976)

Mineral detritus (mainly silicates)		Metal bonding mostly in inert positions
Heavy metal -hydroxides -carbonates -sulphides		Precipitation as a result of exceeding solubility product in the water course
Clay minerals (sorption)	pH	Physico-sorption (elec. attraction) Chemical sorption [exchange H^+ in $SiOH$, $AlOH$ and $Al(OH)_2$]
Bitumen, lipids Humic substances Residual organics	pH	Physico-sorption Chemical sorption ($COOH^-$, OH^- groups) Complexes
Hydrous Fe/Mn- oxides	pH	Physico-sorption Chemical sorption Coprecipitation by exceeding the solubility product
Calcium carbonate	pH	Physico-sorption Pseudomorphosis (supply and time) Coprecipitation

Finally, effective load versus total load of a contaminant must be considered. A river with high suspended sediment concentration of low contaminant concentration relative to the water phase may contribute more to total loading than a river with low suspended load of high contaminant content. Thus, on a weight per weight basis, concentration of 2,4-D may be higher in the suspended sediment, but because of the low suspended sediment concentrations, most 2,4-D is moved in the aqueous phase (Chacko and Gummer, 1978).

EXAMPLES AND INTERPRETATION

River Regimes and Sediment-Contaminant Chemistry

Contaminated rivers, whether the Saskatchewan or the Rhine, have three basic geochemical regimes: catchment,

contamination and estuarine (Jonasson and Timperley, 1975).

The first regime is the catchment or source of much of the suspended load that is transported by the river system. The river collects its natural background load of nutrients and heavy metals from geological sources in its headwaters. Theoretically, there should be no contaminants, but long-range transport of contaminants and long-range effects of acid rain have already affected many pristine areas. Nevertheless, the geology of the enclosing bedrock and soils of the catchment area determine the basic chemical and, to a large extent, physical nature of the suspended load (Brunskill *et al.*, 1975). Natural contamination by nutrients is usually confined to low-lying fertile plains such as the Prairies, although as noted earlier, apatite phosphorus can predominate natural phosphorus loads in mountain areas such as southern British Columbia (Williams, 1973). Natural heavy metal contamination related to mineralization is widespread, and many elements including Hg and As are elevated in natural bottom sediments (Allan, 1975) or suspended sediments (DeGroot and Allersma, 1975).

The second is the contamination regime or the river length along which occur all human activities involving pollution from industrial, agricultural and urban domestic sources. Usually, nutrient, toxic metal and pesticide contributions to rivers from these cultural sources far outweigh any input of "natural" origin. Relatively clean sediments entering the contamination regime of a river may rapidly acquire a pollution load from both point and non-point sources. The sediments may become trapped in sedimentation traps which today are often man-made (reservoirs). The effect is well developed in the Rhine River (Fig. 3) where progressively increasing heavy metal concentrations develop downstream in the clay size fraction of the bottom sediments. Chemistry in the contaminated regime of rivers can be complex. For example, in the natural state, heavy metals have distinct geological associations or correlations but when a metal is derived solely from an industrial source, interrelationships and correlations begin to fail (Fig. 4) or become more complex (Förstner, 1977). Furthermore, in the contamination regime, changes occur in the phases in which contaminants are held in sediments. In Rhine sediments, the contaminants are concentrated in the humate, hydroxide and carbonate fractions (Fig. 5), and under future changing chemical environments, release and recycling may occur.

The third river regime is made up of the distributary, delta and estuarine zones. This regime may appear irrelevant except at shorelines, but the occurrence of large lakes or reservoirs results in internal estuary development at many

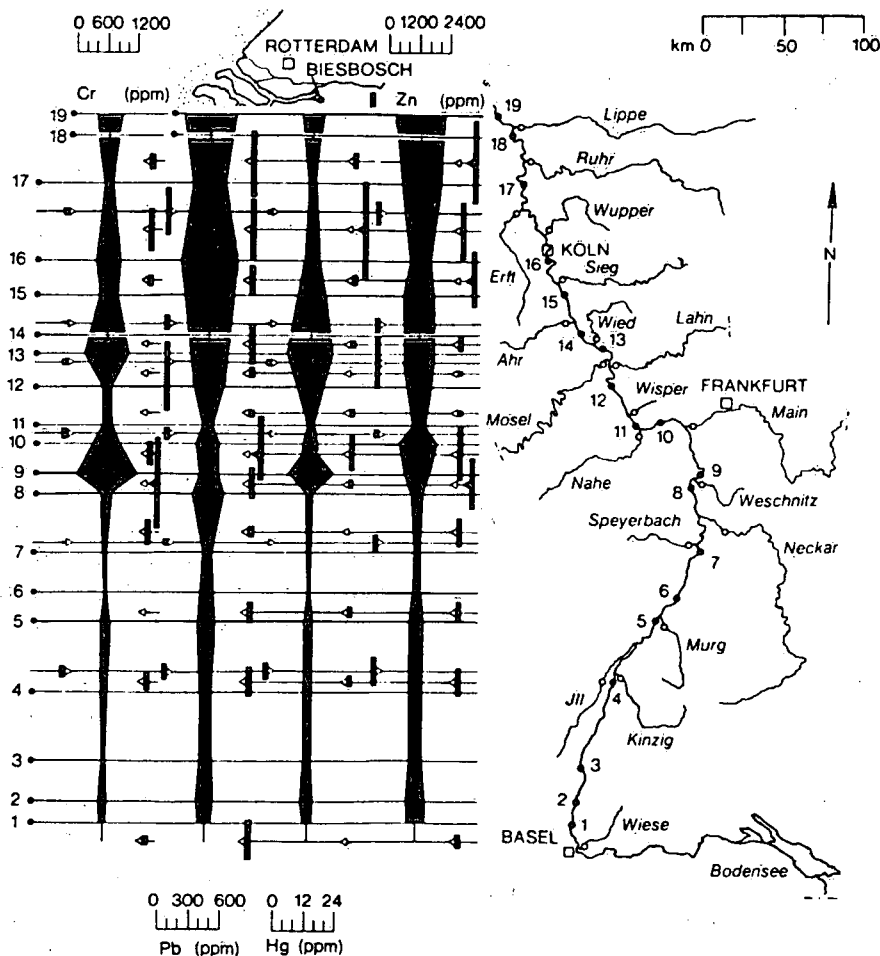


Figure 3. Heavy metal concentration in the pelitic fractions of Rhine River bed materials (Förstner and Müller, 1976).

points in a river system. For example, in western Canada most of the major rivers in the region terminate in large

freshwater deltas. Examples include the Saskatchewan River delta in Cedar Lake, the Red River delta in Lake Winnipeg, the Peace-Athabasca delta in Lake Athabasca as well as small deltas such as that of the Qu'Appelle River in Pasqua Lake, Saskatchewan, and even smaller examples. Delta sediments may be rich in sulphide-sulphur because of excessive plant growth and decay. Many heavy metals such as Hg, Zn and Cu are firmly fixed as metal sulphides and may thus accumulate in delta sites. If the water level drops, exposing the delta, oxygenation of the sediment may cause the release of the metals. River hydrographs in the Prairies can be particularly favourable for such complex precipitation-solubilization cycles of this type.

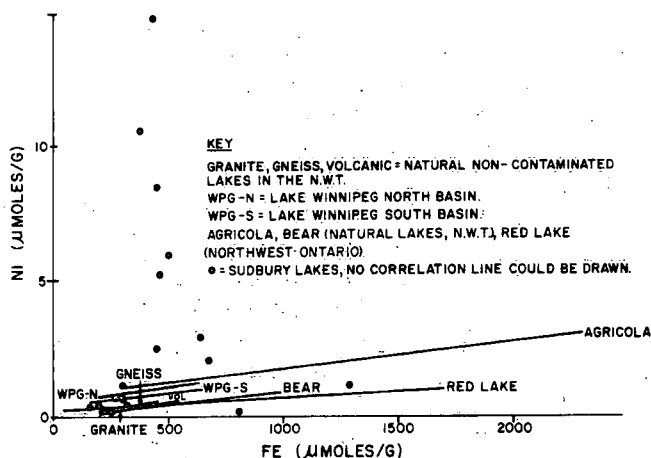


Figure 4. Linear correlation plots for nickel versus iron in lake sediments in Canada (Allan and Brunskill, 1976).

Nutrient Chemistry of Suspended Loads

Traditionally, the trophic status of lakes or reservoirs has been related to the loading of phosphorus to lakes. Certainly this is the case with naturally oligotrophic lakes influenced by increased cultural inputs of nutrients. Re-

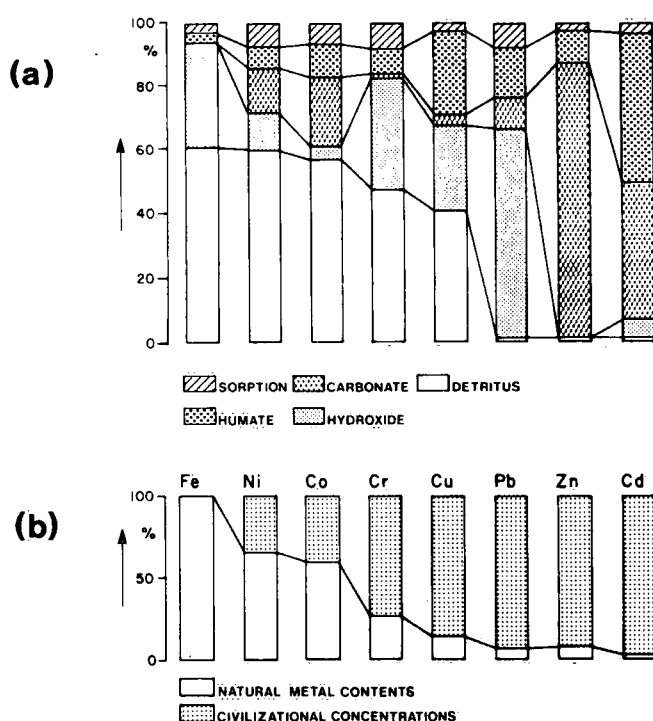


Figure 5. Distribution of (a) bonding types and (b) sources of metals in Rhine River bottom materials (Förstner, 1976).

cently, some evidence has appeared to indicate that in hypertrophic situations, the interrelationships of phosphorus and nitrogen, rather than phosphorus alone, play a role in determining mean summer phytoplankton biomass (Liao and Lean, 1978). Nevertheless, knowledge of nitrogen sediment chemistry (Logan, 1977) and nitrogen cycles is in a relatively primitive state compared with that of phosphorus, which has received the most study over the past decade. Accordingly, the examples discussed here are restricted to phosphorus chemistry of sediments.

Surprisingly, even with the extensive efforts put into study of phosphorus loading and chemistry, questions concerning the exact bio-available content of phosphorus in a river are still largely unanswered and are only now receiving attention (Thomas and McMillan, 1978; Thomas, 1979; Ongley, 1978). Renewed debate has been generated by the PLUARG studies of the Laurentian Great Lakes (IJC, 1978). The problem is that most measurements of phosphorus loading are based on total phosphorus content of river water determined on an acidified sample, including both the suspended and aqueous phases. Alternatively, measurement of soluble phosphorus loading can be made on a filtered sample. Neither method provides a true measure of the biologically available phosphorus load.

To determine the bio-available phosphorus loading in suspended sediment loads, one must first collect sufficient samples for analyses of phosphorus forms and, secondly, have a reliable and proven method of separating phosphorus into the fractions required for accurate interpretation. These requirements are met by the land-based centrifuge systems developed by NWRI and Queen's University and by the techniques developed by NWRI for bottom sediment phosphorus fractionation.

The situation has been studied in detail in two rural stream basins in southeastern Ontario, which are drained by Wilton and Millhaven Creeks (Ongley, 1978). The areas of the basins are 132 km² and 175 km², respectively. Wilton Creek, which was more extensively studied, reflects the rural agricultural situation modified by nutrient atmospheric loadings and is the example used here. Sampling took place on Wilton Creek at four sites, separating the basin into units of characteristic contiguous land uses and fluvio-sedimentary structures. At Queen's University, sampling was event-oriented and was initiated in response to rising water levels indicated by a Telemark water level recorder at the site. As outlined by Ongley (1978),

the scientific objectives of the sampling and analyses were to assess;

- (1) particle-size distributions of suspended sediment within and between storms so that the phenomenon of sediment exhaustion could be related to changes in sediment chemistry;
- (2) the role of channel storage/remobilization by particle-size classes in order to assess the importance of transport continuum down the fluvial system;
- (3) the mineralogy of sub-sieve fraction for a selection of runoff events;
- (4) the role of organic material in flux of phosphorus and trace metals;
- (5) the role of sediment in the transport of phosphorus;
- (6) the role of sediment in the transport of contaminant trace metals; and
- (7) the flux of selected anions.

Practical objectives which derive from these were:

- (1) a better understanding of the spatial and temporal characteristics of sediment-related nutrient and contaminant transmission in fluvial systems, essential for dynamic modelling and for predictive capability of the behaviour of pollutants in the water environment; and
- (2) development of monitoring strategies to optimize data collection for those parameters not normally included in existing surveillance programs but which are now recognized as having potential or proven environmental impact.

A centralized centrifuge operation with mains power was employed. The centrifuge flow rate was 4 L/min. Variations in line voltage can influence centrifuge efficiency. Lower efficiencies occur when total suspended solids are extremely low (0-10 ppm) and during summer operation when organic matter makes up most of the suspended load. As a result, organic matter was under-represented. Laboratory tests of subsieve mineral sediment showed that recovery efficiency was dependent on solids concentration for suspensions of less than 100 ppm at flow rates of 6 L/min. Reduction of flow rate to 4 L/min in 1978 produced recovery efficiencies consistently in excess of 90% during the spring, but again during the summer these declined because of a high proportion of organics and low sediment concentrations.

The problem of efficient organic solids recovery is very important in the role of organic solids as transport media for nutrients, certain trace metals, and especially for organo-chlorine contaminants. One aspect of this is the omission from transmission studies of the growth, decay and flux of mats of filamentous algae (predominantly *Cladophora*) as well as the fine-grained sediment captured in these mats. A limited (in time and space) biomass survey was conducted in Wilton Creek and the organic-sediment complex analyzed for phosphorus and trace metals. Results (Petticrew, 1978) showed that the *Cladophora*-sediment complex accounts for some 2.2% of the annual sediment load in Wilton Creek. The unmeasured *Cladophora*-sediment complex undoubtedly may comprise a very significant amount of the suspended solids load during summer, fall and winter. Studies planned for 1980-82 on the Bow River in Alberta may resolve some of these questions as they relate to nutrient flux in larger rivers (Exner, 1977).

All trends reported here employed an average of the four Wilton Creek sites. The suspended solids ($>0.45 \mu\text{m}$) concentration trend for Wilton Creek, as defined by depth-integrated sampling, shows maximum values of $>180 \mu\text{g/L}$ in the spring and $>140 \mu\text{g/L}$ in the fall. Maximum value in the spring preceded a maximum flow of some 160 cfs. Summer flow values were only a few cubic feet per second and suspended loads fell to nearly 4 mg/L in mid-June. Higher values and scatter in the fall were related to antecedent moisture conditions and rainfall intensity.

Sediment phosphorus forms were determined as described by Williams *et al.* (1976). Although it did not display a strong seasonal trend (Fig. 6), apatite phosphorus (A-P) is most strongly represented in the spring. This was explained by the occurrence of bank and soil erosion during the snowmelt with high values of detrital material. Concentrations of A-P in representative bank and soil samples were between 200 $\mu\text{g/g}$ and 800 $\mu\text{g/g}$. Slumped bank material

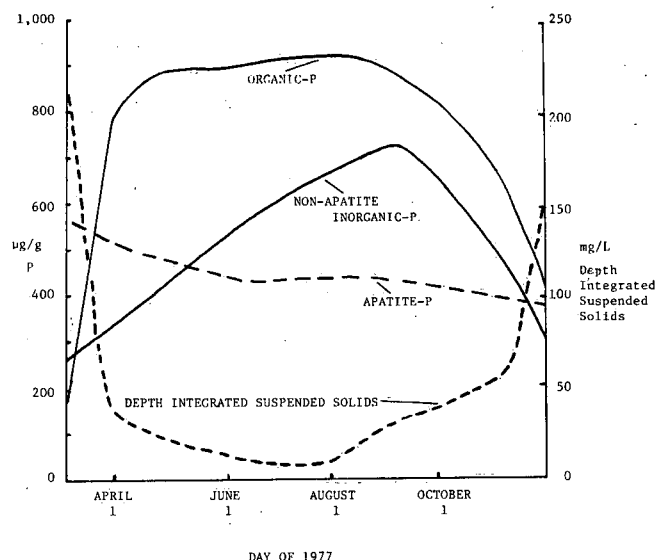


Figure 6. Changes in apatite-P (A-P), organic-P (O-P) and non-apatite inorganic-P (NAI-P) in suspended sediment from Wilton Creek, Ontario. The curves have been statistically fitted to fairly scattered data points but seasonal trends are clear. Note that this is concentration in the suspended load. Quantity of suspended load must also be taken into account to obtain total loading of different forms (compiled from data in Ongley, 1978).

during declining stages of the spring melt provided a source of detrital A-P during storm runoff events for the rest of the year. Non-apatite inorganic phosphorus (NAI-P) showed a pronounced seasonal trend (Fig. 6), rising toward peak values of 700-1100 $\mu\text{g/g}$ during late summer. Values declined in the fall to some 350 $\mu\text{g/g}$ immediately before freezeup in early December. The trend for organic phosphorus (O-P) (Fig. 6) was similar to that for NAI-P except that the organic form rose much more rapidly in the spring, reaching consistently high values as early as May (day 130) compared with August (day 226) for NAI-P. Although a biomass survey was conducted during the July-September period, the early peaking of O-P could reflect the spring bloom of *Cladophora*, which was very evident in Wilton Creek and is reported as commonly occurring in southern Ontario in May and August.

The trend of "% organic matter" as part of the suspended solids load reflected consistently larger percentages of the total solids load for the May-September period despite poor centrifuge recovery of sediment at this time of the year. Although this trend coincided with the period of optimal growth (algal productivity) within the creek, the major peaks could have reflected land use activities upstream (e.g., cattle in the creek) or a flushing of algae during a post-bloom runoff event. Perhaps not coincidentally, the peak value for both O-P and NAI-P occurred

simultaneously with the peak value for “% organic matter” (Fig. 7).

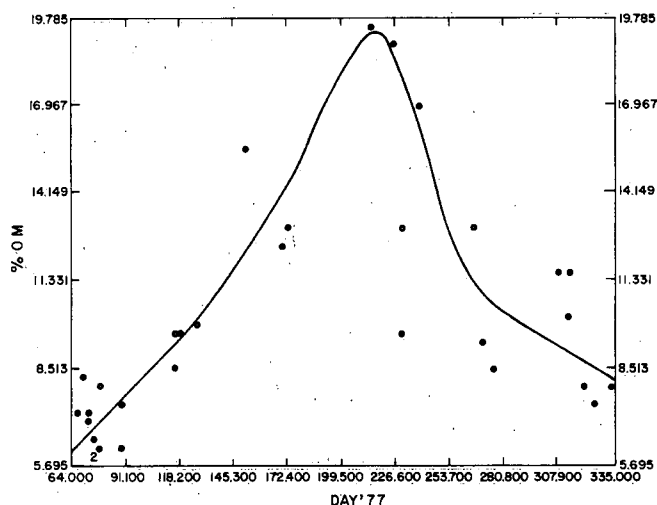


Figure 7. Trend of “% organic matter” (O-M) in Wilton Creek (Ongley, 1978).

For comparison with sediment-related phosphorus forms, standard analyses of total, soluble (i.e., filterable) and total dissolved phosphorus forms were performed on samples of river water. The samples were taken from the pumped water so that these and the centrifuge-recovered solids reflect the same raw water. The soluble reactive phosphorus (SRP = filterable orthophosphate) declined from approximately 14 $\mu\text{g/L}$ in the early spring to $<6 \mu\text{g/L}$ during the summer months (Fig. 8). The trend suggested bio-uptake during the summer-fall period of biomass productivity, with dilution effects associated with runoff events causing the few low values late in the fall. Total phosphorus (T-P) had a spring peak (Fig. 8), reflecting large amounts of apatite phosphorus at a time when the suspended solids concentrations are quite large. From mid-May (day 145) onwards, total phosphorus rose with increasing variability into the late fall. If the interpretation of the T-P trend is correct, values that are obtained for T-P during the growing season are not indicative of potential environmental (in-stream) impact of phosphorus. A similar statement concerning the residual nature of SRP may be made about soluble phosphorus during the growing season. Concentrations of total dissolved phosphorus (TDP) (total phosphorus in a filtered sample) did not indicate any pronounced seasonal trend.

An extremely important comparison that can be made from the Wilton Creek data is the estimate of the amount of particulate phosphorus versus aqueous phosphorus. Whereas the particulate phosphorus [T-P (unfiltered) minus T-P (filtered)] (Fig. 9) showed high spring, low

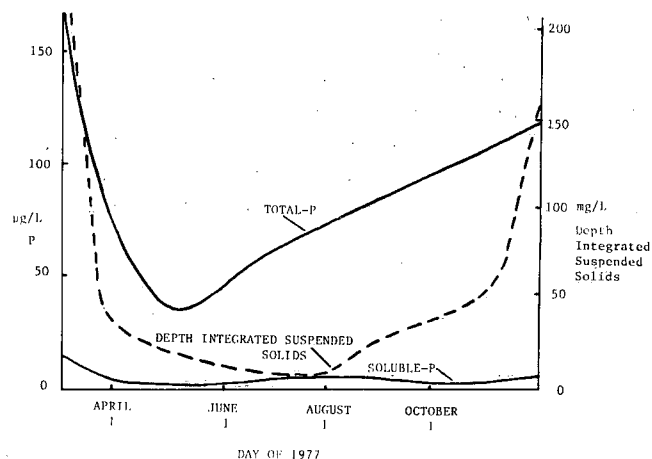


Figure 8. Trends in total soluble-P (filtered) and total-P (unfiltered) in Wilton Creek (compiled from data in Ongley, 1978).

summer and rising fall values, the trend obtained from sediment-related forms (Fig. 6) was the reverse. This apparent inconsistency is a key point in the interpretation of transport mechanisms for contaminants and is of major significance in understanding nutrient and other contaminant loading and transmission processes. The particulate estimate incorporates the quantity of suspended sediment in the water at different periods of the year, i.e., a high suspended load with a low phosphorus concentration may give a greater T-P measurement than a low suspended load with a very high phosphorus concentration. Thus, although there was a doubling of phosphorus content associated with solids during summer (Fig. 10), there was almost a twofold order of magnitude reduction in the concentration of solids through summer, such that the trend in Figure 9 reflects primarily the seasonality of suspended solids

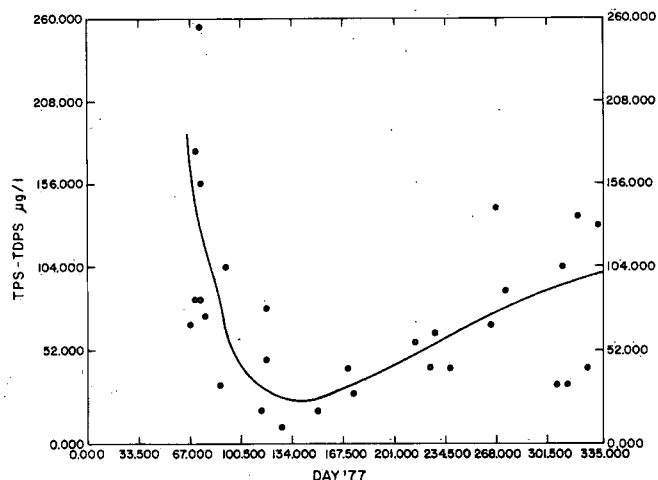


Figure 9. Particulate phosphorus (TP-TDP) trend in Wilton Creek (Ongley, 1978).

concentration. The sediment-related phosphorus trend of Figure 10 illustrates the role of sediment as a phosphorus transport agent during the year. During spring, when suspended solids concentrations are relatively high, the amount of phosphorus in sediment is much less than during the summer when sediment assumes a greater role in phosphorus transport at a time when sediment concentrations are very low. Furthermore, when Figure 10 is considered along with Figure 7, the importance can be seen of organic matter as a phosphorus-transporting agent during the growing season in Wilton Creek.

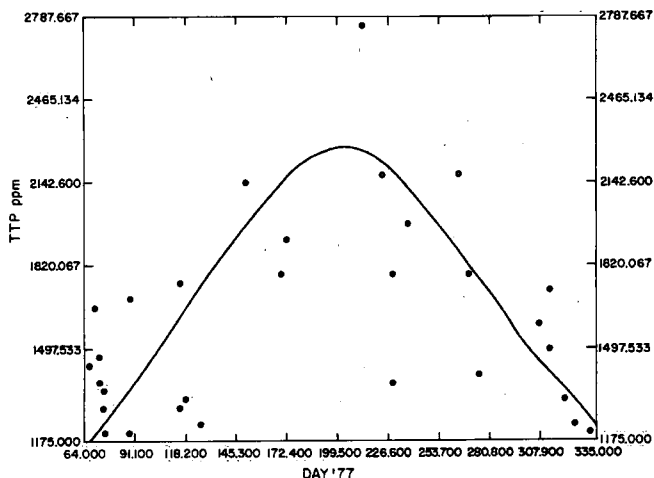


Figure 10. Total phosphorus concentration in suspended sediment from Wilton Creek (Ongley, 1978).

Varying particle size of suspended solids resulted in seasonal trends associated with fine-grained sediment ($<2.0 \mu\text{m}$ clay) and organic matter in Wilton Creek (Fig. 11). Three well-defined clusters emerged. During spring, % clay and "% organic matter" were positively related (% silt is negatively related to "% organic matter"). Moreover, during spring, the proportion of clay relative to silt increased as "% organic matter" increased, reflecting the reduced sediment concentrations occurring later in the spring when there were reduced sources of coarser grained materials. During summer, the proportion of clay was extremely high relative to silt, at which time "% organic matter" was also very high. The summer trend illustrated the practical problem of sampling when much of the suspended load was extremely fine grained and had abundant organic matter with low specific gravity. Fall data tended to cluster between the spring and summer conditions, reflecting decreased biomass production and increased potential for coarser material as the hydrologic contributing area enlarged.

The regional situation in terms of loading of bio-available suspended sediment phosphorus to the Laurentian Great Lakes has also been investigated (Thomas and McMillan, 1978; Thomas, 1979) under PLUARG. Suspended solids were collected using the Westphalia centrifuge system. The sample sites were at mouths of rivers entering the Great Lakes on the Canadian side. Eroding shoreline material was also collected and contained 64% to 86% apatite-P (non-bio-available P) and only 1 to 4% NAI-P (bio-available P). Thomas and Haras (1978) concluded that loading of phosphorus from shoreline erosion was thus

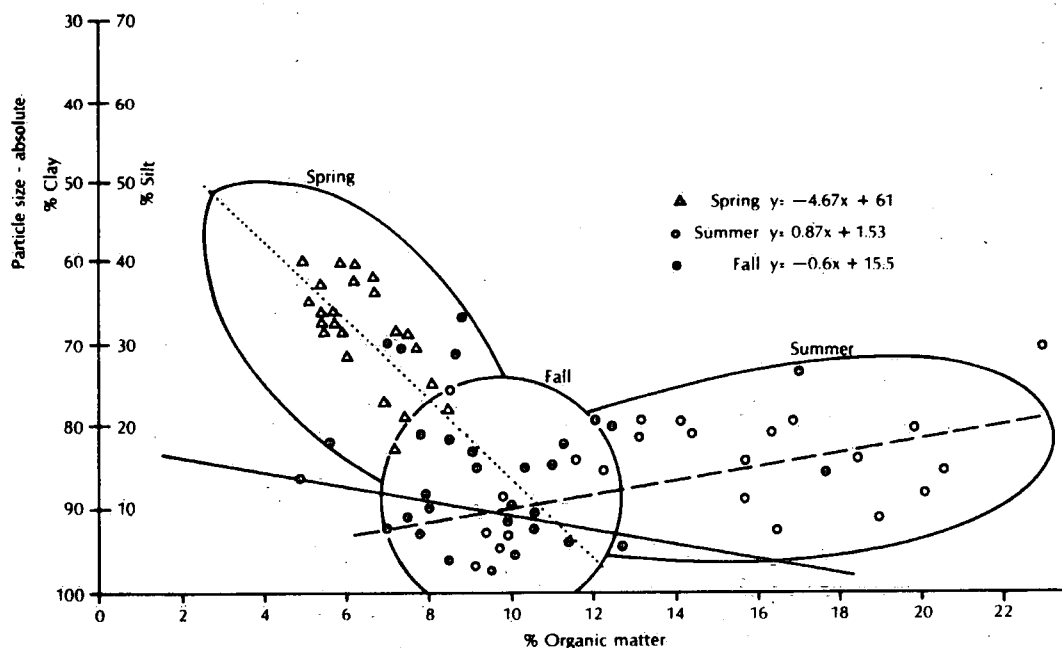


Figure 11. Seasonality of silt-clay ratio and "% organic matter" in Wilton Creek, 1977 (Ongley, 1978).

Table 3. Variability and Mean Concentration of Phosphorus Forms in the Particulate Fraction of Tributaries to the Great Lakes [from Thomas (IJC, 1978)]

	Apatite		Organic phosphorus		NAI-P		Total particulate phosphorus		As percent total particulate phosphorus		
	Mean (mg/kg)	Coefficient of variation* (%)	Mean (mg/kg)	Coefficient of variation* (%)	Mean (mg/kg)	Coefficient of variation* (%)	Mean (mg/kg)	Coefficient of variation* (%)	Apatite (%)	Organic (%)	NAI-P (%)
Monitor streams											
Bronte Creek	391	18.0	633	52.0	447	52.6	1403	35.5	26.6	43.0	30.4
Humber River	491	5.3	680	69.3	669	40.7	1982	40.2	26.7	37.0	36.4
Credit River	450	7.8	461	88.9	481	45.5	1416	46.2	32.3	33.1	34.6
Niagara River	372	22.2	319	6.3	298	21.2	1012	5.7	37.6	32.3	30.1
Grand River	384	12.0	609	39.3	659	29.9	1620	27.3	23.2	36.9	40.0
Cedar Creek	288	39.7	588	31.0	489	27.6	1312	21.1	21.1	43.1	35.8
Thames River	329	29.0	671	56.0	620	35.4	1592	29.0	20.3	41.4	38.3
Saugeen River	366	22.8	348	41.5	259	46.2	966	25.0	37.6	35.8	26.6
Nottawasaga River	416	46.4	706	49.3	508	47.9	1597	29.8	25.5	43.3	31.2
All monitor samples	407	28.3	559	59.3	484	50.1	1460	37.3	28.1	38.6	33.4
Lakes and lake sections											
Lake Ontario North	502	46.8	669	36.4	553	46.6	1742	29.5	29.1	38.8	32.1
Lake Ontario South	448	47.1	1107	111.1	706	91.1	2309	86.2	19.8	49.0	31.2
Lake Erie	392	30.8	433	75.1	492	92.6	1318	52.2	29.8	32.9	37.4
Lake Huron	348	21.7	356	54.2	201	41.8	901	27.6	38.5	39.3	22.2
Georgian Bay	456	17.3	342	41.0	211	46.0	958	22.6	45.2	33.9	20.9
North Channel	426	6.7	252	55.4	242	81.2	815	15.2	49.6	27.4	26.3
Lake Superior	458	12.3	86	38.6	89	67.4	629	16.6	72.4	13.6	14.1

*Coefficient of variation = standard deviation expressed as a percent of the mean.

insignificant in terms of effect on water quality. The mouths of ten rivers were monitored on a monthly basis as a control. Tributaries to the Great Lakes were sampled during the spring runoff when suspended loads were known to be the highest. At the present level of understanding, the most likely consensus is that spring is the best sample time if only one sample run can be funded. (However, with hindsight, it is interesting that this is the time selected when one considers the spring to summer changes in A-P/NAI-P in the previously discussed Wilton Creek data.)

In the ten monitored streams, A-P shows low variability (Table 3) in the lower Great Lakes tributaries and reflects the background phosphorus level of soils in the watershed. Variable land uses and in-stream productivity changes are reflected by changes in O-P and NAI-P. The same rationale of relating land use changes to non-apatite phosphorus ($\text{NAI-P} = \text{O-P} + \text{NAI-P}$) changes in lake sediment cores has been applied to the Great Lakes (Williams *et al.*, 1976) and to western Prairie lakes (Allan *et al.*, 1979). On the other hand, on a percentage basis (Table 3) there is a remarkable consistency for mean annual values of phosphorus forms in the ten monitored streams. Overall, NAI-P, the inferred bio-available fraction, represents a mean 33.4% of the total particulate phosphorus. Values ranged from 26.6% to 40.0% for the Saugeen and Grand rivers, respectively.

The regional spring melt sampling along the Canadian north shore of the Great Lakes (Table 3) shows that NAI-P levels of the lower lakes tributaries are higher than those of the upper lakes (opposite of A-P). A reasonable estimate of the bio-available fraction of the total particulate load of the tributaries of the lower lakes is 33%. This estimate results from the combined influences of land use and Paleozoic sedimentary geology of the area. Similar percentages were determined for O-P and NAI-P loading. As pointed out by Ongley (1978), the interrelationships between suspended load, chemistry and discharge can be complex when studied over the complete open water season. When correlations between bio-available P and general land use or land form were attempted, no clear cause and effect were revealed, perhaps because of individual point sources. Thus, bio-available P cannot be predicted but must be measured for individual watersheds (Thomas, 1979), since it may be related more to specific point source loadings. This is a very important conclusion because it necessitates major expenditures to measure bio-available loads of particulate phosphorus to the Great Lakes on the American side. The United States cannot simply correlate and extrapolate from the Canadian data, i.e., for pollution control purposes. On the other hand, the fact that estimates for overall bio-available P loading can be made may be sufficient for use in total lake mass balance and nutrient-productivity modelling.

The ten monitored streams were sampled at their mouths. By this time, the suspended sediment that had accumulated in the drainage basin in its catchment regime and changed in its chemistry by the contaminant regime had become remarkably consistent in chemical-mineralogical composition. This can be best seen by major element geochemistry (Table 4). The variability observed for major element oxides in the suspended loads of the ten monitored streams was amazingly low. In essence, there is total homogenization by the time the river mouths are reached. This is particularly true for the elements Si, Al, K and Ti (Table 4) which are associated with the layer silicate sorption complex. These similarities imply a consistency in sediment source, mixing and mode of transport. In terms of absolute major element geochemistry, these homogenized samples are very characteristic of their different geological catchment areas as is also the case for much larger rivers such as the Rhine where sediments (mineral residue) reflect Alpine geochemistry even at the delta (DeGroot and Allersma, 1975).

Table 4. Layer Silicate Associated Major Element Oxide Contents of Suspended Sediment Loads [data, other than noted, from Thomas (1979)]

River or creek	SiO ₂ (%)	Al ₂ O ₃ (%)	TiO ₂ (%)	K ₂ O (%)
Bronte Creek	50.7	9.9	0.73	3.2
Humber	46.6	8.2	0.69	2.8
Credit	51.5	10.5	0.77	3.1
Welland	53.1	9.9	0.76	3.0
Niagara	56.3	11.0	0.73	3.2
Grand	46.7	9.5	0.69	2.8
Cedar	52.1	11.7	0.69	3.2
Thames	44.5	10.8	0.63	3.3
Saugeen	37.9	7.2	0.49	2.5
Nottawasaga	44.3	7.2	0.50	2.3
St. Lawrence				
Upper Estuary*	53.0	14.2	1.39	3.1
St. Lawrence				
Lower Estuary*	55.7	15.2	1.23	3.1
Redstone River†	52.8	13.6	0.63	2.6
Mackenzie River				
Delta†				
East Channel	64.3	14.0	0.69	4.1
Mississippi†	70.0	10.5	—	2.3

* From Anglejan and Smith (1973).

† From Wagemann *et al.* (1977).

Heavy Metal Chemistry of Suspended Loads

The data base for heavy metals in suspended loads is even less than the limited results available on nutrients. Analyses of suspended sediments for elements other than nutrients have usually been conducted on only the largest rivers by geochemists studying weathering and sedimentation cycles. The analyses are usually confined to total major elements and expressed as oxides (Table 4). Heavy metal

analyses, for reasons described earlier, have until now been largely confined to bottom sediments from natural or man-made sedimentation traps of drainage systems (Allan, 1975; Förstner and Müller, 1976).

Little is known of the detailed spatial and temporal variations of toxic metal transport in rivers. This is one reason for the importance of the dynamics aspect of the ongoing federal-provincial study of mercury pollution in the Wabigoon River of northwestern Ontario. It is known that total and methyl mercury both move down the system, but the details of phase changes during suspended load transmission are still largely undetermined.

Knowledge of the transfer mechanism for heavy metals can be attained by study of clay-size ($<2 \mu\text{m}$) fractions of river bottom sediments. In the Ems River in Germany, DeGroot and Allersma (1975) showed that

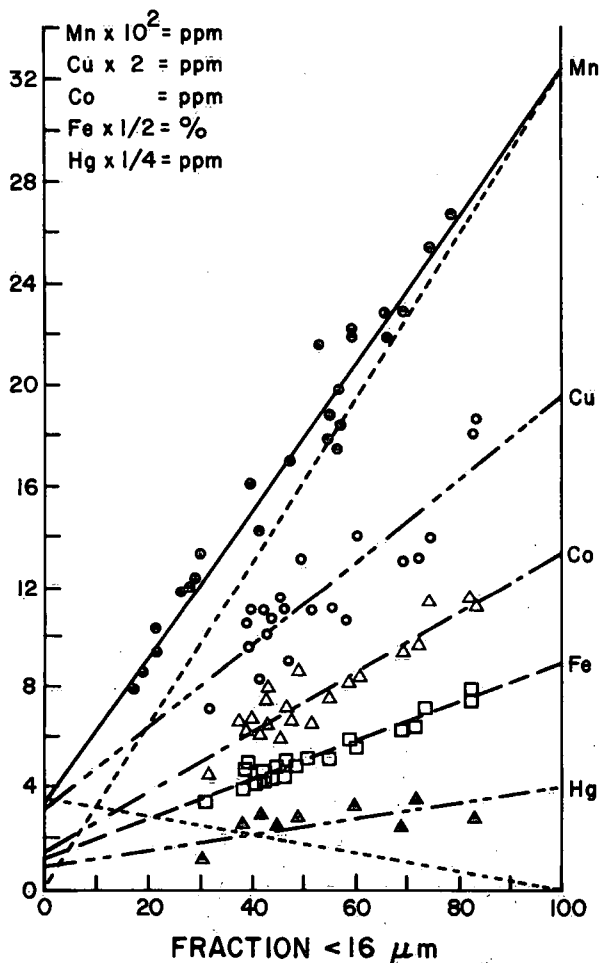


Figure 12. Linear relationships between metal contents and percentage of fraction $<16 \mu\text{m}$ in bed materials from the Ems River (DeGroot and Allersma, 1975).

concentrations of several heavy metals increased with increasing percentage of $<16 \mu\text{m}$ particles [in the medium silt ($20 \mu\text{m}$ to $5 \mu\text{m}$) range] (Fig. 12).

In Wilton Creek, Ontario, Ongley (1978) determined changes for total Zn, Cd, Mn, Pb, Co, Ni and Cu in suspended loads (Fig. 13) during the spring, summer and fall. With the exception of cobalt and to a lesser extent nickel, all other trace metals (Zn, Cd, Pb, Cu and Mn) had significantly higher values during summer and fall storm events at a time when organic matter constituted a significant proportion of the suspended load. Metal concentrations were thus tentatively related to "% organic matter" in recovered solids. Continued examination of the organic component relative to total suspended matter is obviously very significant in terms of the central role played by organics in the flux of trace metals (and pesticides). In addition, estimates of up to 23% organic matter during the summer were extremely low due to the poor suspended load recovery efficiency mentioned earlier and thus the effect may be even more organically controlled than apparent here.

At the regional scale, the distribution of mercury (Fig. 14) and lead in bottom sediments of the Great Lakes (IJC, 1978) closely correlates with inputs from rivers (Table 5). This is an excellent example, on a grand scale, of the close interrelationship of sediment-associated heavy metal transport in rivers and the resulting ability of bottom sediment in sedimentation traps (lakes and reservoirs) to reflect this transport mechanism. There are no better examples, even on a world scale, than those that have resulted from the ten-year commitment by the National Water Research Institute, CCIW, Burlington, to study the sediment geochemistry of the Great Lakes and their Canadian tributaries.

Table 5. Tributary Mercury and Lead Loadings Associated with Sediment (IJC, 1978)

Lake	Metric tons/yr	
	Lead	Mercury
Superior	81 (7.1)*	0.086 (>95)
Michigan	73 (4.0)	0.895 (>95)
Huron	51 (5.0)	0.120 (>95)
Erie	896 (40)	1.530 (>95)
Ontario	209 (33)	0.370 (>95)

*Percent of total tributary load to the lake given in parentheses.

As already mentioned for nutrients and as will be noted later for organo-chlorines, suspended sediment chemistry must be considered along with suspended sediment load and soluble metal load. For example, creeks

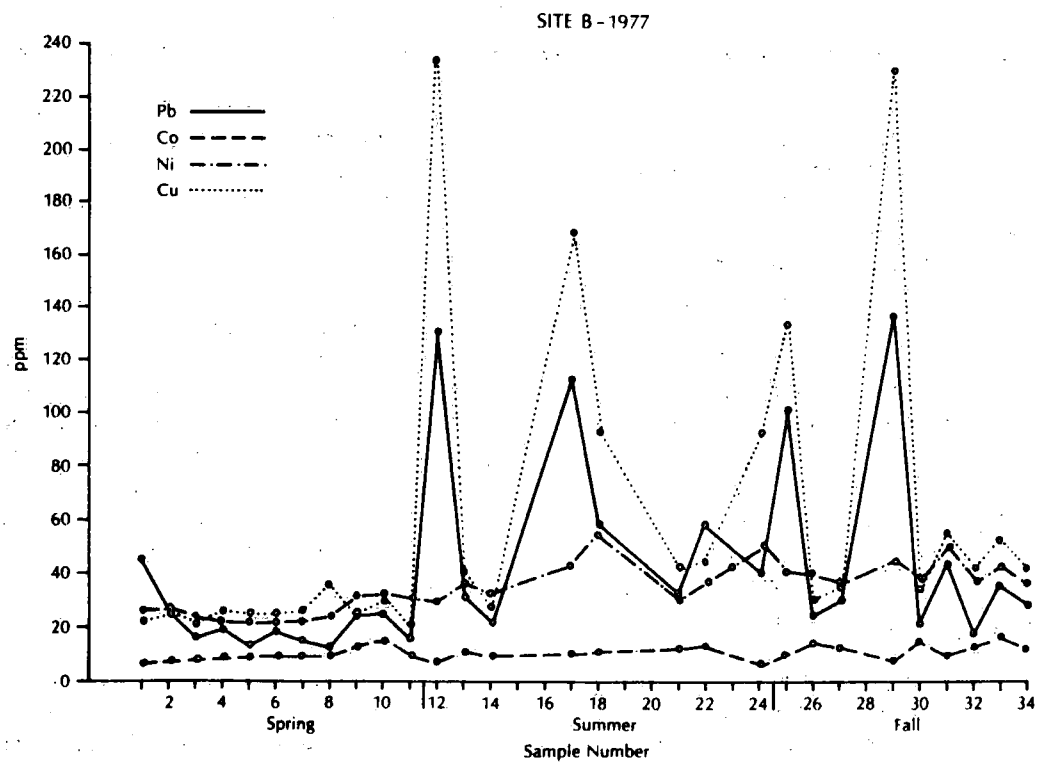
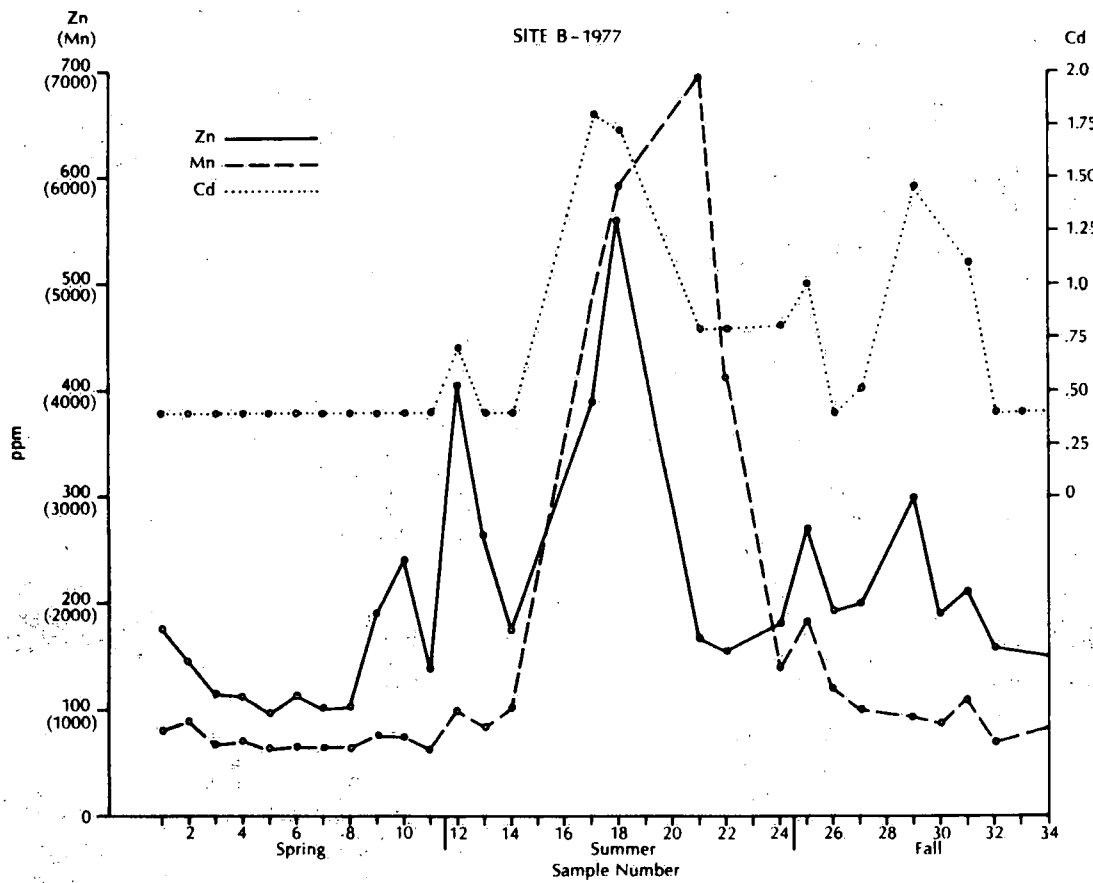


Figure 13. Heavy metal trends in suspended solids in Wilton Creek site WC/2 (site B), 1977 (Ongley, 1978).

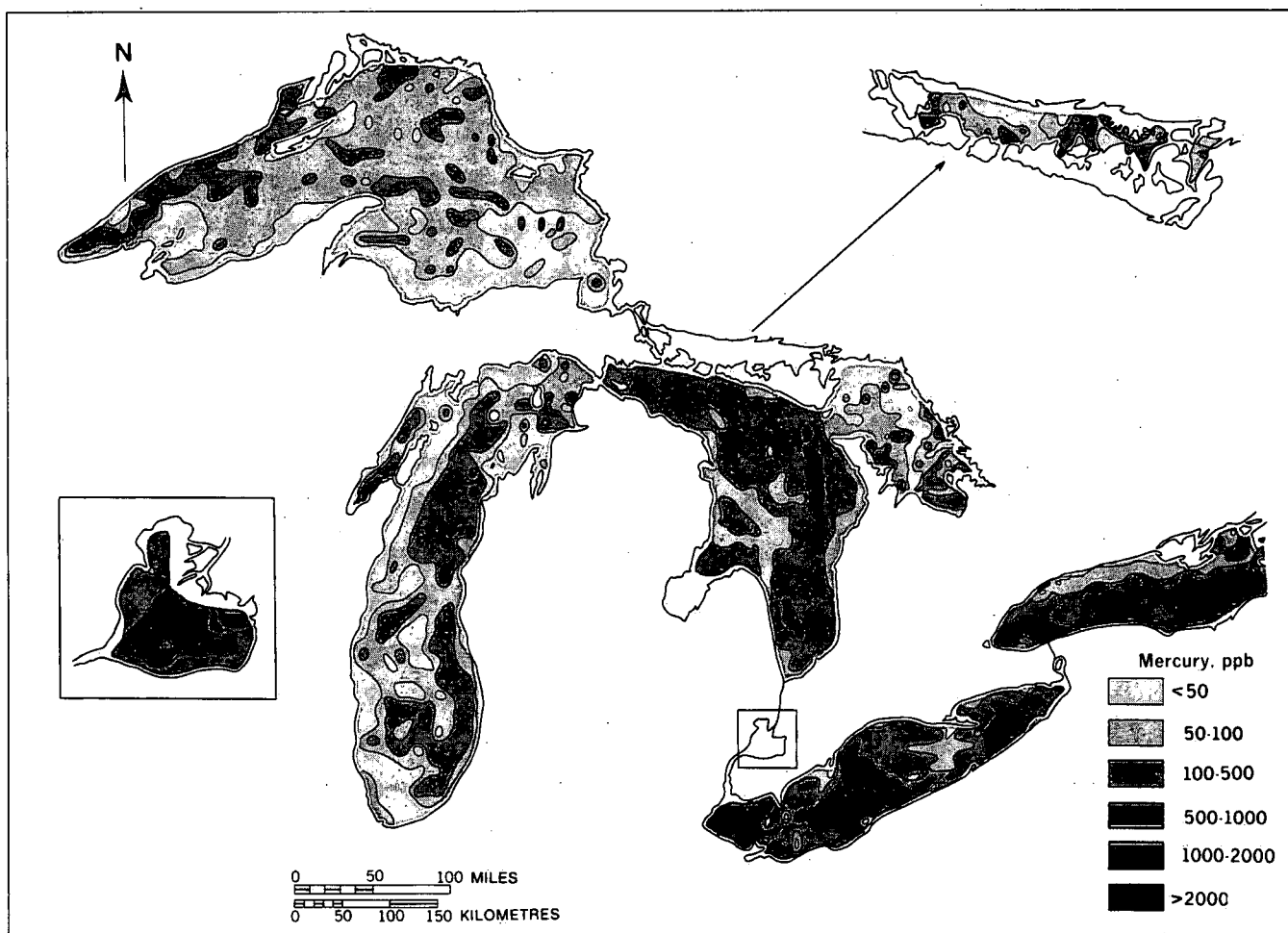


Figure 14. Mercury concentrations in surface sediments of the Great Lakes (ppb = $\mu\text{g/kg}$) [from Thomas (IJC, 1978)].

draining old gold mining areas to the Great Lakes can have very high arsenic concentrations in their suspended sediment (R.L. Thomas, Great Lakes Biolimnology Laboratory, personal communication). Thus, collection and analyses of this sediment detect point source heavy metal pollution of one watershed relative to others. A similar argument was applied to interpretation of arsenic distribution in the bottom sediments of Great Slave Lake (Allan, 1979). On the other hand, the suspended load of an arsenic contaminated stream may be low and background (or less contaminated) streams with much higher sediment concentrations of less arsenic concentration can actually load a particular body of water with more arsenic. A similar argument was used to explain the Hg, As and other heavy metal distribution in the bottom sediment of the south basin of Lake Winnipeg (Allan and Brunskill, 1976).

Finally, as with the phosphorus loading question, we must ask, what is the bio-available fraction of these sediment-related heavy metal loads? In natural streams, most of the heavy metals are present in detrital minerals. In contami-

nated streams, most are likely to be present as hydroxide coatings or carbonates (Fig. 5) and be bio-available or readily recycled under varying physico-chemical and/or bacteriological environments (Jonasson, 1977; Förstner, 1977).

In summary, for pollution control we need to detect the streams with high heavy metal concentrations in their suspended sediment rather than those with high loadings because of high suspended loads. For lake modelling purposes, however, it should be remembered that the high total loadings may be more significant. Most problems involving these interrelationships are site specific and can only be resolved by actual sampling and analyses of suspended loads.

Organo-chlorine Chemistry of Suspended Loads

We again drop an order of magnitude in the data base. Many studies of concentrations of pesticide residues

in river waters are available, and the agricultural literature contains numerous references to related work on soil adsorption of pesticides, degradation processes, airborne release on application and runoff from treated soils.

While it is justifiable to argue that the contribution of organic load to annual sediment load is generally very low, it is during the summer-fall period when pesticide application is in progress that the organic fraction constitutes a very significant portion of the solids load. Although it cannot yet be claimed that pesticide flux is at a maximum during the summer-fall period, the known affinity of organo-chlorine pesticides for fine-grained material and organic solids suggests that the dynamics of the organic and fine-grained load during the summer-fall period must be resolved. Pesticides are still rarely included in sediment studies (largely due to the high cost of gas-liquid chromatography scans). It is, however, known that pesticides of the organo-chlorine family (e.g., BHC's) have low solubility and are readily adsorbed by organic colloids and desorb only slightly (Pionke, 1977; Weber, 1977). Pionke and Chesters (1973) reported that pesticide sorption by algae and aquatic vegetation is rapid, achieving concentrations of 100 to 10 000 times that of the solute phase for a variety of organo-chlorine pesticides.

The Prairies are a major agricultural region of Canada, and agricultural contamination of the limited water resource (the region is semi-arid) by pesticides could have long-term deleterious effects on fish, wildlife and other water uses in the region. The principal sources of pesticides in the Prairies, as elsewhere, are direct and indirect applications (i.e., additions to rivers or lakes to control insects; airborne fallout) of agricultural runoff; industrial discharges; and domestic pesticide usage in urban centres. Weber (1977) reported that organo-chlorine products range from the relatively non-mobile, non-volatile chemicals such as DDT to highly mobile, moderately volatile chemicals such as γ -BHC (lindane). Organophosphorus insecticides are more soluble but their mobility is restricted by complexing with soil colloids.

The fate of organo-chlorines in aquatic systems is little understood. Unlike heavy metals they may volatilize but like heavy metals may interact between aqueous and suspended sediment phases, precipitate or accumulate in sediment or be bio-accumulated. The accumulation of pesticides in bottom sediment is certainly one way by which disappearance from water systems occurs. A bottom sediment sink, however, poses a threat to bottom fauna or flora and does not mean that these substances are irreversibly removed from the system.

Pesticide monitoring programs conducted by the Water Quality Branch of the Inland Waters Directorate,

Western and Northern Region, during 1971 to 1977 revealed a widespread occurrence of 2,4-D; 2,4,5-T; γ -BHC (lindane) and α -BHC as well as more limited distribution of 2,4-DP; aldrin; and β -endosulphan in surface waters of western Canada (Gummer, 1979). Of some 1400 samples analyzed for 13 organo-chlorine pesticides over the six-year period (total of 18 000 plus analyses), positive tests were as follows: lindane (γ -benzene hexachloride) was above detection at least once at 58% of the stations; α -BHC (an isomer of lindane) was above detection at least once at 80% of the stations; 2,4-D was above detection at least once at 59% of the stations; heptachlor was detected seven times, aldrin twice and β -endosulphan once, i.e., only γ -BHC and α -BHC were detected often enough to be of concern. Gummer (1979) makes a convincing argument that γ -BHC and α -BHC are derived throughout the Prairies and in adjacent remote mountain areas as a result of global contamination. The occurrences of chlorophenoxy acid herbicides were predominantly in May and September following periods of the maximum application. Since the water samples were not filtered and were acidified on collection, lack of detection also applies to organo-chlorines sorbed to the suspended sediment fraction. Unfortunately, these Prairie data apply to one point at one time and no valid spatial or temporal information can be extracted. Organo-chlorine pesticides have been less used recently than in the past and possibly it would be more valid to look for them in the bottom sediments of lakes, reservoirs and marshes.

Maximum organo-chlorine concentrations recorded in nonfiltered river water during 1971 to 1977 were 86 ppt lindane in the Qu'Appelle basin (the Great Lakes Water Quality Board has set the objective level for lindane at 10 ppt); 20 ppt α -BHC in the Souris River; 3120 ppt 2,4,5-T in the Qu'Appelle basin; 36.4 ppt Baygon in Sturgeon Creek, Winnipeg, 12 h after aerial spraying for mosquitoes; 4300 ppt and 3400 ppt 2,4-D below Regina and Winnipeg, respectively (Gummer, 1979). These high values for 2,4-D were derived from urban-industrial centres and are possibly related to effluents from pesticide packaging plants. An interesting observation was the detection of 2,4-D at the Alberta-Saskatchewan border. This was traced to effluent from a plant near Edmonton. The plant effluent contained some 4 350 000 ppt 2,4-D but the detection point had been 280 km downstream in the North Saskatchewan River, indicating that transport downstream can occur over major distances.

Another study of pesticide transmission in the Prairie region focused on 2,4-D in the Red River below Winnipeg. Concentrations of 2,4-D in water, suspended sediment, bottom sediment and benthos between the United States border and Lake Winnipeg showed that most of the herbi-

Table 6. Concentration of 2,4-D in Red River Water and Partitioned Suspended Sediments (Chacko and Gummer, 1978)

Location	Date	Partitioned water sample				Supernatant (µg/L)	Total (calc.)† (µg/L)	Total (analysis)‡ (µg/L)
		6000 RPM		18 000 RPM				
		µg/kg	µg/L (x 10 ⁻³)*	µg/kg	µg/L (x 10 ⁻³)			
Red River Floodway	77-7-13	4 (52)¶	0.21	4 (20)	0.08	<0.004	<0.004	0.009
	77-7-29			<4				0.010
Perimeter	77-7-18			Trace**				0.012
	77-8-3			<4				0.099
Lockport	77-7-4	5 (20)	0.1	<4	—	<0.004	<0.004	0.18
	77-7-19			Trace (6.6)				0.12
	77-8-11			<4				0.064
Lower Fort Garry	77-7-6	<4 (22)	<0.088	Trace	<0.039	<0.004	<0.004	0.053
	77-7-21			<4 (9.9)				0.016
	77-8-4			<4				0.067
Selkirk	77-7-4	<4 (38)	<0.16	<4	<0.088	0.006	0.006	0.110
	77-7-25			<4 (22)				0.009
	77-8-4			<4				0.024
Goldeye Lake	77-7-11			<4				0.069
	77-7-27			<4				0.036
	77-8-8			<4				0.038
Netley Lake	77-7-11			Trace				0.028
	77-7-27			<4				0.007
	77-8-8			<4				0.036
Assiniboine River Main St. Bridge	77-7-14			<4				0.008
	77-8-2			<4				0.099

*Contribution of 2,4-D to 1 L river water from the sediment partitioned at the given RPM.

† A summation of 2,4-D found in the sediment fractions plus concentration in the supernatant.

‡ The 2,4-D found by analyzing a non-partitioned water sample.

¶ Concentration of suspended sediment in water sample is shown in parentheses and is expressed as milligrams per litre, wet weight.

** Trace—Not in measurable quantity.

Table 7. Pesticides in Suspended Solids Collected at the Mouths of Rivers and Streams on the Canadian Side of the Great Lakes (Frank, 1977)

Contaminant*	Lakes				
	Ontario (1974)	Erie and St. Clair (1975)	Huron (1974)	Superior (1975)	
Samples	53	24	21	48	
Analyzed	34	14	9	5	5
ΣDDT					
Presence	34	14	8	5	5
Mean (ppb)	138	34	160	2.9	2.3
Range (ppb)	2-2380	1.1-115	0-1330	1.4-5.2	1.0-4.1
Dieldrin					
Presence	18	14	1	4	4
Mean (ppb)	1.5	3.6	0.2	0.4	0.2
Range (ppb)	0-6	0.5-13.8	0.0-2.0	0.0-1.5	0.0-0.4
Endosulphan					
Presence	6	11	0	4	2
Mean (ppb)	2.3	5.5	—	0.8	0.4
Range (ppb)	0-35	0.0-18.3	—	0-4.3	0.0-2.0
Heptachlor epoxide					
Presence	0	7	0	2	1
Mean (ppb)		1.2		0.2	<0.1
Range (ppb)		0.0-3.6		0.0-0.6	0.0-0.2
Chlordane					
Presence	0	12	0	4	0
Mean (ppb)		2.9		0.8	
Range (ppb)		0.0-20.0		0.0-1.0	
PCB					
Presence	34	14	9	5	5
Mean (ppb)	194	60	84	20	20
Range (ppb)	2-1800	10-330	20-370	8-30	10-30

* No organophosphorus insecticides found in any suspended solids.

HCB present in 2 of 9 samples from Lake Ontario—mean 1.1 ppb, range 0-5 ppb. No HCB in 2 samples from Lake Huron.

Atrazine in 3 of 34 samples in Lake Ontario—mean 45 ppb, range 0-1110 ppb. No atrazine in 9 samples from Lake Huron (1974).

Table 8. Residues in Five Suspended Solids Taken from the Detroit River in 1974 (Frank *et al.*, 1978)

Contaminant	Constant ppb dry weight basis		
	Mean	Range	S.D.
o,p'DDE	<0.1*	<0.1- 0.2	—
p,p'DDE	5.4	2.0- 12.0	3.9
p,p'TDE	5.2	3.1- 10.0	3.2
o,p'DDT	3.2	0.9- 6.1	1.8
p,p'DDT	4.6	2.1- 7.1	2.3
ΣDDT	18.5	10.0- 27.0	7.6
PCB	72	30-100	28

*Mean of parameter at detection limit; no S.D. given.

Table 9. Residue in a Core Taken from Station U-42 in Western Basin of Lake Erie (Frank *et al.*, 1978)

Years	Depth (cm)	Content in freeze-dried sediment (ppb)		
		p,p'DDE	p,p'TDE	PCB
1969-71	0-2	19.0	53.0	340.0
1966-68	2-4	9.0	20.0	10.0
1963-65	4-6	1.5	2.0	6.0
1961-63	6-8	2.5	1.0	10.0
1958-60	8-10	2.0	ND	ND
1956-58	10-12	ND	ND	1.0
1953-55	12-14	ND	ND	ND
1827-1952	14-112	ND	ND	ND

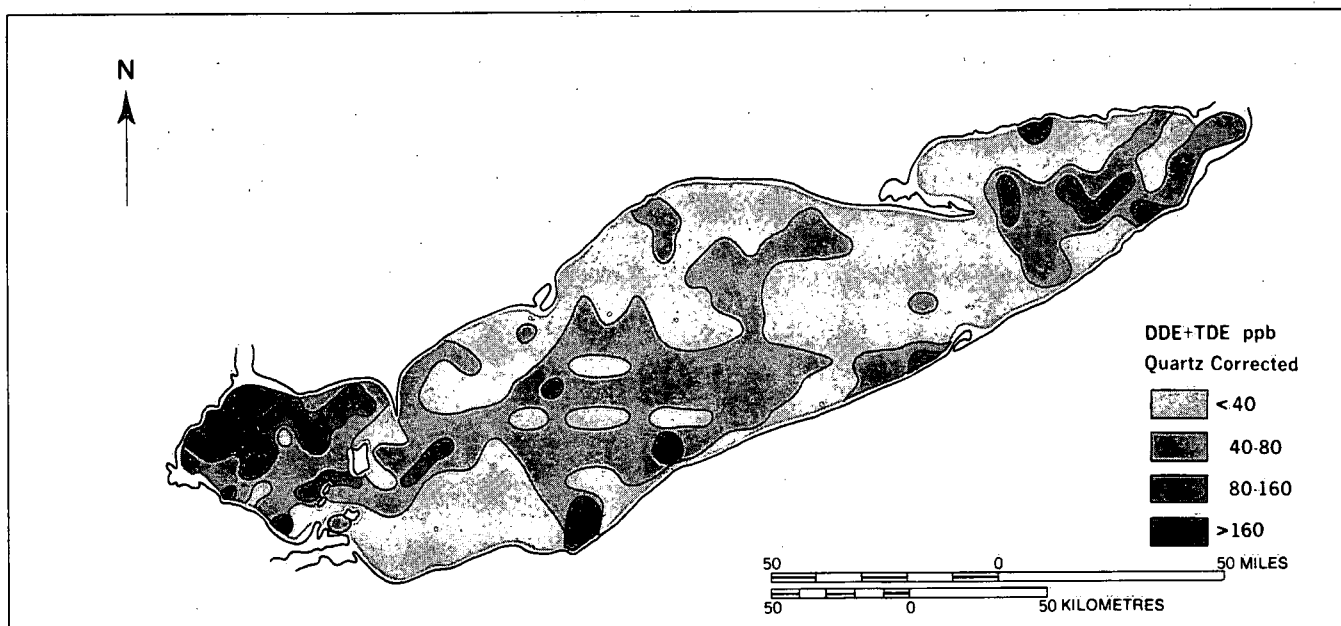


Figure 15. Quartz corrected DDE + TDE (ppb) in Lake Erie bottom sediment (Frank *et al.*, 1978).

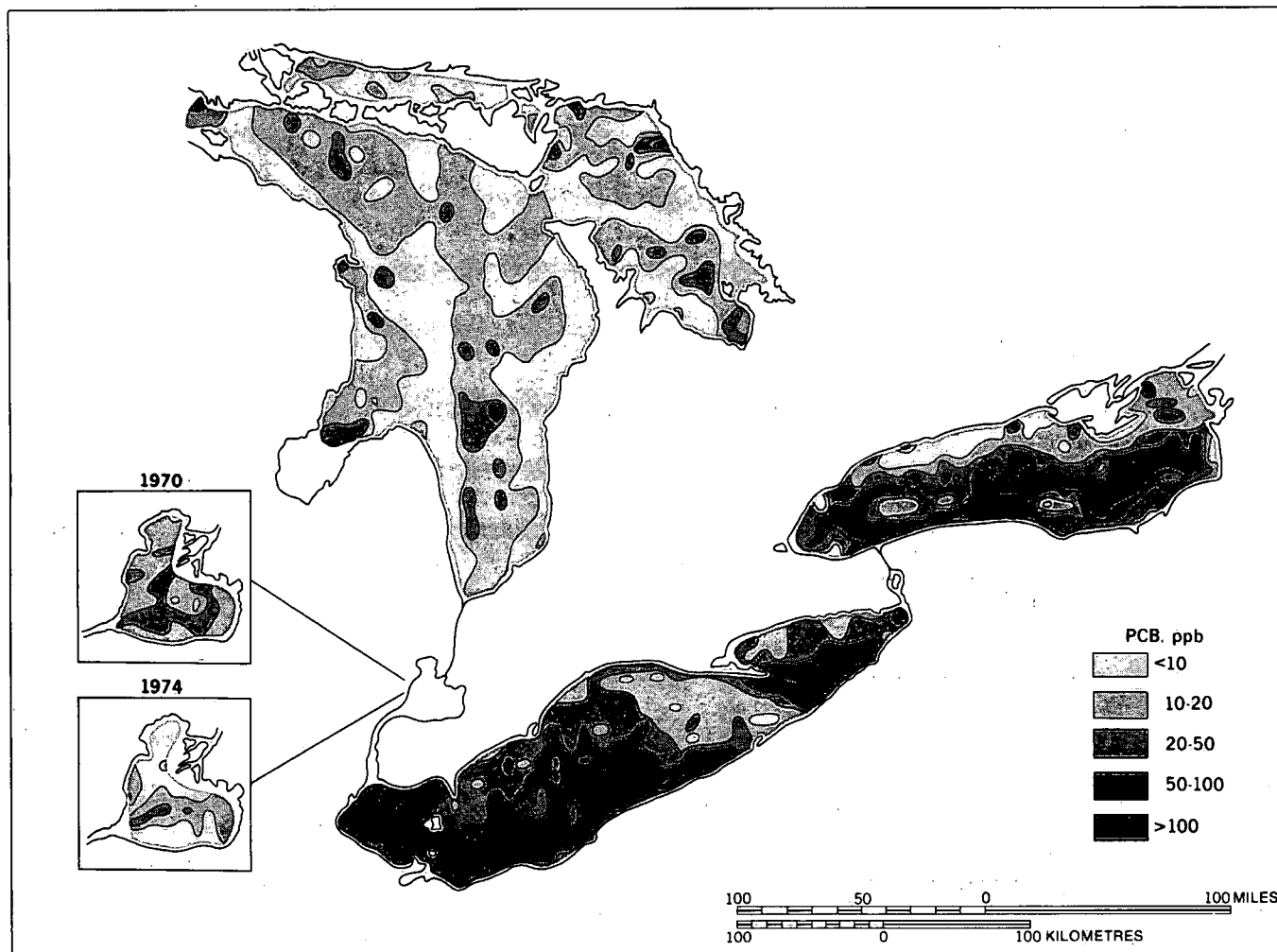


Figure 16. PCB concentrations in surface sediments of Lakes Huron, Erie and Ontario (ppb = $\mu\text{g/kg}$) (IJC, 1978).

cide was in the water phase, some was in the suspended sediment and the rest was not detectable in the bottom sediment and benthos, i.e., less than the detection limit (Table 6). This agrees with literature statements on aqueous transport of 2,4-D (Pionke, 1977; Weber, 1977).

No examples of large-scale regional studies of suspended sediment organo-chlorine transport exist for the Prairie region. In the Canadian drainage area of the Laurentian Great Lakes (Table 7), suspended solids from river mouths were analyzed between 1974 and 1976. During the spring runoff, samples were collected by high-speed centrifugation (Westphalia system). Sixty-two streams were sampled (Lake Ontario, 34; Lakes Erie and St. Clair, 14; Lake Huron, 9; Lake Superior, 5). Dieldrin and DDT were found in most samples (Table 7). Samples of suspended sediment from the Detroit River, a major source of contaminants to Lake Erie, had high concentrations of DDT and PCB's (Table 8). Comparison of these 1974 values with those in a sediment core from the west end of Lake Erie (Table 9) shows them to be less than the concentrations between 1969 and 1971. On a grander scale, the distributions of DDE plus TDE (Fig. 15) and PCB's (Fig. 16) in Lake Erie bottom sediments clearly reflect extensive pollution from source rivers, probably in the form of suspended sediment loading. The important point to note is that the organo-chlorine suspended sediment chemistry of rivers eventually has an important relationship to that of the bottom sediments in downstream sedimentation traps such as lakes, reservoirs or marshes.

CONCLUSIONS

Drainage sediment contamination by nutrients, especially phosphorus, and by heavy metals, especially mercury and arsenic as well as many other transition elements, has been well documented in the last decade. Studies of dredged and cored bottom sediments from lakes, reservoirs, rivers and estuaries are relatively widespread. The bottom material field is today moving from a stage of investigation of total concentrations to one in which the form of nutrients and heavy metals is emphasized. This is particularly so in terms of bio-availability of nutrients and heavy metals. Although nutrient bio-availability has been much researched by soil scientists, heavy metal bio-availability is still very much in its infancy and is primarily tackled by experts in environmental geochemistry.

Bottom sediment geochemical studies, except with small coring devices, have seldom been limited by sample size. The same is not true for suspended sediment studies in which sample size has until recently been limiting. Traditional suspended sediment sampling devices used by water

resource agencies such as the U.S. Geological Survey or the Water Survey of Canada seldom provide sufficient sample (25 g) for intensive biogeochemical-mineralogical study of contaminant transmission pathways. The problem of sample size has now been effectively reduced by the satisfactory performance of experimental land-based continuous-flow centrifuge procedures developed by CCIW and Queen's University to collect suspended sediments in the Great Lakes drainage basin.

It is clear from the PLUARG data base that a significant proportion of the particulate fraction loaded to the Great Lakes is bio-available and may be used in algal productivity. There are, however, complicated spatial and temporal trends in changes of nutrient forms in the suspended load as a function of flow regime and annual biomass cycles. Organic content of summer and fall suspended loads is thought to be particularly significant in terms of transmission of nutrients, heavy metals and pesticides.

Whereas some data exist on nutrients and heavy metal transmission characteristics in suspended loads, the data base on pesticide transport is extremely limited. Larger samples are needed for extraction, and pesticide pathways in aquatic systems are complex because of biodegradation, rapid removal to sediments, isomerization and hydrolysis. Water quality monitoring in the Prairies showed a need to elucidate the extent of persistent pesticide contamination of bottom sediments deposited in transmission features of Prairie rivers. There is a need to conduct detailed series sampling of selected rivers to determine the spatial (time of travel), temporal (seasonal flow) and water-sediment geochemical controls on transmission processes and pathways, characteristic of biologically productive drainage systems, such as those in the Prairie region of Canada.

One aspect not developed here is the grey area of colloidal particles and their role on nutrient, heavy metal and pesticide transmission in rivers. Even with high-speed field centrifugation, suspended load is still defined as $>0.2\text{-}\mu\text{m}$ particles. The effluent from these centrifuges can still contain mineral or organic material varying in size up to 2000 \AA , and although bacteria are removed, neither high molecular weight organic acids (humic and fulvic) nor colloidal Mn and Fe oxides and hydroxides, which transport heavy metals and also probably pesticides, will be removed. With heavy metals such as Hg, Cu and Pb, which have a high affinity for fulvic acid, few of the metals may actually be present in solutions simply as hydrated cations. Separation and analyses of colloids, however, require fractionation techniques such as filtration in Sephadex columns, and the level of study is much more complex than the particulate-non-particulate situation described herein.

In studies of transmission controls and characteristics of the contaminants, suspended sediment in rivers should be collected from the same body of water at different locations as it flows downstream. This permits interpretation of mineral-suspended-sediment/organic-suspended-sediment/biota-water interactions, deposition and regeneration of contaminants, and effects of transmission features. Such a study involves detailed knowledge of flow characteristics of specific rivers and residence times of lakes and reservoirs. Series sampling on a flow regime or event basis can become a complicated and expensive endeavour, yet such data are needed to provide the type of geochemical data required for modelling of contaminant pathways. Without this information, models will be highly speculative at best and, at worst, an exotic mathematical exercise in futility. In a recent article (Wolman, 1977), Professor Wolman of Johns Hopkins University in Baltimore states:

Choices among policy alternatives (relevant to society's interest in protection of the environment and management of natural resources) require much better information on the distribution and composition of non-point sources of pollutants, on the relation of pollutants to sediment behavior, on the mode of transport and storage of exotic man-made pollutants, and on the relationship between biota and sediment in water bodies. Concepts of mass balance and models of the sediment system as a whole are essential to evaluations of the virtues and drawbacks of proposed private and public actions. Vast sums of money rest on the outcome of these analyses.

The highly variable temporal and spatial character of erosion and sedimentation processes must be emphasized in the predictive exercise of environmental impact assessment. Validation or testing of the predictive capacity of our current knowledge can only be achieved by field observation. This does not imply massive data collection programs but rather an integration of model building, laboratory study, and continuity of study in carefully selected field areas.

ACKNOWLEDGMENTS

I am indebted to my friends and colleagues who generously provided figures and tables based on their research: Dr. R.L. Thomas, Director, Great Lakes Biolimnology Laboratory, CCIW; Professor E.D. Ongley, Geography Department, Queen's University, Kingston; and Dr. J.D.H. Williams, Research Scientist, National Water Research Institute, CCIW.

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