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ON GREAT LAKES POLLUTION
FROM LAND USE ACTIVITIES**



**INTERNATIONAL
JOINT
COMMISSION**

SOURCES, STORAGE AND TRANSPORT
OF HEAVY METALS IN AGRICULTURAL
WATERSHEDS

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HEAVY METALS IN AGRICULTURAL WATERSHEDS

BY

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SUMMARY

The objective of this project was to determine and assess the relationship between concentrations of selected heavy metals in streamwater, suspended sediments, bottom sediments and soils within selected agricultural watersheds, with the aim of elucidating storage and transport mechanisms for trace elements.

Soil profile samples of the major soil types of each of the 6 agricultural watersheds were obtained for nutrient and trace metal analysis. Analyses of total metal concentrations (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, Zn, Al and Fe) and DTPA extractable metals (Cd, Cu, Ni, Pb and Zn), as well as total carbon, organic carbon, total nitrogen, total phosphorus and pH were performed. To demonstrate field variability and the effectiveness of our sampling system, six replicate soil samples were taken within the same soil pit for most sites. In addition, four soil pits within the same soil type separated by at least 1 mile were sampled in one watershed. The replicate soils were analyzed for total concentrations of Cr, Cu, Mn, Ni, Pb, Zn, Al, Fe, C and N. Composites of the A horizons from each major soil of each watershed were used for the extraction of HA's and FA's. Ultimate analyses, functional group analyses, chemical degradation and identification of products were performed on each sample.

Bottom sediments were obtained from the mouths of the watersheds in 1975 and 1976. The same analyses as performed on the soil samples were performed for the bottom sediments.

Streamwater was collected in each watershed several times during the summer and fall of 1976. Samples were divided into total, particulate ($>.45\mu$) and dissolved ($<.45\mu$) fractions. Each fraction was analyzed for total and organic carbon, total nitrogen and sulphur, and total concentrations of Al, Fe, Cd, Cr, Cu, Mn, Ni, Pb, Se and Zn.

Average soil concentrations for 10 metals and 2 non-metals were determined for the soil samples. Weighted average metal concentrations were determined for each watershed. The average Ap soil concentrations were as follows:

4.7 \pm 2.3 ppm As; 51.5 \pm 17.1 ppm Cr; 17.3 \pm 6.3 ppm Cu; 47 \pm 18 ppb Hg; 558 \pm 273 ppm Mn; 19.4 \pm 6.2 ppm Ni; 22.5 \pm 4.2 ppm Pb; 0.35 \pm 0.11 ppm Se; 84.3 \pm 23.5 ppm Zn; 5.85 \pm 1.00% Al; 2.78 \pm 1.15% Fe; 2.33 \pm 1.02% C; 3.02 \pm 1.80% organic matter; 0.20 \pm 0.10% N; 657 \pm 277 ppm P; 19.6 \pm 10.2% clay and 6.6 \pm 0.6 pH units. Values for B and C horizons are available in Table 3.

Concentrations of the metals measured in soils were within the ranges reported for soils by other researchers and appeared to be natural levels.

There was a positive correlation for most metals between concentrations found in the Ap and C horizons. This relationship was strongest for Se and Pb, 2 metals that tended to accumulate in the Ap horizons but still reflected the C horizon values. As, Cr, Cu, and Ni in bottom sediments were significantly correlated with C horizon concentrations while Zn, Pb and Mn in bottom sediments were correlated with Ap horizon values.

Some total metals, such as Cr, Ni, Pb and Zn, were positively correlated with clays, Al and Fe, while others, such as Cu and Hg, were positively correlated with organic matter.

Within a single soil pit, Al and Fe had the least variability in the replicate samples, while Cu and Ni had the most. Soil B horizons were more variable than Ap or C horizons. The watersheds with the highest metal concentrations showed the least variability.

In watershed 10 - a watershed with high metal concentrations and low metal variability - the A horizon was more variable in metal content than either the B or C horizon; however, the variability for sites separated by several miles was nearly the same as for samples within the same soil pit.

Bottom sediments had lower metal concentrations than watershed soils while suspended sediments had higher metal concentrations. This is largely due to the clay and organic matter content variations. Suspended sediments are enriched in clay and organics while bottom sediments were lower in both compared with soils.

For the metals in soils and bottom sediments, there were wide ranges of values between watersheds but there were very small fluctuations within each watershed. This was the case for both total and DTPA extractable metals.

DTPA extracts, which measure plant availability, showed the highest extractable metal contents were in the Ap horizons - 5.5% total Cu, 2.1% total Ni, 5.5% total Pb and 1.5% total Zn. The DTPA extractable Cu, Pb and Zn were twice as high in bottom sediments as in soils. DTPA extractable and total metals were not significantly correlated.

Organic matter - HA's and FA's - extracted from soils, bottom sediments and suspended sediments were structurally similar to each other and to organics extracted in other parts of the world. The binding capacities of organics extracted from bottom sediments were lower than those from soils; however, for Cu and Zn, these organics may be binding a proportionately greater quantity of metal.

The 6 agricultural watersheds were grouped as 2 groups on the basis of metal distribution throughout the soil profile. Soils in Essex County (1 and 13) had the highest metal concentrations in the C horizon while the south central Ontario watersheds had the lowest metal concentrations in the

C horizons. This grouping of watersheds was also evident in the relationships of heavy metals in bottom sediments and soils.

Of the fertilizers examined, trace metals were detected only in phosphate fertilizers. Low levels of Cu, Co and Ni were found in phosphate fertilizers but the levels did not increase as the amount of phosphate increased. Cd, Zn, Cr and Fe increased with the amount of phosphate.

Aerial fallout, applications of phosphate fertilizer and manure disposal have the potential to raise present soil metal levels by 0.1%, 0.005% and 0.5% per year, respectively. With the removal of metals from the soil by erosion, leaching and plant uptake, increases in metal levels would take a considerable number of years to detect.

Generally, 65% Cu, 50% Pb and Zn and 35% Ni in bottom sediments were bound in chemical forms that under severe ecosystem stress could be liberated into a readily useable form. When soluble metals were added to the soils and sediments, they reacted first with the carbonates to form co-precipitates and then the more strongly bound forms - hydrous oxides and organic matter. As the metal additions continued, more of the metal remained in the water soluble and exchangeable forms. Phosphorus, although it affects the solubility of metals, did not appear to affect the binding of the metals.

There were no correlations between metals and other elements in the streamwater when the values for all the watersheds were averaged. However, on an individual watershed basis, some correlations were observed but there was no consistent pattern. Of the few particulate samples obtained during 1976, metal values were higher in the particulate than in the soils or bottom sediments, undoubtedly a reflection of particle sizes. Similar values for particulates were obtained during the spring runoff period of 1977.

With respect to metals, no evidence was found to relate agricultural activity to metal concentrations in either terrestrial or aquatic ecosystems. The metal levels were a reflection of the soil types present and their geochemical composition.

INTRODUCTION

Under the 1972 Water Quality Agreement between Canada and the United States, the Pollution from Land Use Activities Reference Group (PLUARG) was charged with answering the following: 1. were the boundary waters being polluted?; 2. from what sources and in what quantities were pollutants entering the lake?; and 3. what remedial measures would alleviate the problems? Since agriculture covered such a large proportion of the basin, Agriculture Canada, Ontario Ministry of Agriculture and Food and Ontario Ministry of the Environment funded projects to delineate the contributions from agricultural sources.

The major objective of this study (Project 9) was:

To determine and assess the relationship between concentrations of selected heavy metals in stream waters, suspended sediments, bottom sediments, soils and soil amendments within selected agricultural watersheds, with the aim of elucidating storage and transport mechanisms.

Sites for collection of samples were located within the six agricultural watersheds - 1, 3, 4, 5, 10, and 13 (Detailed Study Plan). This study dealt with the elements Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se and Zn, with in-depth investigations being carried out on Cd, Cu, Ni, Pb and Zn. Water, suspended sediments, bottom sediments and soil samples were collected by investigators in Projects 7, 8 and 9, after consultation with the project leaders. A detailed mapping of the soil series present in each of the six agricultural watersheds was prepared by Acton et al., 1978 (Project 7) while the mineralogical characterization of the sediments and soils was the objective of Project 8 (Wall, 1978).

The following experimental data were obtained: 1. total concentration of Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se and Zn in soils, bottom sediments and suspended sediments; 2. DTPA extractable concentrations of Cd, Cu, Ni, Pb and Zn in soils and bottom sediments; 3. total concentrations of Cd, Cu, Pb and Zn in filtered and unfiltered water samples; 4. elemental analysis such as C, N, P, S and pH determination on soils and sediments; 5. concentrations and analytical characteristics of humic and fulvic acids in selected bottom sediments, suspended sediments and soils; 6. total levels of selected metals in fertilizer stocks.

The experimental data provided the following information: 1. background levels of heavy metals in soils; 2. prediction of the heavy metal

storage capacity of organic and inorganic matter in stream waters, bottom sediments, suspended sediments and soils; 3. establishment of relationships between heavy metal contents of water, suspended sediments, bottom sediments and soils; 4. correlation of clay content and organic matter content of suspended sediments, bottom sediments and soils with respective metal concentrations; 5. establishment of relationship between the nature of humic and fulvic acids in bottom sediments and adjacent soils in an attempt to gain insight into the sources (soil erosion or in situ formation) of these organic components; 6. identification of agricultural sources of heavy metals based on analysis of fertilizer materials, and data anticipated from questionnaires distributed to farmers within the watersheds, dealing with fertilizer, animal waste and sewage sludge usage; 7. overall statement regarding the important mechanisms of heavy metal transport and storage, operative within the selected agricultural watersheds.

DATA COLLECTION

Sampling

Six agricultural watersheds in Southern Ontario were selected for this study. Short descriptions are presented in Table 1. More complete descriptions of these watersheds are given in the Detailed Study Plan, 1974. It was anticipated that the diversity of agricultural practices in these 6 watersheds would permit extrapolation of results to the Great Lakes Basin. Sampling sites for soils were located within the major soils of each watershed. The number of soils sampled in each watershed ranged from 2 in watershed 10 to 7 in watershed 1. The soils are described in Appendix Tables 1, 2 and 3. Soil pits measured approximately 100 cm x 150 cm. Soil samples were collected for trace elemental analyses by collecting discrete horizons with plastic or Teflon coated utensils. Sampling was from the bottom upward in the profile. Approximately 1 kg of each horizon was sealed in a plastic bag and shipped to the laboratory. Soil replicates were obtained by collecting 6 samples (at least one per face) from each primary horizon (ie. only 1 A horizon, 1 B horizon and 1 C horizon) in a soil pit. In watershed 10, four sites were located at least a mile apart within the same soil series and were sampled in the same manner. Soil samples for humic substances extraction were collected from the surface soils only. Twenty separate samples were composited for each surface sample to be used for humic substances extraction.

Sediment sampling stations were located slightly upstream of the MOE gauging station in areas when movement on the streambank would not contribute to sediment load in the water. A bimonthly sampling scheme was adopted. Bottom sediments were collected from the mouth of the watershed using a hand-held plastic corer (Sutton, 1974). Bottom sediments ranged in depth from 5-20 cm. Samples were collected across the underwater width of the stream until approximately 1 kg was obtained. The cores were placed in plastic bags for shipment to the laboratory.

Suspended sediments were obtained in the same location and at the same time as the bottom sediments in 1976. A battery operated pump was used to obtain 20 l of suspended sediment at each station. Event samples were occasionally obtained, in addition to the regular bimonthly samples.

During the spring runoff period of 1977, suspended sediment samples were obtained from 4 of the agricultural watersheds by the centrifugation method available at Canada Center for Inland Waters at Burlington. 450 l of water was obtained at approximately the time of the spring peak

TABLE 1.

AGRICULTURAL STUDY WATERSHEDS

	<u>NAME</u>	<u>COUNTY</u>	<u>SOIL TYPE</u>	<u>AREA (km²)</u>	<u>PRIMARY AGRICULTURAL ACTIVITY</u>
AG 1	Big Creek	Essex	Clay	51.8	Cash Crops
AG 3	Little Ausable River	Huron	Clay, loam	54.1	Pasture & Forage Crops
AG 4	Canagagigue Creek	Wellington	Silt loam, clay loam	18.9	Pasture & Small Grains
AG 5	Holiday Creek	Oxford	Loam	29.5	Pasture & Forage Crops
AG 10	Twenty Mile Creek	Lincoln	Clay	29.8	Pasture
AG 13	Hillman Creek	Essex	Loamy fine sand	20.7	Horticultural & Cash Crops

runoff and centrifuged to remove the sediment. Samples before and after centrifugation were obtained also.

Chemical Analyses

Once at the laboratory, soil and bottom sediment samples were poured into plastic trays and allowed to air dry. Samples were thoroughly mixed, divided into quarters and diagonally opposite quarters combined. Half the sample was prepared for mineralogical and physical properties, and the other half for chemical properties. Only the chemical properties were examined in this project. All soil and bottom sediment samples were sieved through a 2 mm nylon sieve, sediments to conform to the definition of bottom sediments established by PLUARG, and soils to conform to analytical methods. Samples were analysed for total carbon (Leco Furnace), carbonates (pressure transducer), total sulphur (oxygen flask combustion), total nitrogen, total phosphorus and pH (CaCl_2).

For total metal analysis, the samples were ground to pass through a 300 mesh sieve. 1.000 gram of oven-dry sample was placed in a 100 ml teflon beaker, and 20 ml concentrated HNO_3 was added. The solution was covered and gently boiled for $\frac{1}{2}$ hour on a hot plate at $100\text{--}150^\circ\text{C}$. After cooling, 20 ml concentrated HClO_4 was added and the solution gently boiled for $\frac{1}{2}$ hour on a hot plate at $200\text{--}250^\circ\text{C}$. After cooling, 20 ml concentrated HF was added and the solution covered and boiled for $\frac{1}{2}$ hour on a hot plate at 80°C . The covers were removed and the heat gradually increased to 250°C as the HF evaporated. The beaker sides were washed down with 25 ml 1N HNO_3 and boiled again to dissolve the residue. After cooling, the solution was made up to 50 ml with distilled water and the trace elemental concentrations determined by atomic absorption spectrophotometry. Reagent blanks and standard rock and soil samples were run with each batch of samples. Several quality control checks were run throughout this study to determine the precision of our analytical laboratory. From the standard deviations and the means, one could determine the necessary number of samples to be analyzed to maintain a given precision. For Cu, Mn, Ni, Pb, Zn, Al and Fe (over 10 ppm) only one sample was necessary to maintain $\pm 10\%$ precision. Samples were at least run in duplicate for this study. Concentrations below 10 ppm required greater numbers of duplicates to maintain $\pm 10\%$ precision. Cr also required at least 2-3 duplicates because of an analytical problem with perchloric acid.

Mercury analyses were conducted on 5 g soil or sediments in modified flasks. Vanadium pentoxide (0.1 g) was heated for 5 minutes with 5 ml concentrated HNO_3 . 5 ml H_2SO_4 was added to the solution and the heating and refluxing continued for 30 minutes. After cooling, 3-4 drops of 50% hydrogen peroxide were added. When room temperature was reached, the apparatus was washed with 2% sulphuric acid (30-40 ml), catching the washings. The digest was filtered through prewashed glasswool into a 100 ml volumetric flask and made up to volume with 1.0 N H_2SO_4 . The mercury concentration was determined by flameless atomic absorption (modified method of Malaiyandi and Barrette, 1970).

Selenium analyses were conducted on 0.2 g samples after wet digestion with HNO_3 and HClO_4 . 5 ml HNO_3 and few glass beads were added to the sample in a Kjeldahl flask. After 30 minutes at room temperature, 2 ml HClO_4 was added and the flask placed over low heat for 20 minutes. Heat was increased until fumes of HClO_4 evolved and digestion continued for a further 15 minutes. After cooling, 2 ml 1.0N HCl was added and the flasks were placed in 100°C waterbath for 15 minutes. The digest was transferred to 50 ml pointed tubes fitted with Teflon stoppers and the volume brought to 25 ml. A solution of 5 ml 1:1 formic acid and 5 ml 0.04 M Na_2 EDTA in 10% $\text{NH}_2\text{OH}\cdot\text{HCl}$ were added and the solution titrated to pH 1.8 with 4N NH_4OH . After 10 minutes on a 50°C waterbath, 5 ml 0.1% DAN (2, 3 - diaminonaphthalene) was added and incubated a further 30 minutes at 50°C. After cooling, 5 ml cyclohexane was added and the tubes were shaken for 5 minutes. The water phase was drawn off, the cyclohexane was transferred to a cuvette and the fluorescence was measured (Levesque and Vendette, 1971).

Arsenic was analyzed by the Ontario Ministry of the Environment Laboratories (MOE). Flameless atomic absorption was employed after arsine generation from a nitric-sulphuric acid digest of the samples.

Extractable metal concentrations were determined on DTPA extracts of the soils and sediments (Lindsay and Norvell, 1969). 10 g soil or sediment was shaken with 20 ml 0.005 M DTPA (diethylene triamine pentacetic acid), 0.01 M CaCl_2 and 0.1 M triethanolamine at pH 7.3. After filtering the suspension, Cd, Cu, Ni, Pb, and Zn were measured by atomic absorption spectroscopy directly on the filtrate.

For the extraction of fulvic and humic acids, 300 grams of air dried sediment were placed in a 4 l beaker and 0.1 N HCl was added to decompose the carbonates which may interfere with the extraction of organic matter. Once the evolution of CO_2 stopped, the sediments were centrifuged, washed twice in distilled water and centrifuged again. Washed sediments were placed in a narrow necked polypropylene flask and 3 l 0.5 N NaOH was added. The air in the flask and samples was displaced by nitrogen and samples were left to stand for 24 hours with intermittent shaking. Samples were centrifuged at 2,000 rpm for 30 minutes and the supernatant was retained. The pH of the supernatant was adjusted to pH 2 by the addition of 6 N HCl, and the solution was allowed to flocculate for 24 hours. The solution was centrifuged and the supernatant (fulvic acid) was freeze dried separately from the residue (humic acid).

At that point the HA's still had very high ash contents. To lower the ash, HA's were shaken for 24 h with an aqueous solution containing 0.5% (w/v) HCl + 0.5% (w/v) HF. Following this treatment, the residues were centrifuged, washed free of Cl^- and freeze-dried.

Sediment FA fractions contained large quantities of NaCl crystals resulting from the neutralization of NaOH with HCl; the lower the organic content of the sediments, the higher was the NaCl content of the FA fractions. After freeze drying, the sediment FA's were dissolved in

about 500 ml distilled water, transferred to seamless dialyzing tubing and dialyzed against distilled water until no further Cl^- was detected by AgNO_3 . This treatment lowered both FA yields and ash contents.

HA's and FA's were extracted from surface soil samples in the same manner except that the treatment to reduce carbonates was omitted.

Moisture and ash were determined on all samples by drying for 24 hours at 105°C and heating for 4 hours at 750°C respectively. The samples were also analysed for carbon and hydrogen by dry combustion, nitrogen by Dumas method, sulphur by oxygen flask combustion and oxygen by difference.

Total acidity, total carboxyl groups, total phenolic OH groups and E_4/E_6 ratios were determined on the samples when sufficient material was available (Schnitzer 1972). For total acidity 50 mg samples were equilibrated with 20 ml 0.185 N $\text{Ba}(\text{OH})_2$ under nitrogen for 24 hours. Excess $\text{Ba}(\text{OH})_2$ was back titrated to pH 8.4 with 0.35 N HCl to determine the concentration of dissociable protons on the humic acids.

The procedure for total carboxylic groups involved equilibrating 50 mg sample with 50 ml 0.2 N $(\text{CH}_3\text{COO})_2\text{Ca}$ under nitrogen for 24 hours. The supernatant was back titrated to pH 9.8 with 0.1 N NaOH to determine the concentration of carboxylic acid groups.

Total phenolic - OH groups were attributed to the difference between total acidity and total carboxylic groups.

Visible light spectra were examined by the E_4/E_6 ratios. 1.0 g of sample was dissolved in 10 ml of 0.05 N NaHCO_3 and optical densities were measured at 465 and 665 nm on a Spectronic 20 spectrophotometer. Infra red spectra (4000 to 800 cm^{-1}) of 1 mg of material in 400 mg KBr pellets were run on the samples (Schnitzer 1972).

Total metal concentration of the extracted HA's and FA's were analyzed as described for soils and sediments.

Suspended sediments were obtained from the mouths of the six agricultural watersheds during 1976. Twenty liter carboys of each sample were shipped to Ottawa for analysis. Six liters of water were freeze dried after the water was thoroughly mixed. This sample was designated as total sediment. An additional 6 l was centrifuged at 2000 rpm for 30 minutes to remove the large particles, and then the supernatant was passed through a $.45\mu$ filter. The filtrate (particle size $<.45\mu$) was freeze dried and was designated dissolved ($<.45\mu$). The residue on the filters and the centrifuged particles were combined, freeze-dried and were designated particulate ($<.45\mu$).

After freeze drying, the samples were analyzed for moisture, ash, total and organic carbon, total nitrogen, total sulphur and total concentrations of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, and Zn by the methods previously described.

TABLE 2.

EXTRACTION SCHEME FOR METAL FORMS

METAL FORM	SEDIMENT: EXTRACTANT RATIO	EXTRACTANT
SOLUBLE	1:5	Deaerated double distilled water
EXCHANGEABLE	1:5	1N MgCl ₂ pH 7
CARBONATE	1:25	1M HOAc
MANGANESE OXIDES	1:25	0.1M NH ₂ OH.HCl in 0.01M HNO ₃
ORGANIC	1:25	30% H ₂ O ₂ and 0.1M HNO ₃
IRON OXIDES	1:25	1.0M NH ₂ OH.HCl in 25% HNO ₃
CRYSTALLINE	1:50	HF, HClO ₄ , and HNO ₃

The remaining 8 l of suspended sediments were used for the isolation of organic materials from water. Suspended and dissolved humic material were precipitated by adding an excess of $Pb(NO_3)_2$ and the resulting lead humates were separated by centrifugation at 2000 rpm for 15 minutes. Lead humates were collected and composited for each watershed during the 1976 sampling season.

To remove the lead, the lead humates were suspended in distilled water, an excess of sodium sulphide was added and the pH was lowered to 9 with HCl. After stirring for 1 hr, the lead sulphide formed was filtered and the pH of the filtrate was adjusted to 1 with HCl. Nitrogen was bubbled through the solution to remove excess H_2S . Any precipitated sulphur compounds were filtered off and the clear filtrate was freeze dried.

After drying, the humate was dissolved in 50 ml of isopropanol and 20 ml of distilled water. Any precipitate was removed by centrifugation and the supernatant was dried on a rotary evaporator. This was repeated several times until no further sulphur precipitated. The humates obtained from the watersheds (when sufficient sample was available) were treated similarly to FA's extracted from soils and bottom sediments.

Particulate samples obtained by centrifugation during the 1977 spring runoff were freeze dried, and then analyzed for the same elements as the 1976 suspended sediment samples. Water samples obtained before and after centrifugation were analyzed for suspended solids and total metals by MOE laboratories.

A composite of the bottom sediments collected from each watershed was used to examine the forms of metals in bottom sediments. Modifications of the methods of Gupta and Chen (1975) and Gibbs (1973) were used.

The sequence of extractants to differentiate soluble, extractable, carbonate bound, manganese oxide bound, iron oxide bound and organically bound metals is listed in Table 2. Only Cd, Cu, Ni, Pb and Zn were examined. Each sample was sequentially extracted with each of the 6 extractants. The samples were washed with distilled water and centrifuged between extractions.

To examine the fate of metals applied to these watersheds, A horizon soils and bottom sediments from watershed 1 (Big Creek) and watershed 4 (Canagagique Creek) were incubated with the following, either singly or in combination: 100 ppm P; 5 ppm Cd; 250 ppm Zn; 100 ppm or 250 ppm Cu; 100 ppm or 250 ppm Ni; 100 ppm or 250 ppm Pb. Samples were incubated with P for 4 weeks, and then with metals for a further 6 weeks. Controls, with no additions, were included in each step. Soils were incubated at approximately 80% field capacity while bottom sediments were covered with 1 cm of water. After 10 weeks, samples were dried and sieved through a 2 mm plastic sieve. These samples underwent the series of extractions previously mentioned.

Bulk fertilizers stocks used to blend fertilizer mixtures for use in Essex county were sampled from local distributors for metal content. The samples were collected in paper envelopes, and duplicate one gram samples were digested in 10 ml 2 N HCl until boiling. The samples were cooled, filtered through No. 42 Whatman paper and the residue was leached with 2 N HCl to give a final volume of 25 ml. An IL 250 atomic absorption spectrophotometer was used for quantification.

EXPERIMENTAL RESULTS

Soils

A pedological description of the soils found in the six agricultural watersheds has been prepared by Project 7 (Acton et al., 1978). The mineralogical aspects of these soils are presented in Project 8 (Wall, 1978). The emphasis in this report has been placed on trace element analyses in these watersheds.

Total Trace Element Concentrations

The total concentrations of Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Zn, as well as total nitrogen, phosphorus, carbon, organic carbon, pH, clay, organic matter and carbonates are given in Appendix Table 4 for each soil sampled. The division of soil sites into luvisols, gleysols and brunisols is given in Appendix Table 2. The percentage of each watershed represented by each soil series is given in Appendix Table 3. The average metal values for all the soils sampled in Southern Ontario are given in Table 3. The weighted average values for each watershed for each horizon are given in Table 4.

The mean concentration of As in the soils studied was 4.7 ± 2.3 ppm for the A horizon, 6.3 ± 4.4 ppm for the B horizon and 4.4 ± 2.7 ppm for the C horizon. These values are within the range reported by Frank *et al.* (1976) as average for Southern Ontario Soils. Ranking the watersheds for decreasing concentrations of As gave the following (Figure 1):

A HORIZON 10 > 1 > 13 > 5 > 3 > 4
B HORIZON 10 > 13 > 5 > 3 > 1 > 4
C HORIZON 13 > 1 > 10 > 3 = 4 > 5

The average concentration of Cd in Southern Ontario soils could not be calculated from our results as the majority of values were below the limit of detection (0.3 ppm). The Cd values were up to 1.0 ppm on some of the soils with a high clay content. Frank *et al.* (1976) reported 0.56 ± 0.69 ppm as average for Southern Ontario soils.

The mean concentration of Cr in the soils studied was 51.5 ± 17.1 ppm for the A horizon, 54.7 ± 17.6 for the B horizon, and 49.6 ± 21.9 ppm for the C horizon. These values were higher than those reported by Frank *et al.* (1976) as normal for Ontario soils - 14.3 ± 8.5 - but some of the difference is due to the mild digestion technique of Frank *et al.* Ranking the watersheds for decreasing concentrations of Cr gave the following (Figure 2):

TABLE 3. AVERAGE ELEMENTAL COMPOSITION FOR SOILS IN AGRICULTURAL WATERSHEDS OF SOUTHERN ONTARIO

	A HORIZON	B HORIZON	C HORIZON
ARSENIC (ppm)	4.7±2.3 (2.0-13.0)	6.3±4.4 (1.2-20.0)	4.4±2.7 (1.0-12.0)
CADMIUM (ppm)	* (1.0-0.1W)	* (1.7-0.1W)	* (1.0-0.1W)
CHROMIUM (ppm)	51.5±17.1 (26.2-76.4)	54.7±17.6 (29.7-82.5)	49.6±21.9 (24.4-78.9)
COPPER (ppm)	17.3±6.2 (11.3-28.8)	25.5±3.9 (20.3-31.2)	24.3±7.2 (20.4-35.2)
MERCURY (ppb)	47±18 (12-100)	36±16 (6-68)	20±11 (1-94)
MANGANESE (ppm)	557.7±273.4 (242.2-905.5)	625.4±133.2 (485.1-826.9)	528.9±69.9 (432.7-563.5)
NICKEL (ppm)	19.4±6.2 (10.2-28.8)	30.9±9.6 (18.4-42.0)	25.8±11.8 (12.4-46.2)
LEAD (ppm)	22.5±4.2 (16.7-28.9)	19.7±3.2 (14.1-23.2)	17.6±4.3 (13.1-24.9)
SELENIUM (ppm)	0.35±0.11 (0.23-0.49)	0.18±0.06 (0.11-0.25)	0.14±0.11 (0.06-0.36)
ZINC (ppm)	84.3±23.5 (50.2-121.2)	83.7±20.7 (51.0-93.6)	69.4±23.1 (43.0-103.4)
ALUMINUM (%)	5.85±1.00 (4.34-7.08)	6.50±0.86 (4.97-7.52)	5.50±1.28 (4.06-7.12)
IRON (%)	2.78±1.15 (1.57-4.88)	3.22±0.72 (2.19-4.41)	2.73±0.83 (1.90-3.78)
CARBON (%)	2.33±1.02 (0.90-3.75)	0.72±0.30 (0.23-1.16)	3.50±1.13 (2.20-5.15)
ORGANIC MATTER (%)	3.02±1.80 (0.16-9.44)	0.66±0.50 (0.00-2.33)	0.37±0.25 (0.08-1.03)
NITROGEN (%)	0.20±0.10 (0.01-0.38)	0.06±0.02 (0.01-0.10)	0.03±0.02 (0.01-0.07)
PHOSPHORUS (ppm)	657±277 (66-2709)	457±224 (143-1058)	465±105 (175-653)
CLAY (%)	19.6±10.2 (5.3-39.0)	32.1±15.7 (1.7-58.1)	26.7±13.5 (2.0-57.2)
pH	6.6±0.6 (5.2-7.6)	7.2±0.6 (5.1-7.6)	7.5±0.2 (7.1-8.0)

* cannot average since values below criteria of detection.

TABLE 4. WEIGHTED** AVERAGE ELEMENTAL CONCENTRATIONS OF SOILS IN EACH AGRICULTURAL WATERSHED

	A HORIZON					
	AG1	AG3	AG4	AG5	AG10	AG13
ARSENIC (ppm)	5.5	4.3	3.8	4.4	6.8	5.4
CADMIUM (ppm)	0.9	*	*	*	*	*
CHROMIUM (ppm)	63.6	80.2	51.7	49.3	62.8	26.0
COPPER (ppm)	24.5	26.5	18.5	16.0	16.4	13.2
MERCURY (ppb)	40	81	52	50	44	29
MANGANESE (ppm)	266.5	686.9	889.5	807.5	2535.5	307.3
NICKEL (ppm)	28.7	29.7	19.0	16.7	22.7	9.5
LEAD (ppm)	24.8	25.2	21.3	22.1	29.3	21.3
SELENIUM (ppm)	0.62	0.41	0.32	0.30	0.42	0.32
ZINC (ppm)	120.4	98.3	75.0	84.9	125.1	53.7
ALUMINUM (%)	6.38	6.92	5.78	5.86	7.10	4.29
IRON (%)	2.69	2.95	2.71	2.61	5.03	1.45
CARBON (%)	2.56	3.28	2.78	2.63	3.24	1.42
ORGANIC MATTER (%)	3.4	4.7	4.3	4.2	3.9	2.2
NITROGEN (%)	0.22	0.29	0.24	0.26	0.24	0.11
PHOSPHORUS (ppm)	645	739	550	978	1668	810
CLAY (%)	30.5	33.5	23.5	19.2	36.1	8.0
pH	6.5	7.4	6.7	6.8	6.2	6.2

* cannot average since values below criteria of detection

** weighted with respect to areas occupied by different soils of each watershed.

TABLE 4 (cont'd)

	B HORIZON					
	AG1	AG3	AG4	AG5	AG10	AG13
ARSENIC (ppm)	4.1	4.5	3.9	4.6	6.3	4.9
CADMIUM (ppm)	1.0	*	*	*	*	*
CHROMIUM (ppm)	79.4	64.9	44.4	46.9	83.0	26.6
COPPER (ppm)	35.6	26.8	21.6	23.4	31.9	27.2
MERCURY (ppb)	38	32	43	37	32	28
MANGANESE (ppm)	640.8	580.8	704.9	743.7	575.0	703.8
NICKEL (ppm)	57.8	37.3	24.6	23.7	42.6	24.1
LEAD (ppm)	20.4	21.4	16.9	18.8	23.3	18.5
SELENIUM (ppm)	0.35	0.19	0.09	0.12	0.22	0.13
ZINC (ppm)	120.8	82.9	68.9	71.1	115.4	68.7
ALUMINUM (%)	8.10	6.93	5.82	6.42	7.46	5.54
IRON (%)	4.07	3.22	3.08	3.25	4.44	2.71
CARBON (%)	0.69	1.07	0.64	0.96	0.77	0.25
ORGANIC MATTER (%)	0.60	0.82	1.15	0.53	1.54	0.18
NITROGEN (%)	0.07	0.06	0.06	0.04	0.09	0.02
PHOSPHORUS (ppm)	336	551	522	660	608	349
CLAY (%)	44.0	42.2	34.3	20.8	48.5	18.2
pH	7.4	7.5	6.5	6.8	6.9	6.7

* cannot average since values below criteria of detection

TABLE 4 (cont'd)

	C HORIZON					
	AG1	AG3	AG4	AG5	AG10	AG13
ARSENIC (ppm)	6.8	3.4	3.4	2.7	5.3	7.8
CADMIUM (ppm)	*	*	*	*	*	*
CHROMIUM (ppm)	78.3	55.7	37.9	26.2	70.5	38.4
COPPER (ppm)	32.7	21.4	20.1	15.6	30.0	25.6
MERCURY (ppb)	28	36	15	8	19	25
MANGANESE (ppm)	510.1	508.2	632.9	525.1	540.8	424.5
NICKEL (ppm)	44.1	20.2	19.3	12.8	30.5	21.8
LEAD (ppm)	17.2	16.2	15.1	13.3	18.6	13.7
SELENIUM (ppm)	0.41	0.12	0.11	0.05	0.09	0.09
ZINC (ppm)	103.7	57.0	59.4	42.4	86.6	65.7
ALUMINUM (%)	6.90	4.47	5.89	4.14	7.08	5.39
IRON (%)	3.48	2.24	2.83	1.81	3.75	2.38
CARBON (%)	2.66	5.16	3.71	4.35	3.27	1.86
ORGANIC MATTER (%)	0.81	0.42	0.25	0.18	0.26	0.29
NITROGEN (%)	0.06	0.04	0.03	0.01	0.06	0.03
PHOSPHORUS (ppm)	338	434	508	430	597	465
CLAY (%)	39.9	30.4	27.4	10.6	57.1	17.9
pH	7.5	7.7	6.9	7.5	7.7	7.5

* cannot average since values below criteria of detection

A HORIZON 3 > 1 > 10 > 4 > 5 > 13
 B HORIZON 10 > 1 > 3 > 5 > 4 > 13
 C HORIZON 1 > 10 > 3 > 13 > 4 > 5

The average concentration of Cu in the soils studied was 17.3 ± 6.2 ppm in the A horizon, 25.5 ± 3.9 ppm in the B horizon and 24.3 ± 7.2 ppm in the C horizon. Frank et al. (1976) reported 25.4 ± 21.5 ppm for agricultural soils. Ranking the watersheds for decreasing concentrations of Cu gave the following (Figure 3):

A HORIZON 3 > 1 > 4 > 10 > 5 > 13
 B HORIZON 1 > 10 > 13 > 3 > 5 > 4
 C HORIZON 1 > 10 > 13 > 3 > 4 > 5

The average concentration of Hg in the soils studied was 47 ± 18 ppb for the A horizon, 36 ± 16 ppb for the B horizon and 20 ± 11 ppb for the C horizon. Frank et al. (1976) determined 0.11 ± 0.18 ppm as average for Southern Ontario. Ranking the watersheds in decreasing concentrations of Hg gave the following (Figure 4):

A HORIZON 3 > 4 > 5 > 10 > 1 > 13
 B HORIZON 4 > 1 > 5 > 3 = 10 > 13
 C HORIZON 3 > 1 > 13 > 10 > 4 > 5

The average concentration of Mn in the soils studied was 557 ± 273.4 ppm in the A horizon, 625.4 ± 133.2 ppm in the B horizon and 528.9 ± 69.9 ppm in the C horizon. These are within the average reported by Frank et al. (1976) of 530 ± 531 ppm. Ranking the watersheds in decreasing concentrations of Mn gave the following (Figure 5):

A HORIZON 10 > 4 > 5 > 3 > 13 > 1
 B HORIZON 5 > 4 > 13 > 1 > 3 > 10
 C HORIZON 4 > 10 > 5 > 3 > 1 > 13

The average concentration of Ni in the soils studied was 19.4 ± 6.2 ppm for the A horizon, 30.9 ± 9.6 ppm for the B horizon, and 25.8 ± 11.8 ppm for the C horizon. Frank et al. (1976) reported a mean Ni concentration of 15.9 ± 16.0 ppm. Ranking the watersheds in decreasing concentration of Ni gave the following (Figure 6):

A HORIZON 3 > 1 > 10 > 4 > 5 > 13
 B HORIZON 1 > 10 > 3 > 4 > 13 > 5
 C HORIZON 1 > 10 > 13 > 3 > 4 > 5

The average concentration of Pb in the soils studied was 22.5 ± 4.2 ppm in the A horizon, 19.7 ± 3.2 ppm in the B horizon and 17.6 ± 4.3 ppm in the C horizon. This pattern of the A horizon with the highest Pb concentration is evident in 18 of the 24 soils. Frank et al. (1976) reported 14.1 ± 9.5 ppm for non-fruit producing soils. Ranking the watersheds in decreasing concentrations of Pb gave the following (Figure 7):

A HORIZON 10 > 3 > 1 > 5 > 3 = 13
 B HORIZON 10 > 3 > 1 > 5 > 13 > 4
 C HORIZON 10 > 1 > 3 > 4 > 13 > 5

The average concentration of Se in the soils studied was 0.35 ± 0.11 ppm in the A horizon, 0.18 ± 0.06 in the B horizon and 0.14 ± 0.11 ppm in the C horizon. Selenium showed this pattern of high surface concentrations in 21 of the 24 soils. Ranking the watersheds in decreasing order of Se concentration gave the following (Figure 8):

A HORIZON 1 > 10 > 3 > 4 = 13 > 5
 B HORIZON 1 > 10 > 3 > 13 > 5 > 4
 C HORIZON 1 > 3 > 4 > 10 = 13 > 5

The average concentrations of Zn in the soils studied was 84.3 ± 23.5 ppm for the A horizon, 83.7 ± 20.7 for the B horizon and 69.4 ± 23.1 for the C horizon. Frank *et al.* (1976) reported 53.5 ± 34.3 ppm Zn in Ontario soils. Ranking the watersheds in decreasing order of Zn concentration gave the following (Figure 9):

A HORIZON 10 > 1 > 3 > 5 > 4 > 13
 B HORIZON 1 > 10 > 3 > 5 > 4 > 13
 C HORIZON 1 > 10 > 13 > 4 > 3 > 5

The average concentration of Al in the soils studied was $5.85 \pm 1.00\%$ for the A horizon, $6.50 \pm 0.86\%$ for the B horizon and $5.50 \pm 1.28\%$ for the C horizon. Ranking the watersheds in decreasing concentrations of Al gave the following:

A HORIZON 10 > 3 > 1 > 5 > 4 > 13
 B HORIZON 1 > 10 > 3 > 5 > 4 > 13
 C HORIZON 10 > 1 > 4 > 13 > 5 > 3

The average concentration of Fe in the soils studied was $2.78 \pm 1.15\%$ in the A horizon, $3.22 \pm 0.72\%$ in the B horizon and $2.73 \pm 0.83\%$ for the C horizon. Frank *et al.* (1976) reported the mean Fe values of $1.45 \pm 0.76\%$, which were not total values due to the extraction procedure. Ranking the watersheds in decreasing concentration of Fe gave the following:

A HORIZON 10 > 3 > 4 > 1 > 5 > 13
 B HORIZON 10 > 1 > 5 > 3 > 4 > 13
 C HORIZON 10 > 1 > 4 > 13 > 3 > 5

Ranking the watersheds in decreasing quantities of clay gave the following (Figure 10):

A HORIZON 10 > 3 > 1 > 4 > 5 > 13
 B HORIZON 10 > 1 > 3 > 4 > 5 > 13
 C HORIZON 10 > 1 > 3 > 4 > 13 > 5

Fig. 1. Total arsenic concentration of soil and bottom sediment for agricultural watersheds. Values weighted from area occupied by each soil series within each watershed.

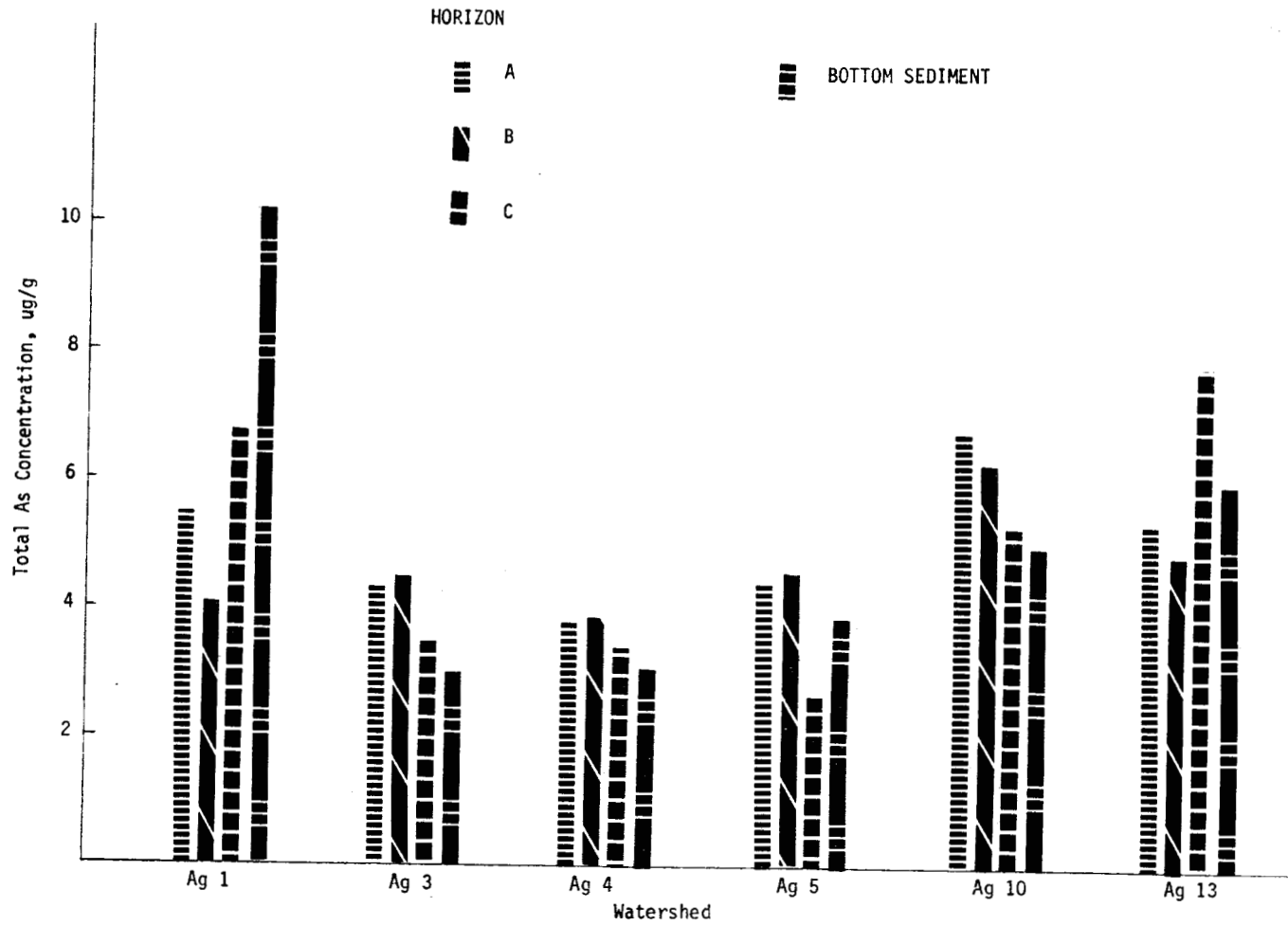


Fig. 2. Total chromium concentration of soil and bottom sediment for agricultural watersheds. Values weighted from area occupied by each soil series within each watershed.

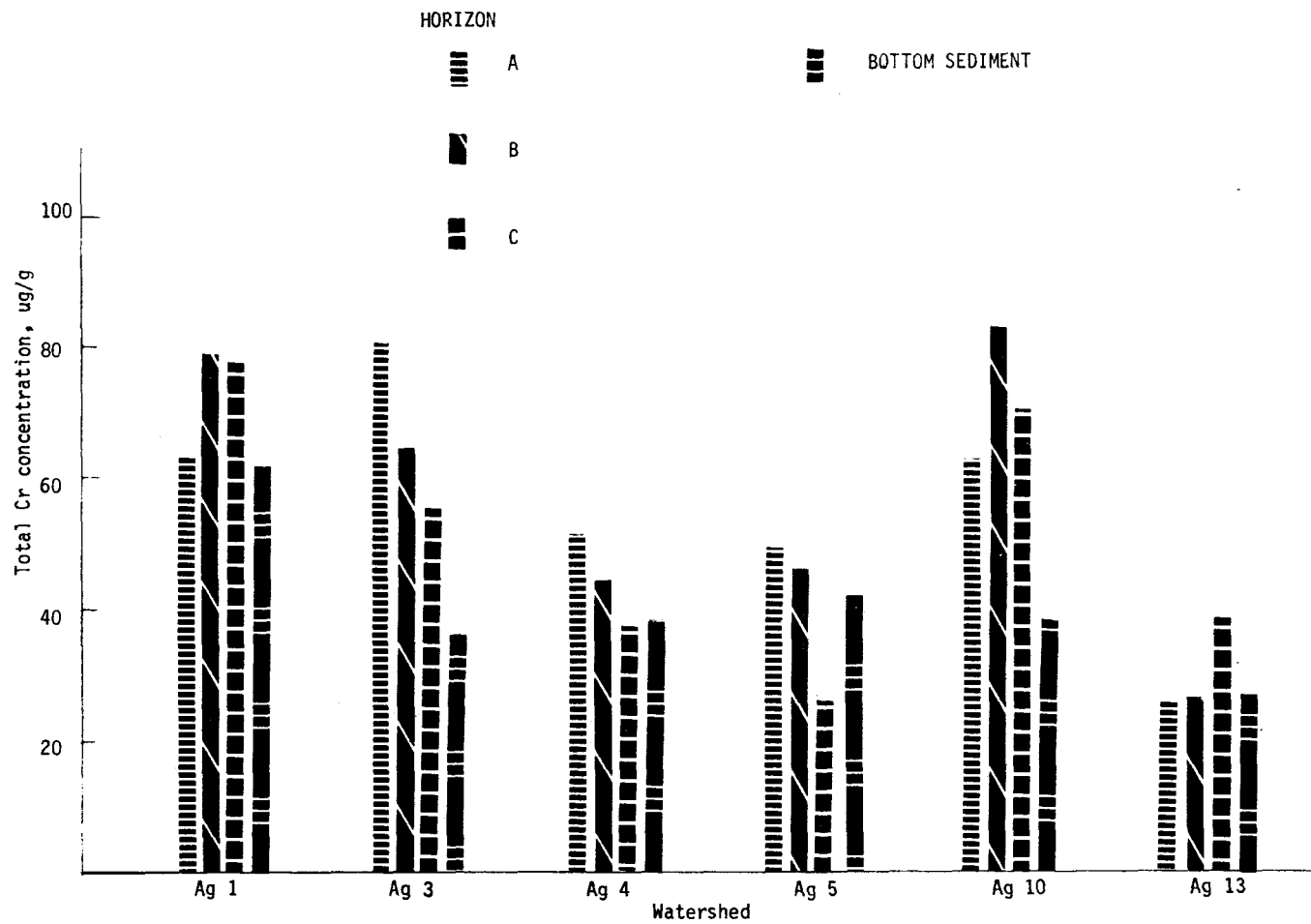


Fig. 3. Total copper concentration of soil and bottom sediment for agricultural watersheds. Values weighted from area occupied by each soil series within each watershed.

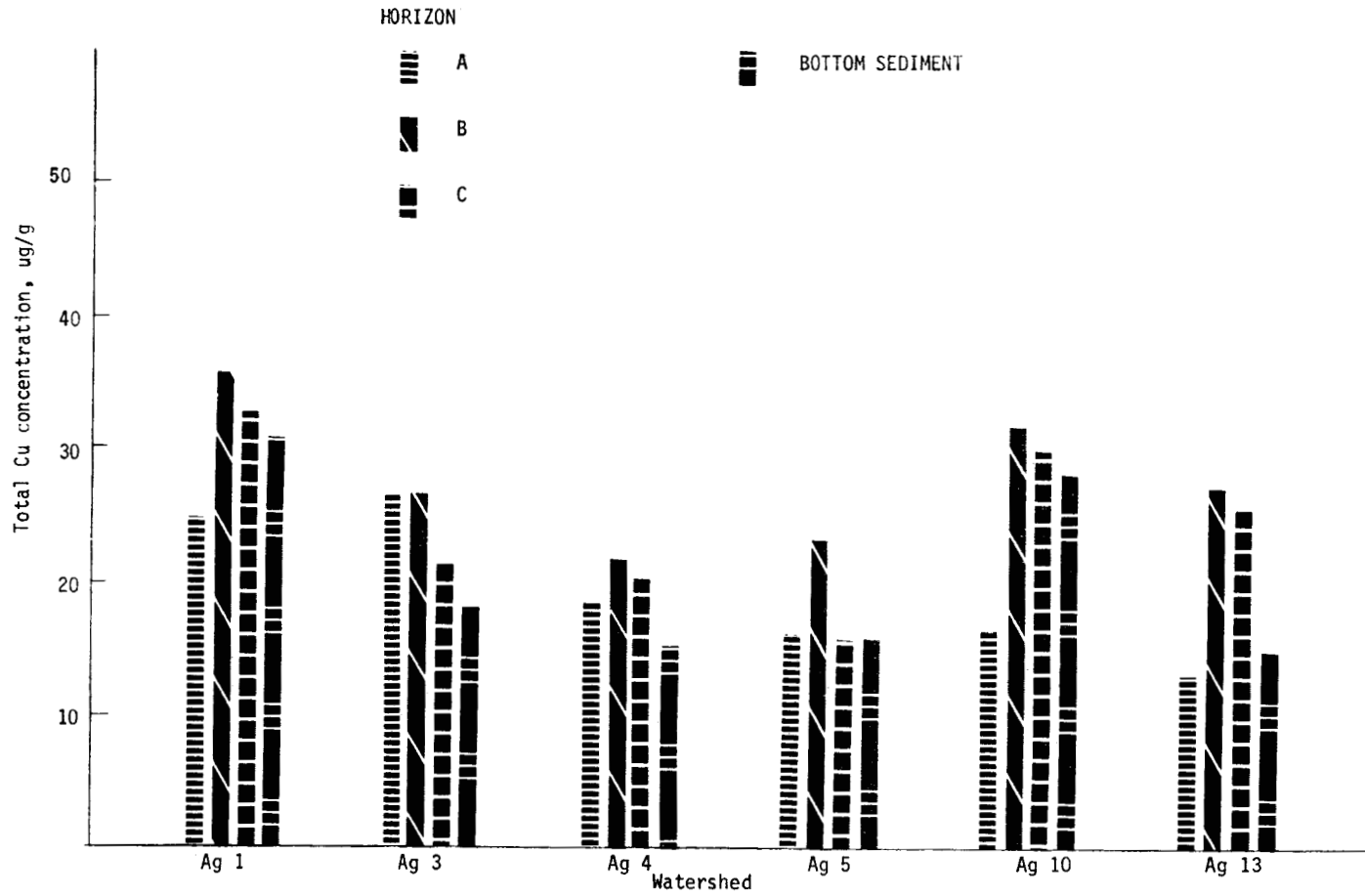


Fig. 4. Total mercury concentration of soil and bottom sediment for agricultural watersheds. Values weighted from area occupied by each soil series within each watershed.

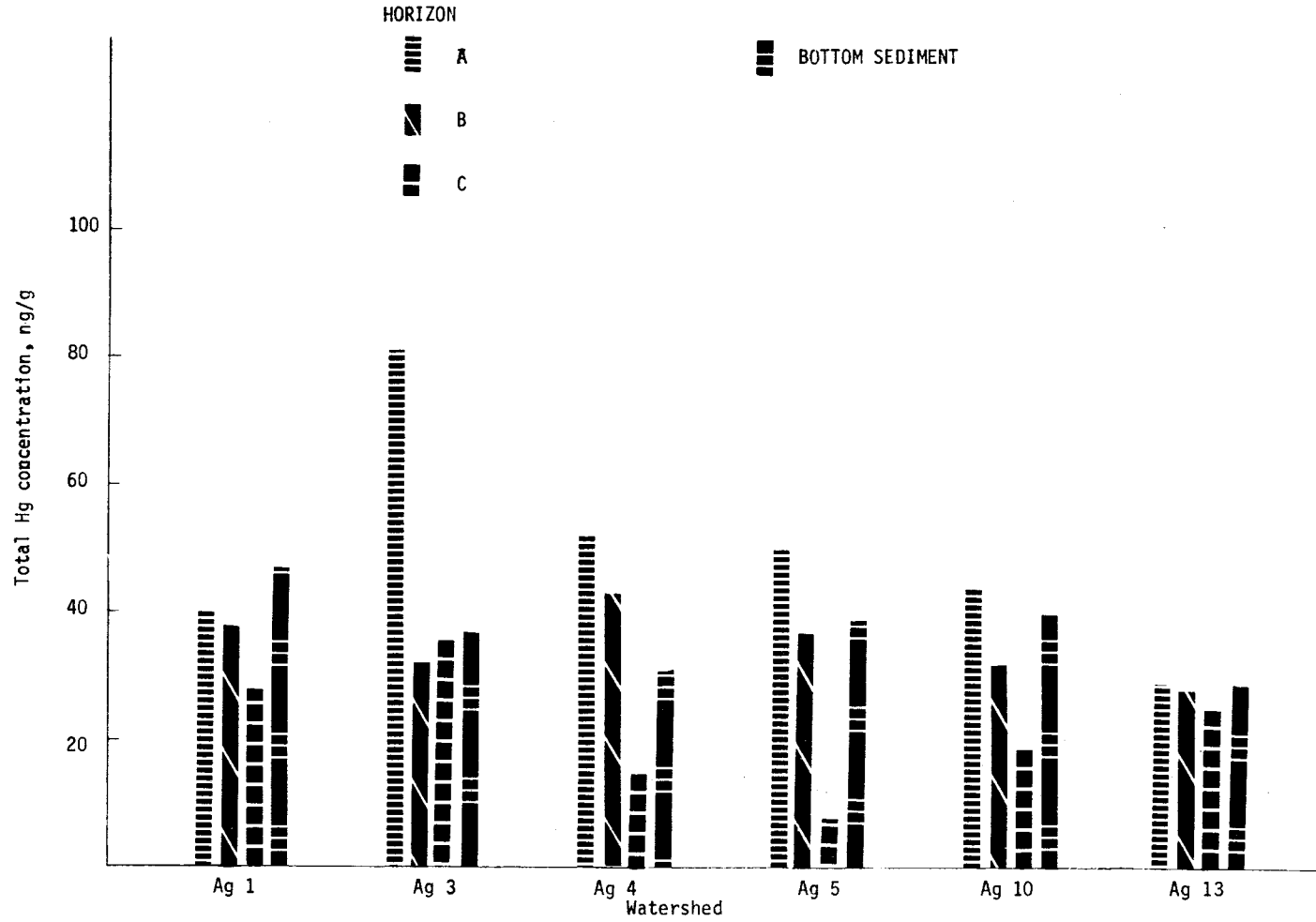
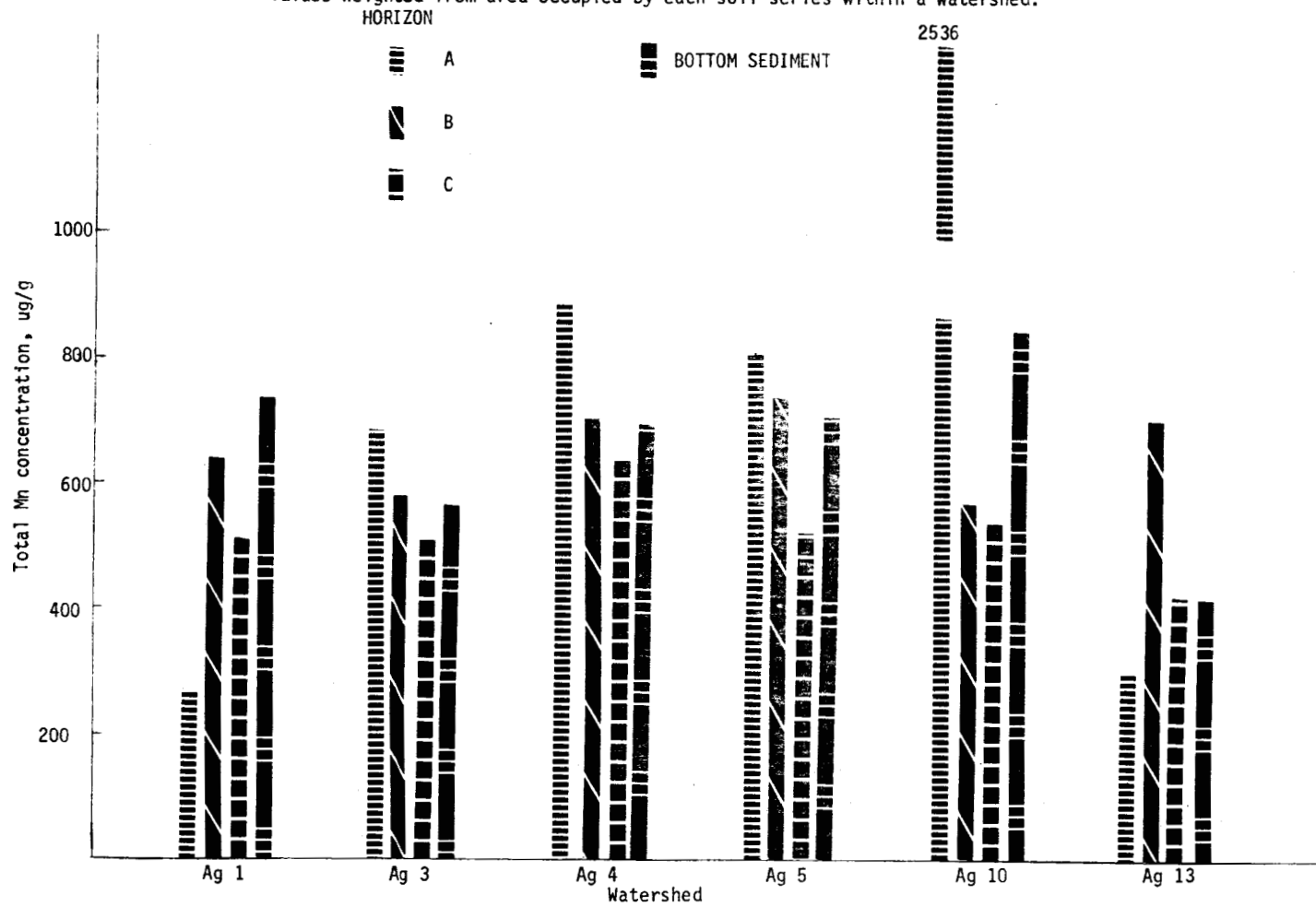


Fig. 5. Total manganese concentration for soil and bottom sediment for agricultural watersheds. Values weighted from area occupied by each soil series within a watershed.



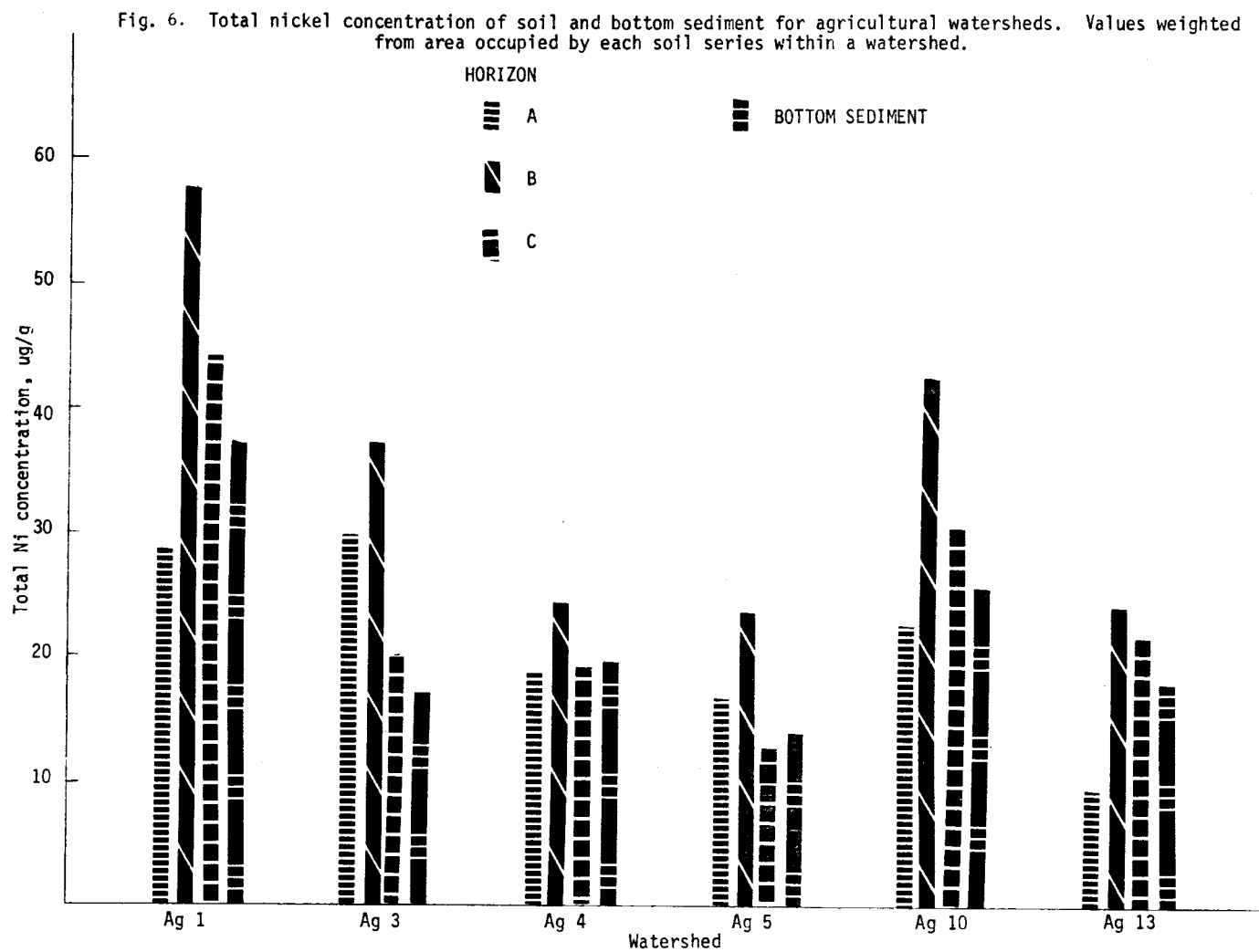


Fig. 7. Total lead concentration of soil and bottom sediment for agricultural watersheds. Values weighted from area occupied by each soil series within a watershed.

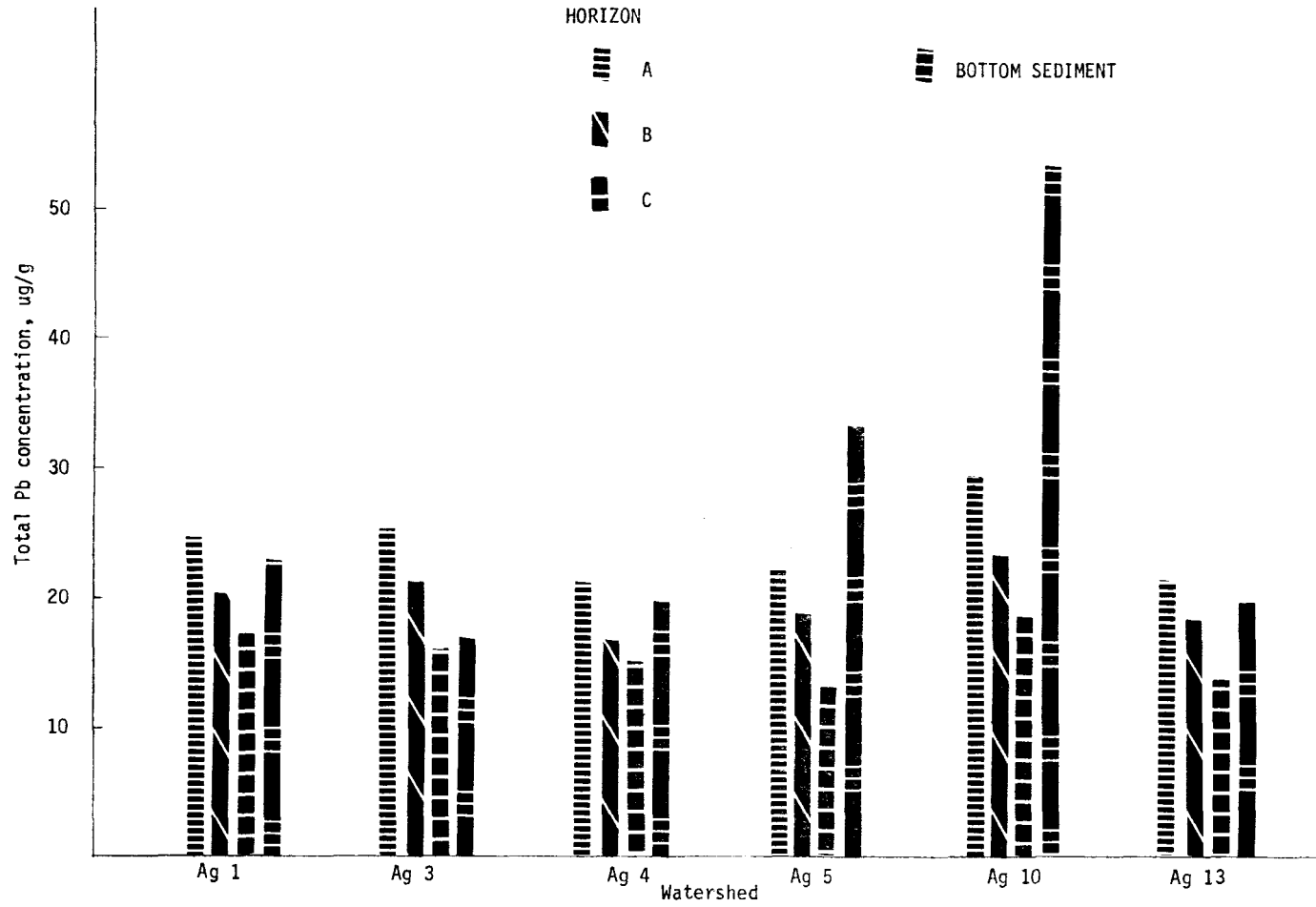


Fig. 8. Total selenium concentration of soil and bottom sediment for agricultural watersheds. Values weighted from area occupied by each soil series within a watershed.

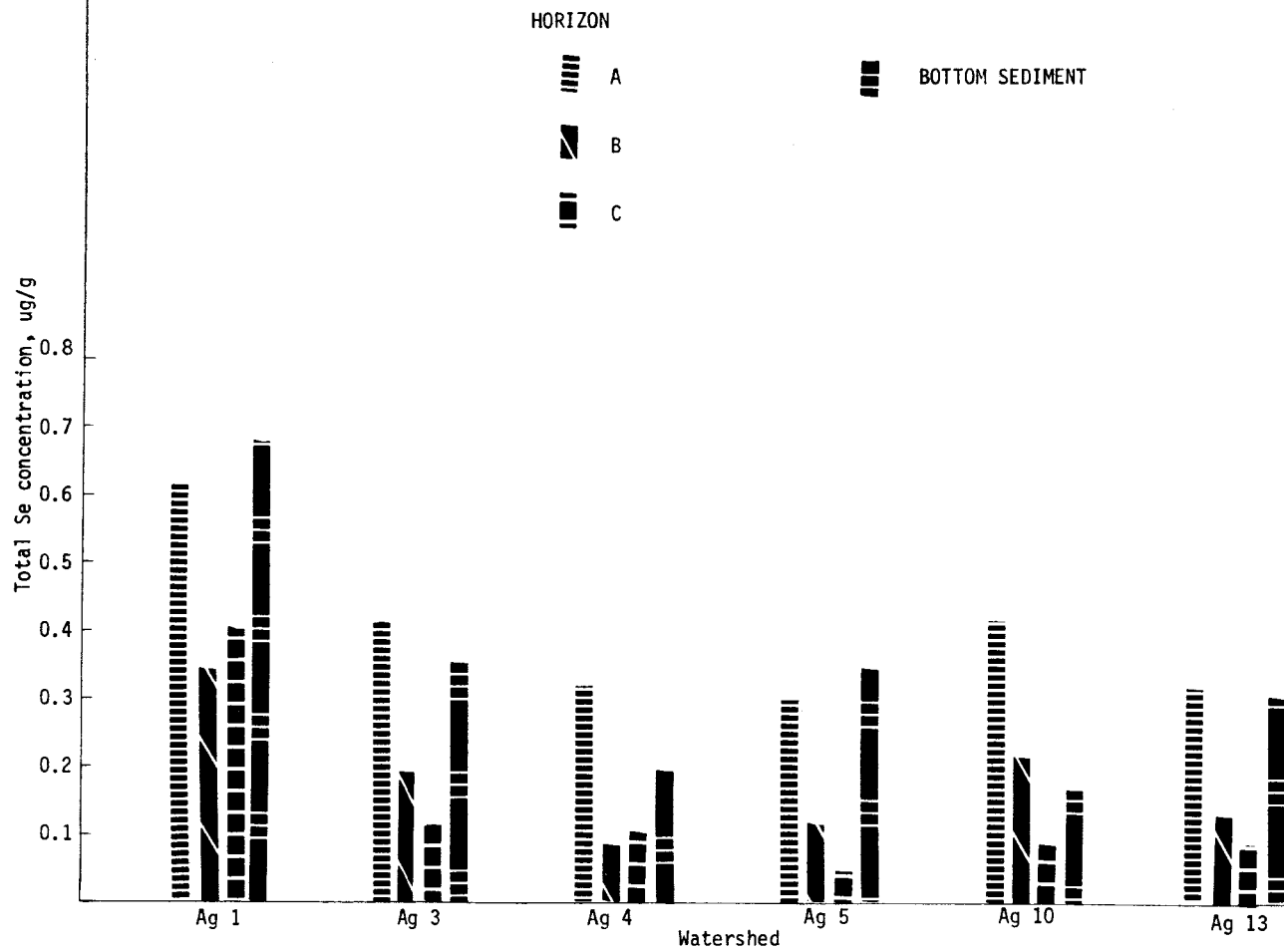


Fig. 9. Total zinc concentration of soil and bottom sediment for agricultural watersheds. Values weighted from area occupied by each soil series within a watershed.

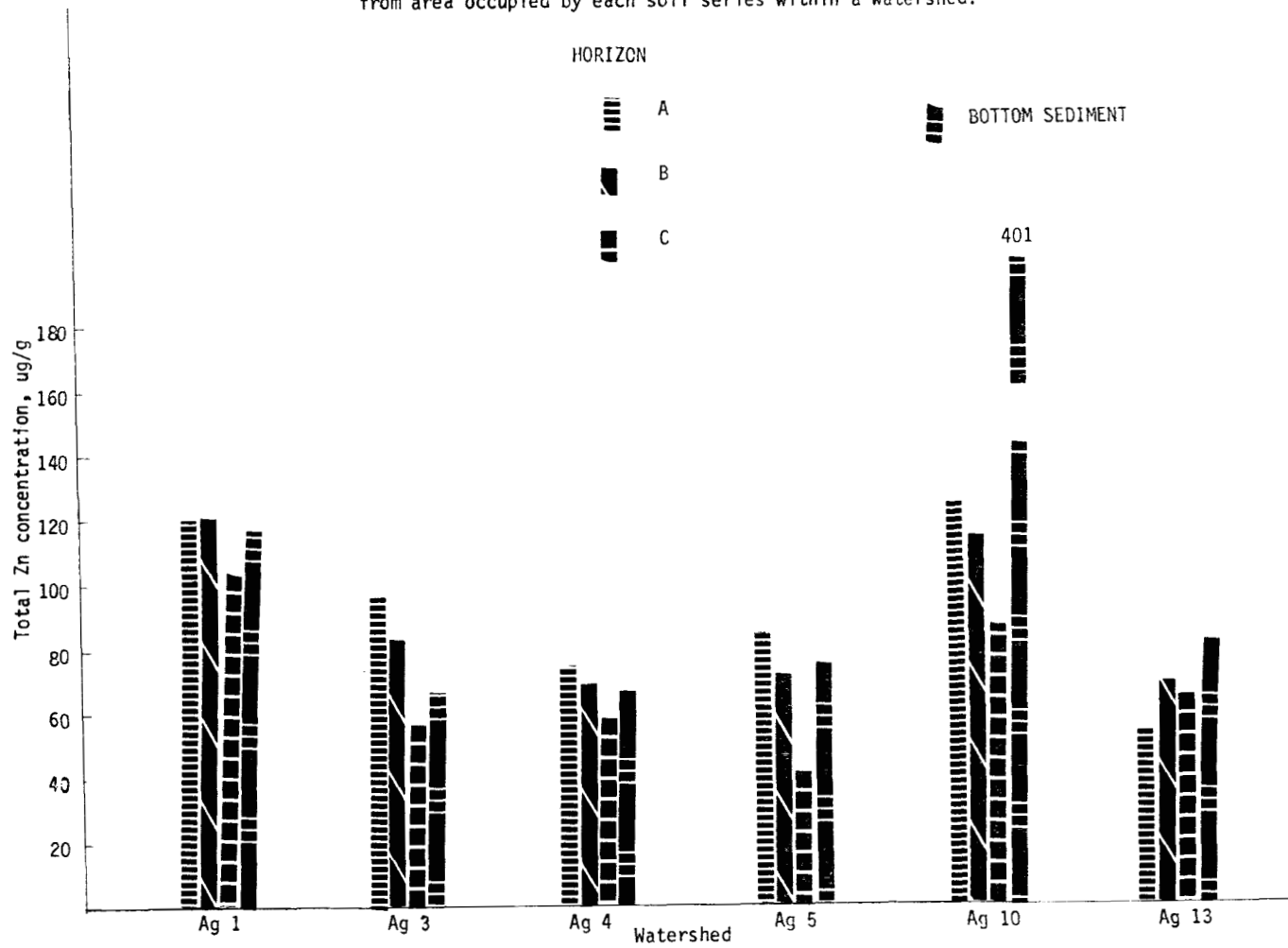
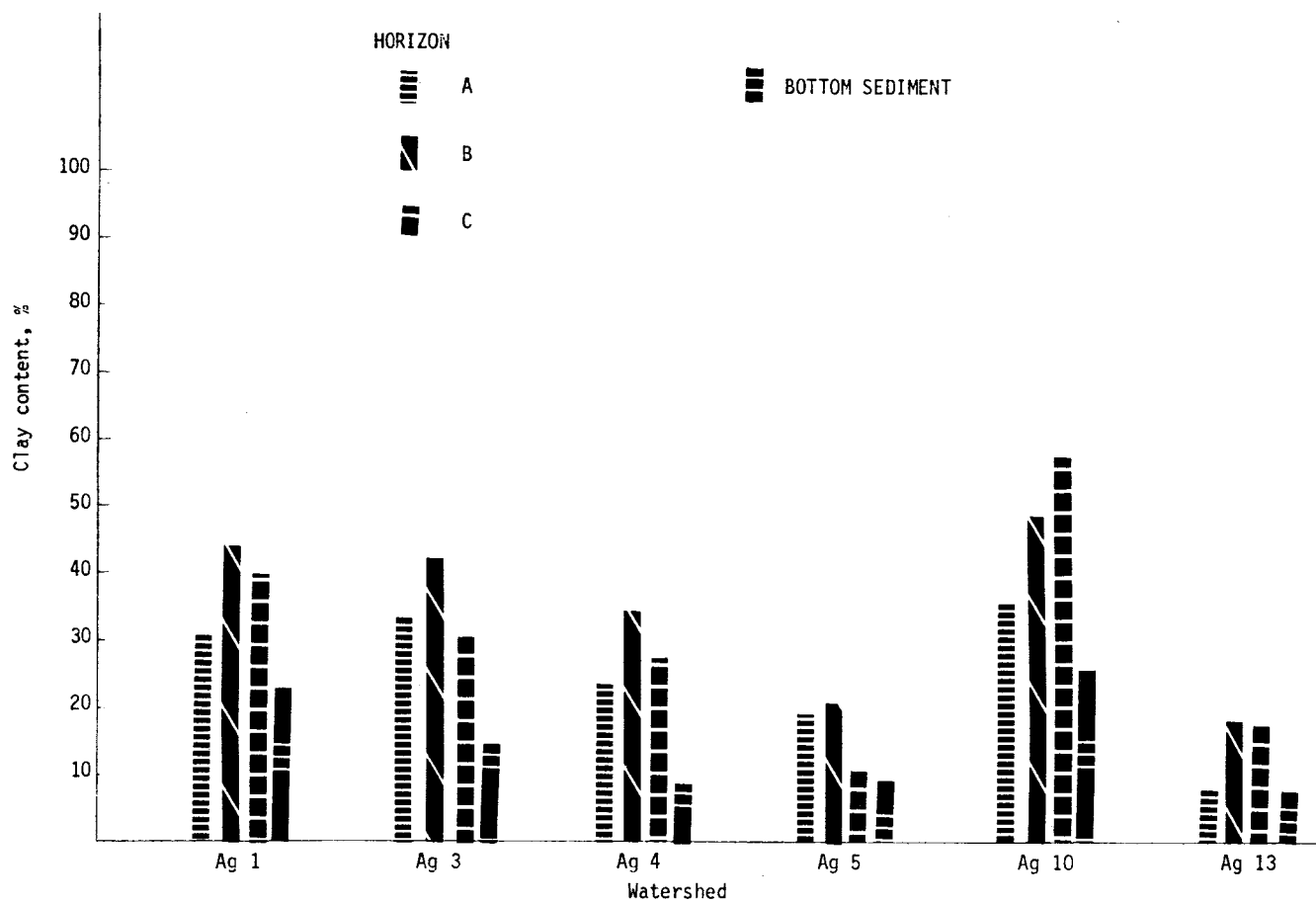


Fig. 10. Clay content of soil and bottom sediment in selected agricultural watersheds. Values weighted from area occupied by each soil series within the watershed.



Carbon, nitrogen, phosphorus and organic matter of each soil were more site specific; average soil values and weighted watershed soil averages are given in Tables 3 and 4. Carbon and organic matter were highest in the surface horizon but the carbon, due to carbonates, was also often high in the C horizon. Total nitrogen and phosphorus were usually highest in the surface soils reflecting the higher organic matter in that horizon; however, in watershed 10, the P values were highest in the C horizon, perhaps due to increased natural phosphorus in this watershed.

Correlation coefficients for trace metals and nutrients with clay, organic matter, carbonates, Al, Fe and Mn are given in Appendix Table 5 for Ap horizons. Correlation coefficients for the individual gleysols and luvisols for each horizon are given in Appendix Tables 6 and 7. The soil order of each soil site are given in Appendix Table 2.

Aluminum and iron correlated positively with clay; 85% of the aluminum and 53% of the iron variation is accounted for by the clay content. Mn was not correlated with clay. It was anticipated that hydrous oxides of Al, Fe and Mn as coatings on clays, as well as part of the clay composition, would be more strongly correlated. The correlation of Al and Fe accounted for 64% of the variation while Mn and Fe accounted for 65% of the variation. However Mn and Al were poorly correlated (14%). Therefore, it could be expected that properties that correlated with clays would also correlate with Al and Fe. These included the metals Cr (particularly with Al 67%), Ni (71%), Pb (particularly with Fe 53%) and Zn (particularly with Fe 65%).

Organic matter correlated positively with total carbon (31%) and total nitrogen (79%), although total nitrogen also showed 49% of variation explained by Al. Copper (45%), and Hg (77%) showed positive correlations with organic matter.

Total phosphorus was positively correlated with total Mn (64%).

DTPA Extractable Metals

The DTPA extraction method is a measure of the availability of metals in soils for plant growth. Since root growth is most active in the A horizon and organic matter is highest in the A horizon, the highest metal availabilities are usually found in the A horizon. The DTPA extracts of the soils from the 6 agricultural watersheds follow this pattern of higher availability in the A horizon than the B or C horizons (Appendix Table 8).

Approximately 5.5% of the total Cu in the A horizons was extracted by DTPA. The gleysolic soils had 7.4% DTPA extractable Cu while the brunisolic and luvisolic soils had about 5%. Only 2.1% of the total Ni was DTPA extractable, with a slightly higher amount from the gleysols (2.8%). Approximately 5.5% of the total Pb in the Ap horizon was extracted by DTPA.

TABLE 5.

AVERAGE CHEMICAL COMPOSITION AND FUNCTIONAL GROUP ANALYSIS OF HA'S¹ AND FA'S²
EXTRACTED FROM WATERSHED SOILS AND SEDIMENTS

	C %	H %	N %	S %	O %	E4/E6	Total Acidity meq/g	Total Carboxyl meq/g	Total Phenol meq/g
Soil HA's ¹	52.9	6.2	3.6	0.9	36.4	4.5	9.3	5.0	4.3
Sediment HA's ¹	56.0	6.7	5.7	2.7	28.9	3.8	6.8	2.9	3.9
Ideal HA's ¹	56.2	4.7	3.2	0.8	35.5	4.8	6.7	3.6	3.9
Soil FA's ²	44.7	6.5	3.7	1.6	43.5	5.1	12.2	6.5	5.7
Sediment FA's ²	38.7	6.3	4.4	1.3	49.6	4.4	8.1	2.5	5.6
Suspended FA's ²	40.9	4.9	1.5	7.8	44.9	*	*	*	*
Ideal FA's ** ²	45.7	5.4	2.1	1.9	44.8	9.6	10.3	8.2	3.0

* Insufficient sample

** from Schnitzer (1977)

HA - Humic Acid

FA - Fulvic Acid

The range of the extractable Pb was greater among the soil orders - brunisols had 9.4%, gleysols had 6.9% and luvisols had 4.3% of the total Pb extractable. Only 1.5% of the Zn was extractable with DTPA with very little difference between the soil groups.

There was no strong correlations between DTPA extractable metal and clay, organic matter, Al, Fe or pH, although clay gave significant correlations ($r=+0.54$ for Cu, $r=+0.57$ for Ni) (Appendix Table 9). Similarly, the correlations between DTPA extractable metal and total metal were $r=+0.69$ for Cu, $r=+0.54$ for Ni, $r=+0.05$ for Pb and $r=+0.48$ for Zn.

Humic Substances

The general characteristics of the soils from which humic substances were extracted are given in Appendix Table 10. Their characteristics are similar to those soils previously discussed (Appendix Table 4). The extraction efficiency can be calculated from the organic matter content of the soils. Thus, the organic matter content of the soils analyzed ranged from 21.4 to 50.5 g/kg. Extracted and purified HA's accounted for between 6.0% (watershed 10) and 36.5% (watershed 1) of the initial organic matter, whereas extracted and purified FA's constituted between 3.3% (watershed 10) and 19.9% (watershed 5) of the original soil organic matter. Percentages of the initial organic matter extracted as HA's + FA's were as follows: watershed 1 - 52.4%; watershed 3 - 20.2%; watershed 4 - 36.8%; watershed 5 - 55.8%; watershed 10 - 9.3% and watershed 13 - 41.1%.

Table 5 contains the average elemental composition and functional group analyses of HA's and FA's extracted from watershed soils and "ideal" HA and FA.

The elemental composition of the soil HA's from the 6 watersheds is shown in Appendix Table 11. The widest variations were in C (47.9-56.0%) and O (33.6%-39.8%) contents. When the C analysis for soil was omitted, the average %C for the soils HA's analyzed increased to 53.5%. Data for the remaining elements were relatively uniform. Average elementary analyses for the 6 HA's were similar to those of an "ideal" HA, which is the composite of numerous analyses done on large numbers of HA's extracted from soils occurring under widely differing climatic and geologic conditions.

The elementary composition of the soil FA's resembled that of the "ideal" soil FA (Appendix Table 12).

Data for major oxygen-containing functional groups in the HA's and FA's extracted from the soils in the watersheds are also shown in Appendix Tables 11 and 12. Averages for total acidity, carboxyls, phenolic hydroxyls and E_4/E_6 ratios for HA's were close to similar data for the "ideal" soil-HA. Similar observations were made on the FA's, except for E_4/E_6 ratios, which were appreciably lower than those for the "ideal" soil FA but were close to the E_4/E_6 ratio for the "ideal" soil-HA.

Yields of major types of oxidation products resulting from the different HA's and FA's identified by mass spectrometry are summarized in Table 6. Only small amounts of aliphatics were isolated from the different degradation products. The major compounds produced were benzenecarboxylic and phenolic acids. Similar amounts of benzenecarboxylic acids were formed from the oxidation of one g of methylated soil HA and soil FA. Also, similar but somewhat lower yields of these acids were isolated from bottom sediment HA's and from organic matter in suspended sediments. Bottom sediment FA's produced the lowest yields of benzenecarboxylic acids.

As far as phenolic acids were concerned, the oxidation of soil HA's produced the largest amounts, while lower but similar amounts were formed from soil FA's and bottom sediment HA's. Schnitzer (1977) reports that the major compounds produced by the KMnO_4 oxidation of methylated HA's and FA's extracted from surface and subsurface soils formed under widely differing geologic and climatic conditions were benzenecarboxylic and phenolic acids. He considers these compounds major humic "building blocks". The data presented herein, show that sediment HA's and FA's have the same "building blocks" as soil humic substances. Weight ratios of benzenecarboxylic to phenolic acids, which may be considered to reflect the interrelationship between major "building blocks", are also listed in Table 6. The ratios ranged from 2.2 (for soil HA's) to 5.9 (for suspended sediments). From the data in Table 6 the aromaticity of each set of HA's and FA's was approximated by expressing yields of phenolic + benzenecarboxylic acids as percentages of total yields. Because dialkyl phthalates were not considered structural components, the yields of dialkyl phthalates were subtracted from total yields for the purpose of estimating aromaticities. As shown in Table 6, the aromaticity of the organic matter from the suspended sediments was similar to that of soil HA's, whereas aromaticities of bottom sediment HA's and FA's were lower than those of soil HA's and FA's. Another point of interest is the isolation of relatively large amounts of dialkyl phthalates from bottom sediment HA's and FA's. It is possible that the dialkyl phthalates were environmental contaminants (Schnitzer and Khan, 1972).

The main infrared (IR) absorption bands of soil- and sediment-HA's and -FA's were in the regions of 3400 cm^{-1} (hydrogen-bonded OH), $2960\text{--}2850\text{ cm}^{-1}$ (aliphatic C-H stretch), $1730\text{--}1715\text{ cm}^{-1}$ (C=O of CO_2H , C=O of Ketonic carbonyl), 1620 cm^{-1} (aromatic C=C, COO^- , hydrogen-bonded C=O) and 1050 cm^{-1} (Si-O of silicates). Smaller bands were visible near 1520 cm^{-1} (aromatic C=C), 1440 cm^{-1} (CH_2), 1400 cm^{-1} (COO^-), 1230 cm^{-1} (OH or C-O stretch), 800, 670-660, 570, 530 and 470 cm^{-1} , most likely due to Si-O valence and deformation vibrations and to the presence of iron oxides (Kodama et al., 1977) and aluminum oxides.

IR spectra of watershed soil HA's showed a preponderance of OH and COO^- and, to a lesser extent, of CO_2H group as well as of aliphatic CH_2 groups and silicates (Si-O). IR spectra of watershed soil FA's indicated the presence of substantial concentrations of OH and CO_2H groups and of silicates, which appeared to be strongly associated with the organic matter.

TABLE 6.

 MAJOR COMPOUNDS (mg) PRODUCED BY THE KMnO_4 OXIDATION OF 1.0 g
 METHYLATED HUMIC MATERIAL

Type of Compound	Soil HA's ¹	Bottom Sediment HA's ¹	Soil FA's ²	Bottom Sediment FA's ²	Suspended Sediment
Aliphatic					
Alkanes	5.8 (5.6 - 7.8)	NA (0)	2.3 (0.2 - 5.9)	2.2 (1.0 - 4.2)	2.7 (1.0 - 7.7)
Fatty acids	2.7 (0.9 - 7.6)	NA (1.07)	0.7 (0.3 - 2.6)	0.8 (0.3 - 1.2)	1.8 (0.6 - 4.0)
Carboxylic acids	1.0 (0.2 - 7.1)	NA (.1)	NA (1.3 - 4.4)	NA (1.6 - 8.6)	NA (0)
Phenolic	28.2 (3.1 - 67.7)	12.4 (3.2 - 29.9)	12.7 (3.1 - 29.5)	6.7 (3.3 - 26.3)	7.4 (2.9 - 53.0)
⊗ Benzene-carboxylic	61.2 (51.2 - 198.5)	43.9 (6.8 - 106.0)	57.2 (27.1 - 84.9)	22.6 (7.5 - 70.6)	44.0 (13.9 - 193.5)
Furan	4.8 (1.2 - 8.6)	1.9 (1.2 - 7.7)	3.0 (0.8 - 10.3)	1.2 (0.5 - 1.2)	4.2 (0.8 - 37.5)
Dialkyl phthalates	4.6 (0.6 - 8.6)	29.5 (14.4 - 143.0)	4.3 (1.1 - 9.9)	36.7 (17.7 - 68.3)	5.5 (0.6 - 48.9)
Total	111.2	87.7	78.7	70.2	66.1
Weight Ratio Benzene Carboxylic/phenolic	2.2	3.5	4.5	2.5	5.9
% Aromaticity*	83.9	75.4	94.0	67.5	84.8

* excluding dialkyl phthalates from total weights

NA - not averaged as only 1 or 2 values

1 HA - Humic Acid

2 FA - Fulvic Acid

The concentrations of metals associated with the extracted HA's and FA's are also presented in Appendix Tables 11 and 12. Iron and aluminum are the major metals bound to the HA's and FA's, with much smaller quantities of the trace elements.

Metal Variability Study

Mean values and standard deviations for total metal concentrations in soil replicates are given in Appendix Table 13. The sites used in this part of the study were the same as those reported in the first part of the study and samples were collected at the same time. Values are very similar to those reported in Appendix Table 4. From the standard deviations and the means of each element for each set of replicates, it is possible to calculate the number of replicate samples necessary to maintain $\pm 10\%$ precision. These values are reported in Table 7. Cr was eliminated because there was an analytical problem due to digesting with HClO_4 .

Al and Fe showed the least variation in the replicates, especially in the A horizons. Mn, Pb and Zn showed smaller variation than Cu or Ni. Watersheds 3 and 10 showed the least variation in the majority of metals in the A and C horizons - the two watersheds which usually had the highest metal concentrations. Soil B horizons are often zones of accumulation and can be expected to be more variable. Watershed 4, with lower metal values, showed the highest variation in most metals. It appeared that the higher the quantity of metal in a soil horizon, the lower the variability within the soil pit. It is obvious that each soil reacts in its own manner and it may not be possible to draw more general conclusions from these results. Our study involved at least 2 replicates from each soil pit being analyzed for each value and this appears to be adequate for most metals in most soils.

A part of the replication study was also designed to examine the variability of trace metals within a soil by analyzing replicates from different soil pits. Four sites at least one mile from each other were sampled from Watershed 10. The number of sites required to maintain $\pm 10\%$ precision are shown in Table 8. The A horizon was much more variable when the sites were separated by greater distances. Some of the variability in Cu and Ni may be due to the low concentrations of these metals in the surface soils. The metals in the B and C horizons have about the same variability when the sites were separated by miles as the different sides of the soil pits. Only Ni showed more variation.

Thus, it appears that 1-3 replicates are necessary from each soil pit to maintain $\pm 10\%$ precision but great care should be taken to choose a representative soil site, and perhaps more than one site per soil series should be sampled for trace metals.

Fertilizer Stocks

The total concentration of Cd, Co, Cr, Cu, Ni, Pb, Zn and Fe in fertilizer used in watersheds 1 and 13 are presented in Appendix Table 14.

TABLE 7.

NUMBER OF REPLICATE SOIL SAMPLES REQUIRED TO MAINTAIN $\pm 10\%$ PRECISION
 VALUES ARE AVERAGES* FOR EACH WATERSHED

Watershed	Cu	Mn	Ni	Pb	Zn	Al	Fe	Average for All Seven (7) Metals
(A Horizon)								
1	1	2	1	2	1	1	1	2
3	1	1	1	1	1	1	1	1
4	6	2	2	2	2	1	1	3
5	1	2	1	2	2	1	1	2
10	1	3	1	1	1	1	1	2
13	<u>2</u>	<u>2</u>	<u>4</u>	<u>1</u>	<u>1</u>	<u>1</u>	<u>2</u>	2
Average	2	2	2	2	2	1	2	
(B Horizon)								
1	4	3	3	3	1	1	2	3
3	1	2	5	1	2	3	3	3
4	9	1	2	2	2	2	3	3
5	5	1	1	3	1	1	1	2
10	2	3	2	1	3	1	2	2
13	<u>2</u>	<u>2</u>	<u>3</u>	<u>2</u>	<u>1</u>	<u>1</u>	<u>2</u>	2
Average	4	2	3	2	2	2	3	
(C Horizon)								
1	1	4	1	3	1	2	2	2
3	1	1	5	1	1	1	1	2
4	3	3	7	4	4	5	5	5
5	2	1	2	2	2	1	1	2
10	1	1	2	1	1	1	1	2
13	<u>2</u>	<u>2</u>	<u>3</u>	<u>1</u>	<u>1</u>	<u>2</u>	<u>2</u>	2
Average	2	2	4	2	2	2	2	

* Rounded to next highest sample

$$N = \frac{(t)^2 \times (C.V.)^2 \times 10^{-4}}{(p)^2}$$

t = confidence limit of 1.96
 C.V. = coefficient of variations
 p = desired precision

TABLE 8.

NUMBER OF SITES REQUIRED TO MAINTAIN METAL LEVELS AT \pm 10% PRECISION

Watershed 10 - Haldimand clay sites (2, 3, 4 & 6)

		Cu	Mn	Ni	Pb	Zn	Al	Fe
A Horizon								
	C.V.	29.7	85.4*	30.1	11.5	19.1	12.6	23.1*
	N	9		9	2	4	2	6
B Horizon								
	C.V.	6.7	8.5	28.4	12.0	16.0	8.3	5.6
	N	1	1	8	2	3	1	1
C Horizon								
	C.V.	7.2	4.6	25.4	14.3	8.1	6.8	10.8
	N	1	1	7	2	1	1	2

* Ferro-manganese nodules were present in some surface soils giving a wide range of values.

Detectable amounts of all metals investigated were found principally in fertilizer containing phosphorus. Ammonium nitrate, potassium sources and dolomite contained <2 ppm Co, <7 ppm Ni and 180-543 ppm Fe and traces of Cd, Zn, Cu and Dr. All fertilizers contained <3 ppm Pb and no detectable metal was found in urea.

The fertilizers which contained phosphorus had 2.8, 4 and 34 ppm Cu, Co and Ni, respectively and the concentration of these elements appeared not to increase with phosphorus content as did the concentration of Cd, Zn and Fe. Of the phosphorus fertilizers, triple superphosphate contained the highest concentrations of Cd, Cr and Zn, namely 9.3, 92 and 108 ppm respectively and monoammonium phosphate contained 11,808 ppm Fe.

As denoted by the standard error of the difference, the metal content of fertilizers of the same nutrient analysis from different distributors did not differ appreciably. This result was expected since, it was discussed later, all distributors received their material from the same outlet. Variance between distributors in the analysis of the fertilizers is probably due to differences in lots from the main supplier.

Bottom Sediments

Total Metal Concentrations

The concentrations of total trace metals and nutrients in bottom sediments are given in Appendix Table 15. Average values for each of the watersheds and values obtained by OMOE for the same watersheds are also given.

There was no discernable seasonal pattern found in the bottom sediments collected in 1976. Although there were great differences in metal concentration between watersheds, there was little fluctuation in concentrations within each watershed. Total carbon, nitrogen, phosphorus, clay, organic matter and carbonates were also generally consistent within each watershed.

Ranking the watersheds in terms of decreasing concentration of metal gave the following:

As	1 > 13 > 10 > 5 > 4 > 3
Cr	1 > 5 > 4 > 10 > 3 > 13
Cu	1 > 10 > 13 > 3 > 5 > 4
Hg	1 > 10 > 5 > 3 > 4 > 13
Mn	10 > 1 > 5 > 4 > 3 > 13
Ni	1 > 10 > 13 > 3 > 4 > 5
Pb	10 > 5 > 1 > 4 > 13 > 3
Se	1 > 3 > 5 > 13 > 4 > 10
Zn	10 > 1 > 13 > 5 > 4 = 3
Al	1 > 10 > 4 > 13 > 5 > 3
Fe	10 > 1 > 5 = 4 > 13 > 3
Clay	10 > 1 > 3 > 5 > 4 > 13

Generally, the ranking by metal concentration reflects the ranking by clay content of bottom sediments with watersheds 1 and 10 having the highest metal concentrations. Watershed 13, with the lowest clay content, ranked higher than expected for As, Cu, Ni and Zn.

Correlation coefficients for bottom sediments are given in Appendix Table 16. Generally, the correlation coefficients were higher when only the watershed averages were used. For example, $r=+0.24$ for Cu and clay individually but $r=+0.96$ for Cu and clay averaged for each watershed.

Clay content was positively correlated with Al, Fe and Mn, the metals that form hydrous oxide coatings on clay particles, as well as form clay minerals. Thus, as in soils, metals that were correlated positively with clay, were also correlated with Al, Fe and Mn, although not always as strongly as in soils. The strongest positive correlation was shown by clay and Cu, accounting for 92% of the variation, while Hg, Ni, Pb and Zn were also positively correlated with clay. Cr and Se showed no correlation with clay, Fe or Al. None of the metals were strongly correlated with organic matter or carbonates in the bottom sediments.

DTPA Extractable Metal Concentrations

The DTPA extractable metal concentrations in bottom sediments are presented in Appendix Table 17. The pattern for the DTPA extractable metals was similar to that of total metals in bottom sediments - the variation in extractable metals from within the watershed was small although there was greater variation between the watersheds. Watershed 10 sediments had the highest concentration of extractable metals.

Cd appeared to be the most extractable metal (up to 50% removed by DTPA) but this may have been exaggerated by the total metal values being so close to the detection limit of the other metals. On the average, 13% of the Cu, 10.8% of the Pb, 3.0% of the Zn and 2.1% of the Ni were DTPA extractable. Except for Ni which was the same for soils and sediments, the bottom sediment DTPA extractable concentrations of Cu, Pb and Zn were double the DTPA extractable quantities found in soils.

The correlation coefficients for DTPA extractions of bottom sediments are given in Appendix Table 18. There were no strong correlations between DTPA extracted Cu, Ni, Pb or Zn and clay, organic matter, pH, total Al, Fe, Cu, Ni, Pb or Zn.

Humic Substances

The chemical analyses of the bottom sediments from which humic substances were extracted are given in Appendix Table 19. The ultimate analysis, functional group analysis and total metal concentrations are given for HA's in Appendix Table 20 and for FA's in Appendix Table 21. Average values for all these measurements for soil and sediment HA's and FA's are recorded in Table 6.

The bottom sediments were similar to those previously described from Appendix Table 15. The most noticeable difference between the soils and sediments was the low organic C content, and subsequent humic yield, from the bottom sediments. HA's extracted from the sediments accounted for between 14.3% (watershed 1) and 48.3% (watershed 13) of the initial organic matter, whereas FA's constituted between 22.2% (watershed 5) and 30.2% (watershed 1) of the original sediment organic matter. Between 44.4% and 78.3% of the initial sediment organic matter was extracted as HA's + FA's.

The bottom sediment HA's tended to have lower C and higher N contents than either the ideal HA's or the watershed soil HA's. The functional groups were about the same as ideal soil HA's, but slightly less carboxyl groups than the soil HA's.

The bottom sediment FA's also had lower C and higher N contents than FA's from soils. The carboxyl content of the FA's extracted from bottom sediments was lower than that of FA's from soils, while the phenolic hydroxyl content of the sediment and watershed soil FA's was similar but higher than that of the ideal soil FA. The E₄/E₆ ratios of sediment and soil FA's were lower than that of the "ideal" soil FA. These last two phenomena are probably related to the relatively high ash content of the soil and sediment HA's and FA's which consisted mainly of silicates, Fe and Al and which we were unable to lower with the procedures that we used.

IR spectra of HA's and FA's extracted from the sediments were very similar to those of soil HA's and FA's. In general, the IR data confirmed the information provided by chemical methods in that they showed that sediment HA's and FA's contained appreciable amounts of oxygen-containing functional groups through which they interacted with metal ions, metal oxides and metal hydroxides to form stable metal-organic complexes. Interactions of the humic materials with silicates were also indicated.

The chemical and spectrophotometric data show that HA's and FA's in suspended and bottom sediments resemble soil HA's and FA's in surface structural features and in ability to form strong metal-organic complexes and to interact with silicates.

Fractionation Experiment

Results of the forms of metals in bottom sediments are given in Appendix Table 22 for Cu, Ni, Pb and Zn. Similar analyses for Cd were performed but the values were too close to the limits of detection to be reliable. A number of extractants were tested but those used by Gupta and Chen (1975) gave the most consistent results. A summary of the results is given in Table 9.

Although bottom sediments from each watershed gave different concentrations for the same chemical form, there were consistent patterns for each metal and their forms.

Only Zn had any detectable water-soluble component and this may have been a combination of interstitial water and H₂O soluble forms. The

TABLE 9.

FORMS OF METALS IN BOTTOM SEDIMENTS*

	Cu	Ni	Pb	Zn
TOTAL ppm	22.8	23.4	23.9	94.3
% WATER SOLUBLE	-	-	-	0.2
% EXCHANGEABLE	2.2	0.6	1.2	0.5
% CARBONATE BOUND	10.6	3.3	21.9	10.1
% MANGANESE OXIDE BOUND	15.2	-	24.5	11.7
% ORGANICALLY BOUND	15.5	14.3	4.9	14.1
% IRON OXIDE BOUND	22.1	17.8	-	16.8
% CRYSTALLINE	34.4	64.2	47.5	49.1

* Average of 6 watersheds

exchangeable concentrations were low for each metal. The crystalline accounted for about half the metal in each sample with Ni the highest in the crystalline. No Pb was detected in the Fe oxide fraction of any sample and Ni was not found bound to Mn oxides. In watersheds 4 and 5, neither Cu nor Ni was found in the Fe oxide fraction. Pb was the lowest of all the organically-bound materials but the highest for the carbonate associated materials. The carbonate co-precipitated metals formed a significant proportion of each sample. (It was anticipated that the mild acid extractant may also be removing some of the hydrous oxide-bound materials).

Generally, 65% of the Cu, 50% of the Pb and Zn and 35% of the Ni were in forms that under severe ecosystem stress could be liberated into a readily useable form. Presently, only the water soluble and exchangeable are likely available to plant growth, but the carbonate-bound are only loosely associated and may become available to organisms or bind more tightly into the other forms.

The results of the experiment incubating the soils and sediments with metals are given in Appendix Table 23. Where the metal was added to the sample either alone or with the other five (5) metals, only the additional metal (i.e. 5, 100 or 250 ppm) is accounted for in the tables. This enables one to see where the addition metal was bound.

Cd added to soils and sediments became associated with the exchangeable form. When the other metals were added, some of the Cd was also present in the water soluble phase. Once again, Cd values were near the detection limits and other forms may have occurred but our instruments were not sensitive enough to detect them.

Cu added to soils and sediments was more evenly distributed between the different forms than Cd but this was probably due to the greater concentrations of Cu added. The percentages of each metal found in each form were approximately the same whether 100 or 250 ppm Cu was added. With the higher metal additions, some Cu also became water-soluble. When the other five metals were added, there was a shift to the tighter binding groups as the weaker sites become filled. One interesting observation was the carbonate association in the soils. The free carbonates in these soils were low and metals were not normally associated with them but after incubation, a large proportion of metal co-precipitated with the carbonates. The sediments, however, had much higher percentages of added metals associated with carbonates than the soils.

The same pattern was repeated for Ni, Pb and Zn: the co-precipitate sites were filled first, and as the amount of added metal increased, the metals filled more tightly bound sites. With the very high levels, some was not bound and appeared readily available as water soluble material. Therefore, as small amounts of metal are added, they occupy the readily available sites first, and this may have implications for the addition of metals to rivers either through runoff or direct aerial input. Our experiment ran for only ten (10) weeks incubation and it was feasible that with longer incubation, there would have been an equilibrium set up to spread the Cu over the various forms available.

The same incubation experiment was run with the addition of 100 ppm P as well as the metals. Although P affects the solubility of many metals (MacLean et al., 1969; Buchauer, 1971), the results were not significantly changed from those reported here and P did not seem to have any effect on the metal binding (Results are available from the authors).

Suspended Sediments

The analytical data for suspended sediments are presented in two manners. Appendix Table 24 shows the concentration of total metals and nutrients in suspended sediments on a dry-matter basis after freeze-drying either the total water or particulate and dissolved fractions. Appendix Table 25 gives the same data on a volume basis. Most samples were obtained during times of low flow. Timing of sampling was difficult and event samples were usually missed, as was the spring runoff peak in 1976. Samples marked with an E were events. The correlations between the metals and yield, total C, organic C, inorganic C, total N, total S, total Al and total Fe are given in Appendix Table 26 for all watersheds combined, Appendix Table 27 for the total water in each watershed and Appendix Table 28 for the dissolved fraction in each watershed.

The total concentrations of metals in the freeze-dried water are generally lower than in soils or bottom sediments; Cu was the exception to this and was often higher in the solids obtained from water. For all the watersheds combined, there were no strong correlations between metal values and the other parameters measured except for Zn and Al ($r=+0.82$). However, individually, each watershed shows different correlations as expressed in Table 10. These values ($r^2 \times 100$) are the percentage of the variation accounted for by a specific interaction. Only values $\geq 50\%$ of the variation ($r=.71$) are recorded in Table 10. There do not appear to be consistent patterns between the watersheds for relationships between elements. It should be recalled that each correlation coefficient is based on only 4-7 samples and may not be valid under stronger sampling program.

The dissolved ($<.45\mu$) metal concentrations are generally lower than the particulate. This difference was most striking for Al and Fe (which are usually particulate in water) where the values were usually less than the reporting limit of 0.1% after filtering.

Very few particulate ($>.45\mu$) samples were obtained because of the low flow and yield conditions. Average values for suspended sediments for each watershed are given in Table 11. Low flow and event samples have been averaged to give some idea of the yearly average metal concentration. Metal contents of the suspended materials are generally higher than the watershed soils or bottom sediments. This is likely a reflection of the particle size of the suspended material; unfortunately, the samples collected were too small to permit particle size analysis.

The concentration of metal ($\mu\text{g}/\ell$) contributed by each fraction are shown in Appendix Table 25. The total concentrations were low but within the ranges reported for natural waters. The concentration data

TABLE 10.

PERCENTAGE VARIATION ($r^2 \times 100$) ACCOUNTED FOR BY
CORRELATION BETWEEN TRACE METALS AND OTHER
STREAMWATER VARIABLES *

Only values $\geq 50\%$ are included.

	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
TOTAL WATER										
AG1 Yield		-53								
Total C	61			61		67				90
Organic C			-58	90		72				
Inorganic C	64		55						83	74
Total N	72		72						86	66
Total S	-88				-66		-81	64		-53
Total Al										85
AG3 Yield	71	76		59		72	58			59
Total C	-59	-59		-74		-71				-94
Organic C	65	64			-79	56	72			
Inorganic C	-77	-76		-81		-83				-90
Total S	-61	-64		-74		-72				-96
Total Al		96		90		96				71
Total Fe	96			92		98			74	
AG4 Yield	88	76	-53							
Total C	-76			71						
Organic C				99		53				
Inorganic C	-88	-61		53						
Total N							53		81	
Total S								-83		
Total Al		83								
Total Fe	83		-81							
AG5 Yield	61									
Organic C						61			61	63
Inorganic C	-56									
Total N									56	56
Total S								-77		
Total Al		77								
Total Fe	77									
AG10 Yield	-50		-72	-81	-82		-81		-72	-67
Total C			77	59	64		64			
Organic C	90		79	85	81		85	67	92	96
Total N	88					90		96	53	69
Total S	-92	-53	-72	-88	-82	-72	-88	-66	-96	-99
Total Al		55	55	64	58	85	64	90	80	92
Total Fe	55								53	56
AG13 Yield					-53				74	
Total C	-96	61								-72
Organic C							-56		-94	
Inorganic C	-71	-77		-71						
Total N		67	67	61		-66	56	77		
Total S	-58						-85		-76	-85
Total Al									85	
Total Fe				98				86		

*For example in AG1, 90% of the variation in total Zn of streamwater can be associated with variations in total C of the streamwater.

TABLE 10 (cont'd)

	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
DISSOLVED FRACTION (.45u)										
AG 1 Total C				-61	76	64				
Organic C			-64		94	90	-69			
Inorganic C				-53				-53	53	
Total N				-55				-90		-77
Total S				76				77		59
AG3 Organic C					-63					
Inorganic C										-62
Total N	-77	-77		-59						
Total S				-62			55			
AG4 Yield	52	52			-67		-76		77	
Total C	72	77			-90		-95		98	
Organic C	64	64			-55				55	
Inorganic C						-58	-64			-76
Total N			-55							
Total S	-82	-82			85		63		-86	
AG5 Yield						-52				
Total C										-64
Organic C					-61				55	
Inorganic C										-59
Total N	52						-55		67	
Total S	-53									
AG10 Yield				-74	-85	-56				
Total C				63	98					
Organic C				76	92	63				
Inorganic C					82					
Total N	96	96		74		90	86		74	74
Total S				-61				-76		
AG13 Yield			-81			76	-72			
Total C	-88		77	-94	-98				-56	
Organic C	-96		88	-96	-88					
Inorganic C	-76			-86	-98				-72	
Total N		59						-66		
Total S			-88			-96			-66	

clearly showed the decrease in Al and Fe values. Values obtained after filtering demonstrate their close association with particulates (Florence and Batley, 1977).

For low flow conditions, the following elements were primarily present in dissolved form ($<.45\mu$): total C, total N, total S, organic C, Cu, Ni, Pb and Se. Mn and Zn appeared more particulate, as their concentrations decreased with filtering. Cd and Cr gave no clear patterns. When the occasional event sample was obtained, most metals were usually higher in the particulate due to the addition of clays from surface erosion into the water. It was unfortunate that most samples were summer low flow samples and more event samples were not obtained because for loading values, the spring runoff and event samples are much more important than summer flow values.

The concentrations for trace metals in water were similar to those obtained by Ihnat (1978) on some of the same samples (Project 9B) except for Cu. Our methods, although precautions were taken, did not take into consideration blanks other than reagent digestion blanks (ie. no field blanks), therefore, our method, although precise, was not as accurate as Ihnat's.

The chemical analyses of suspended sediment collected during the spring runoff period of 1977 are given in Table 12. These spring samples were obtained by centrifugation at CClW rather than filtration through $.45\mu$ filters. A check of the two methods showed that the centrifuge recovered 83 mg/l of suspended sediments while the filtering method recovered 89 mg/l. These are within 10% of each other. It was understood, at the beginning, that some loss of material exists with the centrifuge method, especially some of the smaller particle sizes, but the centrifuge allowed for the processing of greater volumes of water and hence increased the yield. It was normal to process 450 l for each sample. Despite supreme efforts on the part of the sampling team, it was felt that only in watershed 13 was the spring peak sampled adequately. The other watersheds were sampled shortly after the spring sediment peaks, but the large volumes of water that could be processed by centrifugation allowed sufficient sample for analysis to be collected.

The trace elements were higher in the suspended sediment than in either the bottom sediments or soils indicating that the loads of metals leaving the watersheds were greater in the spring than in the summer or fall low flow periods. Cd averaged 1.2 ppm, Cr 96 pp, Cu 49 ppm, Mn 630 ppm, Ni 40 ppm, Pb 60 ppm and Zn 237 ppm. These averages were similar to those obtained in 1976; however, the quantity of sediment lost during the spring runoff indicated that the loads of metals leaving the watersheds was greater in the spring than in the summer or fall flow periods.

TABLE 11.

AVERAGE METAL CONCENTRATIONS (ppm)
OF SUSPENDED SEDIMENTS (1976)

	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
AG 1	3.7	32	72	618	52	92	0.9	218
AG 3	---	80	40	650	48	28	0.6	155
AG 4	4.0	72	34	1380	23	60	0.5	141
AG 5	---	96	93	809	48	48	0.7	213
AG 10	2.5	89	86	1540	40	125	0.2	305
AG 13	---	--	--	----	--	---	---	---
AVERAGE	3.4	64	65	1000	42	71	0.6	206

TABLE 12.

CHEMICAL ANALYSES OF SUSPENDED SEDIMENT COLLECTED DURING
1977 SPRING RUN-OFF PERIODS

	Yield g/l	Ash %	C %	Corg %	Al	Fe	Cd	Cr µg/g	Cu	Mn	Ni	Pb	Zn
AG 3 (22/3/77, 3:00 pm)	35	81.2	5.6	4.0	970	425	0.3	75	32	620	25.5	30	125
AG 4 (17/3/77, 1:00 pm)	19	84.9	5.2	2.6	1365	640	1.5	88.5	47	760	33.5	65	250
AG 10 (16/3/77, 12:00 pm)	62	88.5	3.9	0.8	1850	865	1.5	110	50	605	47.5	50.5	250
AG 10 (21/3/77, 4:30 pm)	31	89.3	3.2	1.3	1855	755	1.3	95	60.5	555	44.5	100	310
AG 13 (4/3/77, 7:00 pm)	306	86.2	4.2	0.5	1865	930	1.0	112.5	59.5	615	52	51	250

DATA ANALYSIS AND INTERPRETATION

Trace metals may be both micronutrients and toxicants. Some of the metals, such as Cu, Zn, V, Se and Mo, are necessary in small quantities for proper functioning of biological organisms but, in slightly higher amounts, they can also severely inhibit growth. The majority of the trace metals are not required for growth, even though they enter biological systems and often tend to accumulate there. Most organisms have a body load of these elements, usually stored in innocuous forms. In recent years, evidence has been confirmed that, under certain environmental conditions, heavy metals are methylated by microorganisms (Wong et al., 1975; Chau et al., 1976) making them more volatile and lipid soluble. With the transformation to an organic form, these metals may easily pass through membranes and can accumulate in different parts of the organisms where they may do greater damage.

Metals in the aqueous environment may be derived from natural geologic weathering of soils or from man's activities. In the Great Lakes region, much of the land is under agricultural management which may affect the metal load entering the lakes. In assessing agriculture's impact on the metal load of the Great Lakes system, several factors had to be considered. First, what are the metal concentrations in the soil materials, bottom and suspended sediments? Second, were they of geologic origin or derived from man's activities? Third, how are these metals stored in the soils and in bottom and suspended sediments? And fourth, by what means are these metals transported from the land to the drainage system and thence to the lakes? This study was an attempt to provide answers to these questions. The speciation of the metals, their biological availability, and toxicology were outside the scope of this study.

Sources of Metals

Soils

Total metal concentrations of the soils were determined in a $\text{HClO}_4\text{-HF}$ digest. The total concentrations of the metals in the watershed soils were within the normal ranges reported for soils (Vinogradov, 1959; Bowen, 1966; Frank et al., 1976; McKeague and Kloosterman, 1974) and were probably of geologic origin. In most cases, watersheds with high clay contents also had high metal contents: sandy soil watersheds had much lower metal concentrations. It also occurred that soils with higher metal and clay contents were more uniform in metal distribution

in the sampling pit than soils with low metal and clay contents, presumably because sandy soils contain coarser grains of unweathered material which may vary greatly in chemical composition. The metals were distributed in two profile patterns - either the highest or lowest metal concentrations were in the C horizon. This grouped the watersheds of Essex County together (C values always highest) and the other watersheds in south central Ontario together (C values always lowest).

Of the metals examined Se, Hg, and Pb were consistently higher in the surface soil (A horizon). Selenium, and Hg have been associated with organic matter, which was higher in the A horizon, leading to their accumulation (McKeague and Kloosterman, 1974; Doran and Alexander, 1977). High concentrations of Pb in surface soils relative to deeper horizons have been reported in both remote and heavily populated areas (National Academy of Sciences, 1972; Whitby, 1974; Vinogradov, 1959) but the reason for this is not readily apparent. Unlike heavily populated areas, the earth's atmospheric load in remote areas would be insufficient to raise the surface Pb values several ppm above that found at deeper depths. This is feasible in heavily populated areas. The surface Pb was not organically related since DTPA extracted only 5% of the total Pb and the fractionation studies (in the sparsely populated Big Creek (AG 1) and Canagagigue (AG 4) watershed soils) showed that organically bound Pb was low (10%). Approximately 87-89% of the lead was associated with the manganese and iron oxide and crystalline fractions, and appeared to be a natural phenomena.

A number of other measurements confirmed that the soil metal concentrations were natural. The DTPA extraction method has often been used on polluted soils since the additional metal does not appear as strongly bound, and areas of contamination often exhibit high DTPA extractable metal concentrations (Rule and Graham, 1976; Silveira and Sommers, 1977; Bingham et al., 1976). All watershed soils showed low concentrations of DTPA extractable metals. The distribution of metals on the different faces of the soil pits (replication study) was more uniform for soils with higher metal concentrations. If the higher concentrations had been contributed by foreign materials, one would expect that, as the quantity added increased, the variability would also increase since additions to large areas would seldom be uniform.

Thus, for the metals studied (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se and Zn), the concentrations in the agricultural watershed soils were within the ranges reported as normal for soils and showed no evidence of metal accumulation from outside sources.

Atmospheric and precipitation

Atmospheric loadings, based on 2 years' rainfall analyses (M. Sanderson), added the following metals to the watershed soils:

Surface Metal Loadings due to Atmospheric Sources (g/ha/year)

	Cu	Pb	Zn
AG 1	84	139	321
AG 3	33	91	365
AG 4	95	44	1263
AG 5	110	73	252
AG 10	29	95	734
AG 13	80	80	256

The highest metal loading (Zn in AG 4) would increase the surface soil Zn (mixed to a depth of 21 cm or 6 in) by 0.67% per year. The majority of the soil metals would only be increased by approximately 0.1% per year - an amount that would require a considerable number of additions to detect.

Fertilizer

Fertilizer applications are another potential source of metal contamination. As recorded in Appendix Table 14, only the phosphate fertilizers contained appreciable quantities of heavy metals. Therefore, based on the usage of phosphate fertilizers in each watershed (Technical Report 5) and the fertilizer analysis, the following loadings were obtained:

Surface Metal Loadings due to Phosphate Fertilizers (g/ha/year)

	Cd	Cu	Ni	Pb	Zn	% area fertilized
AG 1	0.25	0.13	1.46	<0.1	3.33	91
AG 3	0.33	0.14	1.50	<0.1	3.41	90
AG 4	0.23	0.07	0.78	<0.1	1.78	91
AG 5	0.39	0.12	1.30	<0.1	2.96	81
AG 10	0.06	0.04	0.42	<0.1	0.97	79
AG 13	1.08	0.28	3.13	<0.4	7.13	76

Using the highest metal contribution (Zn in AG 13), the increase in surface soil Zn due to fertilizer was 0.005%. Most of the metal additions were much lower and approximately 0.001% of the metal present would be added each year by phosphate fertilizer.

Sludge and manure

Of the 11 agricultural watersheds being monitored by PLUARG, only 32 ha of land in watershed 6 received sewage sludge. Although sludge is probably the most important source of metals to farmland, sludge was

not applied to soils in the 6 intensive watersheds studied; thus, the metal concentrations could not arise from this source.

Manures also contain trace metals. Based on the farm survey (Technical Report 5) and the average metal values published by Webber and Webber (1977), the following estimates of metal additions by manures were made:

Surface Metal Loadings due to Manure (g/ha/year)

	Cd	Cu	Ni	Pb	Zn	% area manured
AG 1	2	56	10	37	433	2
AG 3	18	528	98	325	4,118	20
AG 4	23	784	128	424	5,335	39
AG 5	22	657	123	407	5,125	22
AG 10	24	723	135	448	5,640	19
AG 13	1	17	3	10	129	1

Using the highest metal rate (Zn for AG 10), the Zn content of the soil would be raised 2% per year by manure applications. Generally, manure applications would raise the metal levels about 0.5%. However, the majority of these metals were recycled from the forage crops produced on the same farms, so this may appear artificially high as loading values. Investigation into the levels of metals added to feed as growth stimulants is necessary to put manure loadings into proper perspective.

Thus, it appears that manure disposal could contribute the greatest quantities of metals to the soils, followed by atmospheric sources then phosphate fertilizer. However, because of the recycling phenomena of manures, atmospheric sources are probably the greatest contributor. The loadings presented here are average values for each watershed; assuming a uniform application of materials across the entire watershed. It should be realized that some areas may receive higher quantities of metals than others. For example, manure was only applied to 2% of watershed 1 and 1% of watershed 13 compared to 39% of watershed 4. It should also be considered that these estimates do not include losses from the soil by erosion, leaching or crop uptake. With these losses, even greater numbers of applications (in years) would be needed before any detectable increase in the soil metal levels would be evident.

Transport and Storage

Bottom sediments

Total metal concentrations in bottom sediments were determined similarly to those in soils.

A comparison of average metal concentrations in the soil Ap horizons with the metal concentrations in bottom sediments and suspended sediments is presented in Table 13. Table 14 presents the correlation coefficients

TABLE 13.

AVERAGE METAL CONCENTRATIONS IN SOILS, BOTTOM AND
SUSPENDED SEDIMENTS IN AGRICULTURAL WATERSHEDS

	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppb	Mn ppm	Ni ppm	Pb ppm	Se ppm	Zn ppm	Clay %
SOILS (Ap Horizons)											
AG 1	5.5	0.9	64	25	40	267	29	25	0.62	120	30.5
AG 3	4.3	-	80	27	81	687	30	25	0.41	98	33.5
AG 4	3.8	-	52	19	52	890	19	21	0.32	75	23.5
AG 5	4.4	-	49	16	50	808	17	22	0.30	85	19.2
AG 10	6.8	-	63	16	44	2536	23	29	0.42	125	36.1
AG 13	5.4	-	26	13	29	307	10	21	0.32	54	8.0
BOTTOM SEDIMENTS											
AG 1	10.2	1.2	62	31	47	738	37	23	0.69	117	22.6
AG 3	3.0	-	36	18	37	567	17	17	0.36	67	14.9
AG 4	3.1	-	39	15	31	694	17	20	0.20	67	8.8
AG 5	3.9	-	42	16	39	704	14	34	0.35	75	9.3
AG 10	5.0	0.9	39	28	40	845	26	54	0.17	401	25.6
AG 13	6.0	-	27	15	29	418	18	19	0.31	61	1.4
SUSPENDED SEDIMENTS											
AG 1	-	3.7	32	72	-	618	52	92	0.9	218	90.3
AG 3	-	0.3*	80	40	-	650	48	28	0.6	155	57.6
AG 4	-	4.0	72	34	-	1380	23	60	0.5	141	60.8
AG 5	-	-	96	93	-	809	48	48	0.7	213	79.1
AG 10	-	2.5	89	86	-	1504	40	125	0.2	305	70.3
AG 13	-	1.0*	113*	60*	-	615*	52*	51*	-	250	68.7

- not determined

* Spring 1977 samples

TABLE 14.

CORRELATION COEFFICIENTS FOR SOILS AND BOTTOM SEDIMENTS

	Ap Horizon vs C Horizon	Ap Horizon vs Bottom Sediments	C Horizon vs Bottom Sediments
As	.62	.50	.75
Cr	.57	.43	.58
Cu	.58	.37	.84
Hg	.36	.07	.13
Mn	.35	.66	.63
Ni	.63	.65	.99
Pb	.90	.71	.50
Se	.93	.78	.88
Zn	.65	.67	.50

r = .75 significant at .05 level

for metals in the soil Ap horizon, C horizon and bottom sediments. Generally, the bottom sediments tended to have lower metal levels than the Ap horizons from the same watersheds. This was the case for each of the 9 metals in watersheds 3 and 4, and the majority of metals in watersheds 5 and 10. However, the bottom sediments of watersheds 1 and 13 had higher metal values than the surface soils. The soils from watersheds 1 and 13 also differed from those in the other watersheds in their profile distribution of total metals. Generally soils from watersheds 1 and 13 had higher metal concentrations in the C horizon relative to the A horizon whereas metal concentrations in soils from the other watersheds were reversed. It is unlikely that the bottom sediments would reflect only Ap or C horizons but rather a combination of surface soils, streambanks and streambed materials which would be sorted by water action and influenced by seasonal flow. Such was the case since As, Cr, Cu, Se, and Ni in bottom sediments were better correlated with C horizon values than values in Ap horizons. Nickel in bottom sediments was highly correlated in the C horizon ($r=+0.99$). Likewise Se in the bottom sediments was better correlated with soil C horizons ($r=+0.88$) than Ap horizons ($r=+0.78$). Conversely, Zn, Pb, and Mn values in bottom sediments were better correlated with Ap horizons than C horizons. Even though Pb, Se, and Hg concentrations were higher in Ap than C horizons of soils and were correlated with carbon in the Ap, Hg did not show any correlation between Ap horizon and bottom sediments. The lack of a distinct correlation between soil horizons and bottom sediments may suggest that during periods of normal or low flow streambank erosion predominates while during high flow periods surface erosion dominates resulting in a mixing of the Ap and C horizons in the bottom sediments. Elevated levels of metals in bottom sediments from a polluted source would bear little resemblance to metal concentrations in any of the soil horizons (Perhac and Whelan, 1972; Turekian and Scott, 1967) unless the soils were also polluted.

It was initially estimated that 90% of sediment was contributed by surface soils and only 10% by streambank (W.F. Mildner). It appears evident that the contribution of sediment from streambank and surface erosion differs between watersheds and under different flow conditions.

The forms of metals in the bottom sediments were not the same as in the soils, especially for Cu and Pb. DTPA extracted 13% of the total Cu and 11% of the total Pb from bottom sediments but only 5.5% total Cu and Pb from surface soils. It appeared that more of the Cu and Pb in the bottom sediments was available to extraction by DTPA than in the soils even though the total concentrations were less. The fractionation experiment showed that this difference likely came from carbonate bound materials which could be attacked by the DTPA extractant and, in the case of Cu, organically bound material. Since the carbonates were not present in the Ap horizons and the carbonate materials of the C horizon gave very low levels of DTPA extractable metals, it appears that the metals entered the aquatic ecosystem directly adsorbed to soil particles and/or as soluble metal that underwent both co-precipitation with carbonates and adsorption onto other materials.

Suspended and bottom sediments

Metals in the suspended sediments were higher than metals in the bottom sediments or soils. This was largely due to a difference in particle size - suspended sediments were 60-90% clay, bottom sediments 7-25% and surface soils 8-36% clay. With the smaller particle size and greater surface area for a given weight more metals and other materials could be adsorbed on the surfaces of the suspended sediments than soils or bottom sediments and consequently higher levels were found. Also there was a strong correlation between clay and metals in soils and bottom sediments suggesting clay is involved in primary transport. The bottom sediments had lost much of the finer particles due to sorting by water in the drainage system and were lower in metal content. Thus periods of high suspended sediments were accompanied by higher concentrations of metals transported through the system on clay sized material derived from streambank, bed and surface soils. Mechanisms which raise the suspended load will also increase the metal load.

It was unfortunate that so little suspended sediment was collected because the relationships of suspended sediments within the aquatic environment are unclear. Metal measurements in suspended sediments may vary by 200% over a matter of hours. Angino et al. (1974) stated that suspended sediments were not related to geological but surficial materials and report that suspended sediments are not useful in geochemical prospecting in the same manner as bottom sediments and soils. Suspended sediments are not necessarily related to the geological characteristics of the materials over which they flow.

Organic matter

Another major transport mechanism for metals is their association with organic matter (Garrett & Hornbrook, 1976; Loring, 1976; Thomas, 1972). Heavy metals in bottom sediments have consistently been correlated with organic matter.

The chemical and spectrophotometric data show that HA's and FA's in suspended and bottom sediments resemble soil HA's and FA's in surface structural features, chemical composition and ability to form strong metal-organic complexes as well as to interact with other materials such as clays. From the functional group analysis an estimate of the metal binding capacities of the soil and bottom sediment HA's and FA's were made (Table 15). For example, the average bottom sediment contained per kg, 2.0 g of HA, and 1.6 g of FA. The average CO₂H contents of these materials were 2.9 and 2.5 meq/g respectively. Thus the sum of the product of the HA or FA and CO₂H content gave a total metal binding capacity of 9.8 meq/kg for bottom sediment and 78.9 meq/kg for soil. Since only 37% of the soil organics and 59% of the sediment organics were extracted and 75% of soil organic matter is HA + FA, the total potential metal binding capacity of the bottom sediments was 12.5 meq/kg and of soil 160.0 meq/kg (Whitby and Schnitzer, 1978).

TABLE 15.

ESTIMATED METAL-BINDING CAPACITIES OF BOTTOM
SEDIMENT AND SOIL HA'S AND FA'S

Type of Material	Average Content (g/kg)	Average Organic CO ₂ H Content (meq/g)	Average CO ₂ H Content (meq/kg)	Potential Metal- Binding Capacities (meq/kg)
Bottom Sediment HA's ¹	2.0	2.9	5.8	7.4
Bottom Sediment FA's ²	1.6	2.5	4.0	5.1
Sum of HA's ¹ + FA's ²	3.6		9.8	12.5
Watershed Soil HA's ¹	8.9	5.0	44.5	90.2
Watershed Soil FA's ²	5.3	6.5	34.4	69.8
Sum of HA's ¹ + FA's ²	14.2		78.9	160.0

1 HA - Humic Acids
2 FA - Fulvic Acids

It is unlikely that all of the estimated organic metal binding sites were available for reactions with metal ions in soils and sediments due to binding of the CO₂H groups with hydrous oxides, clay, and other silicates. The fractionation study for soils and sediment suggested that only 11-15% of the metal was organically bound (occupying 1.4% of the binding capacity for soils and 16% for bottom sediments) with the rest distributed between carbonates, iron and manganese oxides and crystalline forms. The CO₂H contents of the bottom sediment HA's and FA's were 2-3 times lower than previously reported values (Schnitzer, 1977) probably because of the higher ash content for sediments than soils which suggests blocking of CO₂H groups by hydrous oxides and silicates in these watersheds. The lower percentage of metal bound to organic matter in soils suggests a reduction in organic binding sites by oxides with time.

Bottom sediments had a lower percentage extractable Cr, Ni and Pb than the soils but contained more organically bound Cu and Zn as determined by direct analysis, H₂O₂, and DTPA extraction (Appendix Table 29). Although HA's and FA's from bottom sediments had a lower amount of binding sites available for metals than organics from adjacent soils, a greater percentage of these sites appeared reactive. These data suggest that humic substances may be in lower concentrations in bottom sediments than soils but they may play a proportionately greater role in the transport of some metals, in this case Cu and Zn.

Dissolved Matter

Insufficient suspended and dissolved organic matter was collected from the watersheds for a complete examination of the binding capacity of this material. In the manner in which suspended particles are mainly clay-sized, there is likely a sorting of organic material in the aquatic environment. In fact, most of the organic carbon was present in the dissolved fraction of the streamwater and only FA, the more water soluble organic, was extracted. Correlations between organic C and metals for total stream water and suspended particulates were not particularly strong but the dissolved fraction usually had organic C positively correlated with metals, i.e.; Cu and Zn.

Weber and Wilson (1975) extracted both HA and FA from river water and found the CO₂H content was 4.7 meq/g for FA and 6.8 meq/g for HA. These values were similar to those we obtained from soils rather than bottom sediments. Functional group analysis of dissolved organics was not possible in this study. During low flow periods, metals such as Cu, Ni, Pb and Se, although present in the particulate, were found primarily in the dissolved fraction (<.45μ) of the streamwater, along with the organic carbon. Kemp (1969) found 25% of the organic matter in Lake Erie and Lake Ontario bottom sediments were HA's and FA's; FA's were 3-4 times greater than HA's, indicating a greater input of FA's due to fluvial transport. One would expect that considerable quantities of soluble metal-organics are lost from the watershed via stream transport during both high and low flow conditions but that particulate transport would be more important during high flow periods.

Suspended sediments and dissolved organic and inorganic materials are good scavengers for removing pollutants from water because of their high surface areas and consequently high binding capacities. Because of these properties they can also retain pollutants for long periods of time and transport them great distances. The opportunity to examine the relationships within the suspended and dissolved materials must await further advances in sample collection and fractionation.

Hydrous oxides

The importance of hydrous oxides in the movement of metals must also be considered. In aquatic environments, the iron and manganese oxides are the primary hydrous metal oxides (Leland et al., 1974). Large quantities of heavy metals occur in manganese nodules in oceans (Burns and Fuerstenau, 1966) and Suarez and Langmuir (1976) found that Mn oxides in Pennsylvania soils contained 10 times the heavy metal content of Fe oxides. Jenne (1968) stated that Mn and Fe oxides were the major controls of Mn, Fe, Co, Ni, Cu and Zn in soils. Based on the methods of Gupta and Chen (1976) and Gibbs (1973), an examination was made of the forms of metals present in the bottom sediments from these watersheds.

The hydrous metal oxides accounted for a large proportion of the metal in the sediment -37% Cu, 18% Ni (no Mn oxide bound), 25% Pb (no Fe oxide bound) and 29% Zn. These hydrous oxides play a vital role in water transport and it was unfortunate a more detailed examination of the suspended sediments could not be made.

Crystalline metal

The major part of the metal (25-75%) was found associated with the crystalline part of the soil or sediment particles and was considered unreactive. Of the metals investigated, the crystalline form accounted for 65% Ni, 50% Pb and Zn, and 35% Cu present in the bottom sediments. Thus a large part of the metal is stored in the sediments in a nonreactive form and is transported solely with the suspended sediments. Since metal concentrations were correlated to clay content it was not unexpected that the crystalline portion would contain the bulk of the metal.

Carbonate metal

The carbonate coprecipitated metal was of more importance in the bottom sediments than in the soils due to the large quantity of carbonates present in the sediments. Dramatic environmental changes, such as a decrease in pH or change in oxidation-reduction potential, would be necessary to release the metals held by the carbonate forms, although the potential for their release under changed conditions exists.

Other forms

Negligible quantities of metals were associated with the readily available water soluble and exchangeable fraction. In fact, for Cu and

Zn, it is vital to plant growth that some of these metals be available.

Metal addition

The fractionation study with added metal was designed to investigate the fate of excess metals if metal loadings to these soils and consequently the sediments were increased. Bioactivity of aquatic metals depends on their solubility (Leland et al., 1974) thus the soluble nitrate forms of the metals were added. In these soils and sediments, and in most other instances, all forms of available sites for metal binding are undersaturated with respect to metals. It was found that as the metal was added the carbonate forms developed first followed by the stronger binding sites (organic and hydrous oxides) then the readily available forms. The implications are that the soil and sediment systems effectively immobilize metal additions up to a point but as the concentration increases the metals are left in a more available form which may later lead to movement through plants and the ecosystem generally.

Although each of the major metal transport mechanisms were covered separately, the various phases, e.g. metal-clay interactions, metal-oxide sorptions, oxide-clay interactions, metal-organic complexes, etc., cannot be separated from one another. Each phase contributes to metal transport and storage although their relative significance may differ under different environments.

The agricultural watersheds in this study were chosen for their variations in agriculture and pollution potential. No major sources of metals were identified in these watersheds and what was found appeared to be of geologic origin. Metal storage appeared to be primarily in the crystalline form in soil and bottom sediments with the rest stored in carbonates, metal hydrous oxides, or organically bound. Little metal was found in a water soluble form or adsorbed on exchange sites. The quantity of metal stored in the crystalline fraction is biologically nonreactive while that in the exchangeable form or associated with the organic material and hydrous oxides may under the right environmental conditions be reactive. A change in pH or oxidation-reduction potential of the water or sediment could result in the release of carbonate, organic and oxide bound metals. Organically complexed metal could be maintained in aqueous solution or associated with suspended sediment. Metal transport occurs primarily on the particulate phase with clay as the reactive transporter.

Agriculture does not appear to be a major source of metal input; however, the possibility remains that increases in metals in the soils, due to atmospheric, fertilizer or particularly sludge sources can lead to increases in both soluble and particulate metals in streamwater and sediments. The potential for these increases should be carefully considered.

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APPENDIX

ABBREVIATIONS USED IN TABLES

ND - NOT DETERMINED

W - DETECTION LIMIT

T - VALUE BELOW CRITERIA OF DETECTION

HA - HUMIC ACID

FA - FULVIC ACID

APPENDIX TABLE 1

GENERAL DESCRIPTION OF SOIL SAMPLE SITES IN AGRICULTURAL WATERSHEDS

Key to Pollutant Transfer Potential of Soils

- GROUP I - high potential for contribution to surface water, low potential for contribution to ground water.
- GROUP II - moderate potential for contribution to both surface water and ground water.
- GROUP III - high potential for contribution to ground water, low potential for contribution to surface water.
- GROUP IV - low potential for contribution to both surface water and ground water.
- GROUP V - high potential for contribution to both surface water and ground water.

WATERSHED 1, BIG CREEK, ESSEX COUNTY

- SITE 1 - poorly drained clay till
(176) - represents the major soil in Watershed 1
- Brookston clay loam series
- Group V pollutant transfer
- SITE 2 - poorly drained clay loam till
(176v) - variant of Brookston clay loam series
- Group V pollutant transfer
- SITE 3 - imperfectly drained sandy material over fine to moderately fine
(165) textured till at 50-100 cm
- Berrian series
- Group IV pollutant transfer
- SITE 4 - 50 cm of sandy material over poorly drained fine to moderately
(176s) fine till
- sandy phase Brookston series
- Group V pollutant transfer
- SITE 5 - 50 cm of gravelly sandy loam to gravelly loam over imperfectly
(175g) drained fine to moderately fine till
- gravelly loam phase Perth series
- Group IV pollutant transfer

SITE 6 - poorly drained clay loam
(176) - unnamed series
- Group V pollutant transfer

SITE 7 - imperfectly drained loam
(175) - unnamed series
- Group IV pollutant transfer

WATERSHED 3, LITTLE AUSABLE RIVER, HURON COUNTY

SITE 7 - poorly drained fine to moderately fine textured till
(216) - Brookston series
- Group V pollutant transfer

SITE 2 - imperfectly drained fine to moderately fine textured till
(235) - Perth series
- Group 1 pollutant transfer

SITE 3 - moderately well drained fine to moderately fine textured till
(234) - Huron series
- Group 1 pollutant transfer

SITE 5 - poorly drained silt loam
(206) - unnamed series
- Group V pollutant transfer

WATERSHED 4, CANAGAGIGUE CREEK, WELLINGTON COUNTY

SITE 1 - poorly drained silty clay loam to silty clay till
(026) - variant of Brookston clay loam series
- Group V pollutant transfer

SITE 2 - imperfectly drained silty clay loam to clay loam till
(025) - Perth silt loam series
- Group 1 pollutant transfer

SITE 3 - moderately well drained clay loam, silty clay loam,
(024) silty clay till
- Huron silt loam and Huron clay loam series
- Group 1 pollutant transfer

SITE 4 - well drained loam till
(013) - Harriston silt loam series
- Group IV pollutant transfer

WATERSHED 5, HOLIDAY CREEK, OXFORD COUNTY

- SITE 1 - poorly drained silt loam, loam till
(046) - Parkhill silt loam series
- Group V pollutant transfer
- SITE 2 - well drained loam to silt loam till
(043T) - Guelph series
- Group IV pollutant transfer
- SITE 3 - imperfectly drained loam to silt loam till
(045) - London silt loam series
- Group II pollutant transfer
- SITE 4 - imperfectly drained loam till
(045) - London silt loam series
- Group II pollutant transfer
- SITE 5 - imperfectly drained loam till over gravelly fine sandy loam
(053) at 50-100 cm
- unnamed series
- Group II pollutant transfer
- SITE 6 - well drained loam till
(043) - variant of Guelph series
- Group IV pollutant transfer

WATERSHED 10, TWENTY MILE CREEK, LINCOLN COUNTY

- SITE 1 - poorly drained fine textured till
(266) - Lincoln series
- Group V pollutant transfer
- SITE 2 - imperfectly drained fine textured till
(265) - Haldimand series
- Group 1 pollutant transfer

WATERSHED 13, HILLMAN CREEK, ESSEX COUNTY

- SITES 1&3 - imperfectly drained laminated silt and very fine sand with
(115) less than 50 cm loam sand and fine sandy loam overburden
- Tuscola series
- Group II pollutant transfer
- SITE 2 - imperfectly drained loamy very fine sand
(105) - unnamed series
- Group III pollutant transfer
- SITE 4 - imperfectly drained medium sand and gravelly sand
- Brady loamy sand series
- Group III pollutant transfer

APPENDIX TABLE 2.

SOIL SITES GROUPED BY SOIL ORDER

LIVISOLS	GLEYSOLS
1-3	1-1
1-5	1-2
1-7	1-4
	1-6
3-2	
3-3	3-7
	3-5
4-2	
4-3	4-1
4-4	
	5-1
5-3	
5-4	10-1
5-5	
5-6	
10-2	BRUNISOLS
13-1	5-2
13-3	
	13-2

APPENDIX TABLE 3.

PERCENTAGE OF EACH WATERSHED CONTRIBUTED BY EACH SOIL SERIES

	SERIES		ACTUAL %
AG1	176	(sites 1, 2, 6)	81%
	176s	(site 4)	1%
	175	(site 7)	7%
	175g	(site 5)	1%
	165	(site 3)	5%
AG3	235	(site 2)	25%
	234	(site 3)	22%
	206	(site 5)	6%
	216	(site 7)	30%
AG4	026	(site 1)	22%
	025	(site 2)	42%
	024	(site 3)	23%
	013	(site 4)	1%
AG5	046	(site 1)	23%
	045	(site 3, 4)	24%
	043	(site 2, 6)	33%
	053	(site 5)	6%
AG10	266	(site 1)	33%
	265	(site 2)	41%
AG13	115	(site 3)	40%
	115s	(site 1)	13%
	105	(site 2)	24%

APPENDIX TABLE 4.

WATERSHED 1 - BIG CREEK, ESSEX COUNTY

TOTAL HEAVY METAL CONCENTRATIONS IN SOILS

	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppm	Mn ppm	Ni ppm	Pb ppm	Se ppm	Zn ppm	Al %	Fe %	C %	N %	P ppm	CLAY %	ORGANIC MATTER %	CaCO ₃ % EST	CaCO ₃ % ACTUAL	pH
SITE 1 (176)																				
Ap	8.5	1.0	67.0	24.5	39	325.0	32.5	24.0	0.51	124.2	6.71	2.85	2.25	0.22	857	39.0	3.31	0.0	4.1	6.2
Bg ₁	12.0	0.6	67.2	31.0	59	490.0	46.0	20.2	0.51	134.0	8.54	3.95	0.61	0.09	211	58.1	0.97	0.0	4.5	6.7
Bg ₂	ND	1.3	82.0	36.0	40	745.0	59.0	20.2	0.40	134.0	8.39	4.42	0.41	0.06	353	52.1	0.55	0.8	4.5	7.5
Ckg	6.4	0.9	95.0	33.2	26	717.5	50.0	16.8	0.28	101.5	7.30	3.72	1.90	0.06	350	46.6	0.69	11.3	9.0	7.5
SITE 2 (176v)																				
Ap	7.6	0.6	51.2	19.5	40	302.5	21.5	26.5	0.37	119.2	5.38	2.21	2.81	0.22	594	25.4	3.80	4.6	4.1	7.2
Bg ₁	12.0	0.6	45.8	16.6	34	382.5	26.5	18.2	0.19	70.8	5.70	2.73	0.45	0.05	156	25.4	0.48	1.3	4.3	7.3
Bg ₂	ND	1.1	82.0	34.4	40	670.0	54.0	20.2	0.20	101.5	8.00	3.75	1.11	0.06	405	45.4	0.69	5.3	5.2	7.5
Ckg	12.0	0.5	69.8	31.5	30	490.0	42.5	16.2	0.35	87.0	6.34	3.05	2.58	0.05	379	35.9	0.83	15.8	20.7	7.6
SITE 3 (165)																				
Ap	3.6	0.5	17.5	5.0	ND	102.5	10.5	14.0	0.51	40.0	3.28	0.83	1.93	ND	248	6.4	2.54	0.0	ND	5.4
Aegj	3.3	0.1W	10.2	10.0	ND	187.5	11.8	9.5	0.03	25.0	5.16	1.40	0.14	ND	66	1.8	0.16	0.0	ND	5.6
Btgj	5.8	0.3T	10.2	15.2	38	210.0	21.5	10.2	0.05	45.8	4.12	1.48	0.48	ND	127	13.2	0.18	2.9	ND	7.0
II Ckg	10.0	0.7	60.0	27.5	26	625.0	48.2	14.0	0.30	110.0	6.94	3.25	3.06	ND	342	42.0	0.72	19.8	ND	7.5
SITE 4 (176S)																				
Ap	3.0	0.7T	35.0	7.5	46	120.0	14.5	16.2	0.37	60.0	4.41	1.18	2.06	ND	335	12.7	2.8	0.0	ND	6.0
Bg	3.5	0.2T	17.5	7.5	36	187.5	20.2	13.0	0.13	50.0	4.78	1.54	0.99	ND	161	15.2	0.5	0.0	ND	6.4
II Bg	19.0	0.5T	70.0	30.0	26	562.5	52.0	19.0	0.39	115.0	7.06	3.78	1.53	ND	362	38.1	1.3	6.5	ND	7.4
SITE 5 (175g)																				
Ap	8.5	0.6T	65.5	17.2	ND	254.0	18.2	27.0	0.43	92.5	5.19	2.04	4.11	ND	564	16.4	4.1	0.0	0.1	6.6
Aegj	13.0	0.5T	79.0	17.5	38	403.0	28.0	21.0	0.69	70.0	5.55	2.72	1.07	ND	220	13.8	0.7	0.0	0.3	6.4
Btgj	20.0	0.3T	84.5	40.8	66	625.0	46.8	22.8	0.28	105.0	7.52	4.12	0.74	ND	234	33.0	0.6	2.9	17.4	7.0
II Ckg	ND	0.1W	93.2	30.5	32	435.0	40.2	19.2	0.46	100.0	6.62	3.38	2.64	ND	363	37.8	0.5	17.6	15.8	7.5
SITE 6 (176)																				
Ap	1.7	1.0	80.0	35.0	50	222.5	37.5	25.8	1.03	140.0	7.74	3.38	2.75	0.29	ND	34.5	3.45	0.0	ND	6.5
Bg ₁	1.2	0.7	80.8	35.0	36	490.0	50.0	24.5	0.52	140.0	8.12	4.12	0.56	0.07	ND	51.6	0.52	2.0	ND	7.1
Bg ₂	3.7	0.8	85.0	40.0	32	725.0	67.2	22.0	0.45	137.5	8.59	4.42	0.59	0.08	ND	39.7	0.55	2.1	ND	7.4
Ckg	2.9	1.0	75.0	35.0	30	362.5	41.5	19.2	0.62	122.5	7.22	3.78	3.62	0.07	ND	38.0	1.03	22.7	ND	7.7
SITE 7 (175)																				
Ap	1.9	0.6T	69.8	20.0	36	200.0	23.2	25.8	0.56	100.0	6.16	2.82	2.37	0.17	ND	21.4	2.73	0.0	ND	6.0
Btg	3.4	1.7	84.8	35.0	50	500.0	57.5	23.2	0.51	135.0	8.39	4.41	0.78	0.09	ND	47.1	0.76	2.6	ND	7.1
Ckg	3.2	0.9	81.2	35.0	26	350.0	42.5	19.2	0.48	127.5	7.34	3.69	2.29	0.06	ND	39.5	0.55	14.8	ND	7.7

WATERSHED 3 - LITTLE AUSABLE RIVER, HURON COUNTY

APP. TABLE 4 (cont'd)

	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppb	Mn ppm	Ni ppm	Pb ppm	Se ppm	Zn ppm	Al %	Fe %	C %	N %	P ppm	CLAY %	ORGANIC MATTER %	CaCO ₃ % EST	CaCO ₃ % ACTUAL	pH
SITE 7 (216)																				
Ap	3.8	1.0	84.2	27.8	81	340.0	29.2	29.5	0.38	92.0	7.74	2.82	2.50	0.24	813	38.0	3.10	5.1	ND	7.6
Bg	3.9	0.4T	57.2	27.8	46	362.5	38.2	28.2	0.25	89.0	7.30	3.12	1.07	0.07	675	41.9	0.55	5.6	ND	7.5
Ckg	3.3	1.0	56.8	21.2	12	527.5	16.0	20.8	0.22	60.5	5.00	2.36	4.36	0.06	445	25.9	0.41	30.9	ND	8.0
SITE 2 (235)																				
Ap	5.1	0.5T	72.5	25.0	95	1085.0	33.2	23.2	0.44	110.0	6.94	3.28	3.75	0.34	740	35.2	5.96	1.9	0.1	7.2
Bt _g j	4.6	0.4T	67.5	25.0	23	745.0	37.2	19.5	0.16	85.0	7.52	3.50	1.09	0.07	547	36.1	1.06	3.5	2.7	7.6
Ckg _j	4.1	0.3T	63.3	21.0	94	522.5	21.5	14.0	0.06	57.5	4.29	2.40	5.81	0.03	436	34.1	0.34	42.1	51.6	7.6
SITE 3 (234)																				
Ap	4.4	0.1W	87.5	22.0	62	810.0	27.0	23.2	0.33	94.8	6.22	2.91	3.22	0.29	549	29.4	4.20	5.6	2.7	7.3
Bt	6.2	0.1W	77.5	29.0	30	720.0	38.0	17.2	0.17	80.8	6.58	3.51	1.33	0.05	533	56.5	1.09	5.2	2.5	7.5
Ckg _j	3.2	0.1W	50.0	21.8	12	452.5	20.2	13.5	0.05	52.0	4.15	2.10	5.55	0.03	403	35.6	0.61	39.0	50.7	7.6
SITE 5 (206)																				
Apk	2.9	0.1W	65.0	43.2	100	290.0	28.0	19.5	0.80	93.5	5.30	2.40	5.54	0.38	1086	20.0	9.44	0.0	7.7	7.3
Bg k ₁	ND	0.2T	45.0	16.0	12	335.0	33.5	14.0	0.15	49.2	3.69	1.63	5.21	0.04	441	14.0	0.00	39.1	40.3	7.5
Bg k ₂	ND	0.2T	45.0	21.0	6	462.5	31.0	11.2	0.14	51.2	3.88	1.48	4.90	0.02	446	14.3	0.08	36.5	44.0	7.5
Ckg	1.3	0.2T	40.0	22.0	6	562.5	35.8	11.8	0.10	55.5	3.81	1.49	5.05	0.02	490	17.8	0.15	37.3	42.7	7.6

WATERSHED 4 - CANAGACIGUE CREEK, WELLINGTON COUNTY

APP. TABLE 4 (cont'd)

	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppb	Mn ppm	Ni ppm	Pb ppm	Se ppm	Zn ppm	Al %	Fe %	C %	N %	P ppm	CLAY %	ORGANIC MATTER %	CaCO ₃ % EST	CaCO ₃ % ACTUAL	pH
SITE 1 (026)																				
Ap	3.8	0.5	52.8	25.8	57	1005.0	22.5	28.0	0.46	97.5	6.62	3.29	3.35	0.34	679	35.1	5.66	0.0	4.7	6.7
Bg ₂	5.5	0.3T	44.5	22.2	30	875.0	31.5	23.0	0.07	100.0	7.26	4.07	0.38	0.03	699	38.1	0.41	1.1	5.2	7.1
Ckg	4.9	0.5	47.8	16.2	21	595.0	18.0	18.8	0.05	66.2	6.89	3.05	1.30	0.03	610	25.8	0.41	8.0	10.3	7.5
SITE 2 (025)																				
Ap	4.2	0.3T	60.0	17.2	57	940.0	19.0	20.2	0.24	69.5	5.82	2.59	2.98	0.22	535	18.7	4.14	4.4	4.3	7.3
Btgj	3.5	0.1W	41.0	19.0	56	550.0	19.0	13.2	0.01	44.2	4.42	2.19	0.84	0.09	420	28.8	2.07	0.0	2.3	6.7
Ckg	3.0	0.4T	41.0	24.5	20	795.0	22.5	16.5	0.14	69.5	6.90	3.39	4.92	0.04	559	27.9	0.21	35.9	40.2	7.1
SITE 3 (024)																				
Ap	4.1	0.4T	49.8	18.0	51	905.0	20.0	21.5	0.39	79.0	6.25	2.96	2.57	0.24	576	26.5	4.14	1.3	4.6	7.2
Btgj	3.9	0.1W	59.8	30.0	45	945.0	32.5	20.8	0.25	93.7	8.01	4.26	0.68	0.06	631	47.6	0.69	2.1	62.3	7.1
Ckgj	3.5	0.1W	32.5	21.4	5	555.0	20.0	12.5	0.14	50.0	4.70	2.40	4.88	0.03	447	35.6	0.21	35.6	27.6	7.6
SITE 4 (013)																				
Ap	4.6	0.1W	40.0	18.5	42	812.5	14.5	24.0	0.18	90.0	5.99	2.72	2.35	0.21	598	18.5	3.24	3.5	ND	7.1
Ae	3.6	0.1W	32.5	15.5	42	807.5	17.2	22.5	0.17	80.0	6.02	2.46	0.36	0.03	322	13.5	0.41	0.9	ND	7.2
Bt	4.8	0.1W	47.0	25.2	58	947.5	25.2	24.0	0.12	100.0	6.86	3.18	1.16	0.05	670	27.3	0.35	7.2	ND	7.2
Ck	2.6	0.1W	24.0	19.2	24	597.5	14.5	21.5	0.02	62.5	4.75	2.30	4.55	0.01	479	17.0	0.14	33.5	ND	7.5

WATERSHED 5 - HOLIDAY CREEK, OXFORD COUNTY

APP. TABLE 4 (cont'd)

	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppb	Mn ppm	Ni ppm	Pb ppm	Se ppm	Zn ppm	Al %	Fe %	C %	N %	P ppm	CLAY %	ORGANIC MATTER %	CaCO ₃ % EST	CaCO ₃ % ACTUAL	pH
SITE 1 (046)																				
Ap	2.3	0.3T	59.5	13.5	50	515.0	17.5	21.0	0.38	106.0	6.55	2.70	3.60	0.34	1507	24.6	5.24	4.2	ND	7.0
Aejg	2.0	0.1W	59.0	10.0	50	665.0	19.0	19.0	0.24	99.8	6.67	3.12	1.35	0.13	1163	20.9	1.79	2.3	ND	7.0
Btjg ₁	5.5	0.1W	61.8	10.4	68	457.5	20.0	17.8	0.07	96.8	6.80	2.52	1.04	0.10	1058	23.0	1.38	1.8	ND	7.0
Btjg ₂	4.9	0.1W	74.0	20.4	26	560.0	24.8	18.0	0.06	70.0	6.88	3.89	0.37	0.03	850	23.5	0.35	1.3	ND	7.1
Ckg	3.5	0.1W	42.0	16.8	10	542.5	15.2	15.8	0.02	48.0	4.80	2.18	3.65	0.01	560	17.6	0.21	26.4	ND	7.5
SITE 2 (043T)																				
Ap	7.1	0.1W	54.2	18.6	50	990.0	18.0	21.0	0.24	77.8	5.99	2.61	2.49	0.26	900	18.1	4.07	1.0	ND	7.0
Btj	5.0	0.1W	40.8	21.7	61	950.0	24.2	20.8	0.09	72.8	6.60	3.05	0.89	0.09	552	20.0	1.17	1.6	ND	7.1
Ck	3.4	0.1W	18.0	15.2	10	542.5	13.8	12.5	0.01	41.2	4.61	1.91	3.55	0.01	487	9.2	0.14	26.0	ND	7.5
SITE 3 (045)																				
Ap	4.8	0.1W	49.5	16.5	43	645.0	15.0	21.2	0.25	73.8	5.81	2.45	2.86	0.25	719	19.1	4.28	2.9	ND	7.0
Aegj	4.9	0.1W	29.5	16.2	40	610.0	17.5	18.5	0.08	61.0	6.05	2.70	0.50	0.05	355	14.3	0.55	1.4	ND	7.2
Btgj	4.8	0.1W	26.5	21.1	30	715.0	19.5	15.0	0.31	58.8	6.15	2.81	1.03	0.03	400	18.9	0.41	5.9	ND	7.3
Ckgj	2.6	0.1W	18.5	15.5	10	595.0	12.8	11.0	0.16	40.2	4.22	1.82	4.11	0.01	448	11.9	0.14	30.2	ND	7.6
SITE 4 (045)																				
Ap	5.0	0.1W	42.0	20.0	64	850.0	16.2	24.0	0.29	82.5	5.42	2.65	1.77	0.25	738	19.2	3.93	0.0	ND	6.2
Btgj ₁	4.6	0.1W	45.5	19.2	42	715.0	19.5	19.0	0.13	72.5	5.72	2.85	0.57	0.05	385	19.1	0.79	0.0	ND	6.5
Btgj ₂	5.0	0.1W	35.0	24.5	36	745.0	23.0	19.0	0.08	75.0	6.20	3.02	0.40	0.05	594	20.5	0.59	0.5	ND	7.2
Ckgj	2.7	0.1W	26.0	18.0	7	522.5	13.2	12.7	0.03	47.8	3.69	1.55	4.16	0.01	464	12.5	0.21	30.3	ND	7.5
SITE 5 (053)																				
Ap	4.2	0.1W	29.5	13.2	49	1035.0	17.0	22.2	0.20	70.0	5.17	2.49	2.02	0.18	707	14.8	3.24	0.0	ND	6.1
Ae	4.2	0.1W	32.8	14.0	34	722.5	17.2	19.5	0.13	60.0	5.57	2.62	0.40	0.04	438	11.3	0.76	0.0	ND	6.0
Bt	ND	0.1W	34.5	30.2	44	910.0	27.0	22.5	0.11	77.5	5.49	3.46	1.15	0.04	787	24.8	0.48	6.5	ND	7.2
Ck	1.9	0.1W	33.0	13.8	4	682.5	10.8	14.0	0.03	50.0	4.05	2.76	3.33	0.01	368	4.9	0.28	23.8	ND	7.3
SITE 6 (043)																				
Ap	4.0	0.1W	42.2	14.5	46	1045.0	15.8	24.0	0.30	77.5	5.35	2.58	2.09	0.19	774	14.1	3.17	0.0	ND	6.8
Ae	3.5	0.1W	29.8	13.5	52	1100.0	15.8	18.5	0.29	75.0	7.50	2.55	0.72	0.07	698	9.9	0.97	0.0	ND	5.9
Bt	5.1	0.1W	43.0	27.8	30	757.5	24.0	19.0	0.12	75.0	6.29	2.92	0.17	0.02	550	17.9	0.21	0.0	ND	5.1
Ck	2.2	0.1W	15.0	15.0	8	592.5	12.5	14.2	0.08	43.5	4.22	2.04	3.22	0.01	466	8.5	0.21	23.3	ND	7.3
II Ck	1.0	0.1W	15.0	13.2	1	375.0	8.5	12.2	0.08	30.5	3.05	0.99	6.83	0.01	250	2.0	0.14	50.6	ND	7.4

WATERSHED 10 - TWENTY MILE CREEK, LINCOLN COUNTY

APP. TABLE 4 (cont'd)

	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppb	Mn ppm	Ni ppm	Pb ppm	Se ppm	Zn ppm	Al %	Fe %	C %	N %	P ppm	CLAY %	ORGANIC MATTER %	CaCO ₃ % EST	CaCO ₃ % ACTUAL	pH
SITE 1 (266)																				
Ap	5.3	0.1W	60.0	15.0	36	385.0	20.5	24.5	0.23	80.0	6.78	3.48	2.76	0.17	396	37.7	3.24	0.0	0.0	6.9
Bg	4.7	0.2W	77.5	25.0	34	575.0	36.8	22.5	0.21	97.5	8.00	4.06	1.08	0.08	637	37.5	2.33	0.0	0.0	6.7
Ckg	5.0	1.0	92.5	30.0	24	505.0	28.5	18.2	0.07	92.5	7.48	3.94	3.05	0.05	624	57.2	0.08	22.5	24.8	7.7
SITE 2 (265)																				
Ap	8.1	0.1W	65.0	17.5	50	4295.0	24.5	33.2	0.58	162.5	7.36	6.29	3.63	0.30	2709	34.8	4.51	0.0	ND	5.7
Btgj	7.6	0.1W	87.5	37.5	31	575.0	47.3	24.0	0.22	130.0	7.02	4.75	0.52	0.10	584	57.5	0.90	0.0	ND	7.0
Ckg	5.6	0.1W	52.5	30.0	14	570.0	32.2	19.0	0.11	90.0	6.75	3.59	3.45	0.06	575	57.1	0.41	24.0	ND	7.7

WATERSHED 13 - HILLMAN CREEK, ESSEX COUNTY

APP. TABLE 4 (cont'd)

	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppb	Mn ppm	Ni ppm	Pb ppm	Se ppm	Zn ppm	Al %	Fe %	C %	N %	P ppm	CLAY %	ORGANIC MATTER %	CaCO ₃ % EST	CaCO ₃ % ACTUAL	pH
SITE 1 (115S)																				
Ap	6.4	0.1W	20.0	13.8	36	255.0	9.8	23.2	0.39	57.5	4.35	1.42	1.67	0.12	1011	7.6	2.69	0.0	ND	6.4
Aegj	2.9	0.1W	34.2	10.6	20	607.5	13.2	12.0	0.15	60.2	4.79	1.99	0.41	0.03	314	10.9	0.48	0.0	ND	6.4
II Btgj	9.4	0.4T	25.5	30.5	39	837.5	26.0	21.8	0.19	77.0	5.76	2.90	0.28	0.03	307	20.0	0.14	0.0	ND	6.7
II Ckgj	8.0	0.1W	47.0	25.2	39	342.5	21.5	16.2	0.08	69.8	5.35	2.31	0.83	0.03	474	9.7	0.28	5.0	ND	7.5
SITE 2 (105)																				
Ap	4.3	0.1W	27.0	9.5	30	175.0	9.2	22.0	0.25	49.8	3.89	1.28	1.03	0.09	510	5.3	1.79	0.0	ND	5.2
Bm ₁	3.0	0.1W	31.0	8.5	12	245.0	12.2	9.8	0.28	31.8	4.49	1.56	0.24	0.02	178	1.7	0.62	0.0	ND	5.8
Bm ₂	4.0	0.1W	17.0	8.5	12	381.5	8.7	9.8	0.16	23.8	3.88	1.09	0.17	0.01	143	2.0	0.21	0.0	ND	6.1
Bg	3.3	0.1W	17.0	14.0	3	397.5	12.5	10.2	0.11	35.0	4.42	1.70	0.11	0.01	216	3.2	0.14	0.0	ND	6.6
Ckg	4.3	0.1W	18.5	17.2	3	355.5	14.0	10.8	0.03	50.5	3.60	1.69	2.62	0.01	383	5.4	0.35	18.2	ND	7.5
SITE 3 (115)																				
Ap	4.4	0.3T	35.5	14.2	18	467.5	9.2	17.8	0.24	49.5	4.40	1.59	1.20	0.11	609	10.0	1.66	0.0	ND	6.4
Aegj	2.6	0.3T	15.5	8.4	12	235.0	9.8	10.5	0.11	34.0	4.38	1.38	0.18	0.01	181	7.0	0.48	0.0	ND	6.4
II Btgj ₁	10.0	0.1W	54.5	31.2	53	497.5	25.5	17.5	0.16	65.2	5.90	2.88	0.28	0.04	289	23.3	0.35	0.0	ND	6.8
II Btgj ₂	ND	0.3T	33.8	29.0	24	647.5	27.2	17.5	0.09	73.2	5.78	2.96	0.28	0.02	493	18.9	0.28	0.0	ND	6.7
II Ckgj	9.4	0.1W	35.0	30.8	12	600.0	26.5	11.0	0.15	67.2	6.44	2.88	3.16	0.04	494	38.6	0.28	22.5	ND	7.5

APPENDIX TABLE 5.

CORRELATION COEFFICIENTS FOR SOIL Ap HORIZONS

	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn	C	N	P	Al	Fe	Mn
CLAY	.003	*	.79	.57	.41	.84	.62	.33	.76	.44	.65	.08	.92	.73	.29
ORGANIC MATTER	.12	*	.41	.67	.88	.46	.08	.39	.38	.90	.89	.16	.31	.33	.18
CARBONATES	.56	*	.40	.09	.07	.17	.09	-.28	.13	.19	.25	-.28	.31	.06	-.04
Al	.08	*	.82	.58	.39	.80	.73	.32	.78	.42	.70	.22	-	.80	.37
Fe	-.16	*	.58	.38	.25	.57	.50	.26	.81	.43	.51	.37	.80	-	.81
Mn	-.20	*	.14	-.01	.10	.13	.68	.01	.50	.22	.29	.44	.37	.81	-

r = .37 significant at .05

r = .48 significant at .01

APPENDIX TABLE 6.

CORRELATION COEFFICIENTS FOR LUVISOLIC SOILS (n = 9)

	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn	C	N	P	Al	Fe	Mn
<u>Ap HORIZON</u>															
CLAY	.18	*	.80	.79	.70	.91	.58	.31	.84	.70	-.55	-.42	.94	.82	.61
ORGANIC MATTER	.35	*	.64	.66	.68	.80	.41	.15	.61	.81	-.49	.30	.73	.55	.40
Al	.16	*	.77	.82	.70	.82	.70	.17	.86	.65	-.05	.44	-	.86	.63
Fe	.35	*	.55	.50	.49	.63	.80	.33	.94	.53	-.35	.78	.86	-	.92
Mn	.46	*	.28	.19	.34	.39	.67	.28	.79	.40	-.44	.92	.63	.92	-
<u>B HORIZON</u>															
CLAY	-.11	*	.87	.55	.05	.75	.42	.47	.68	.39	.58	.13	.64	.78	.07
ORGANIC MATTER	-.10	*	.40	.19	-.14	.15	-.18	-.10	-.05	.40	.66	.18	.02	.10	-.14
Al	-.59	*	.78	.68	.11	.76	.71	.75	.83	.19	.24	-.13	-	.87	.35
Fe	-.35	*	.85	.87	.12	.82	.81	.62	.91	.17	.25	-.04	.87	-	.33
Mn	-.36	*	.03	.23	.03	-.16	.56	-.01	.15	.25	.30	.34	.35	.33	-
<u>C HORIZON</u>															
CLAY	.26	*	.62	.77	.18	.76	.23	.47	.63	.12	.88	.04	.67	.67	-.12
ORGANIC MATTER	-.06	*	.74	.58	.17	.80	.16	.57	.71	-.17	.49	-.07	.49	.52	-.36
Al	.40	*	.62	.88	.06	.86	.45	.72	.87	-.42	.82	-.20	-	.91	-.03
Fe	.35	*	.68	.77	.10	.79	.52	.66	.84	-.31	.78	-.18	.91	-	.05
Mn	-.27	*	-.50	-.40	-.28	-.31	-.22	-.36	-.33	.44	-.02	.24	-.03	.05	-

r = .41 significant at .1
r = .48 significant at .05
r = .61 significant at .01
r = .72 significant at .001

APPENDIX TABLE 7.

CORRELATION COEFFICIENTS FOR GLEYSOLIC SOILS (n = 9)

	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn	C	N	P	Al	Fe	Mn
<u>Ap HORIZON</u>															
CLAY	.52	.33	.66	.23	-.18	.57	.82	-.01	.45	-.30	-.56	-.06	.87	.86	.35
ORGANIC MATTER	-.19	-.61	.01	.61	.71	.03	-.26	.38	-.02	.98	.85	.51	-.27	.01	.27
Al	.23	.39	.84	.32	.01	.63	.74	.21	.51	-.20	-.21	.05	-	.84	.25
Fe	.27	-.03	.63	.37	-.07	.51	.68	.20	.48	.07	-.29	.03	.84	-	.49
Mn	.09	-.25	-.08	.03	.01	-.16	.44	-.20	.02	.20	.33	.31	.25	.49	-
<u>B HORIZON</u>															
CLAY	.11	.76	.52	.72	.87	.67	.68	.56	.83	-.68	.84	-.60	.85	.71	.42
ORGANIC MATTER	.27	-.12	.38	.04	.25	.08	.28	.20	.25	-.20	.94	-.10	.39	.35	-.07
Al	-.09	.56	.73	.68	.83	.61	.70	.49	.83	-.89	.76	-.68	-	.93	.48
Fe	.06	.42	.67	.51	.64	.47	.54	.37	.79	-.93	.50	-.68	.93	-	.64
Mn	-.02	.42	.19	.31	.14	.34	.06	.07	.57	-.50	.29	-.77	.48	.64	-
<u>C HORIZON</u>															
CLAY	.29	.74	.96	.76	.73	.49	.34	.29	.76	-.41	.87	-.20	.83	.89	-.02
ORGANIC MATTER	.32	.37	.36	.64	.73	.60	.31	.92	.72	-.29	.42	-.92	.46	.47	-.31
Al	.11	.66	.80	.60	.81	.38	.54	.38	.80	-.75	.77	-.42	-	.98	-.04
Fe	.15	.73	.88	.70	.89	.42	.55	.45	.86	-.63	.80	-.46	.98	-	-.12
Mn	.02	-.18	.06	-.25	-.23	.06	-.26	-.52	-.31	-.40	-.64	.46	-.04	-.12	-

r = .52 significant at .1
r = .60 significant at .05
r = .73 significant at .01
r = .85 significant at .001

APPENDIX TABLE 8.

DTPA EXTRACTABLE METAL CONCENTRATIONS (ppm) IN SOILS

		Cd	Cu	Ni	Pb	Zn
WATERSHED 1						
Site 1	Ap	0.35	2.98	1.94	2.75	3.72
	Bg1	0.16	2.27	0.60	1.22	0.70
	Bg2	0.25	1.48	0.44	1.18	0.44
	Ckg	0.14	1.48	0.28	1.16	0.30
Site 2	Ap	0.29	1.60	0.84	2.96	6.71
	Bg1	0.19	0.64	0.23	1.12	0.31
	Bg2	0.15	1.47	0.28	0.88	0.29
	Ckg	0.03	1.20	0.19	0.78	0.31
WATERSHED 3						
Site 7	Ap	0.13	2.68	0.25	1.32	0.74
	Bg	0.04	1.49	0.20	1.49	0.18
	Ckg	0.04	1.16	0.08	0.72	0.18
Site 2	A	0.15	1.42	0.49	1.09	1.65
	Aeg	0.07	1.32	0.26	0.71	0.27
	Btg1	0.09	1.70	0.30	0.68	0.28
	Btg2	0.07	0.83	0.20	1.03	0.14
	C	0.05	0.37	0.12	0.80	0.04
Site 3	Ap	0.11	0.67	0.18	1.02	0.64
	Bt	0.07	0.80	0.16	0.72	0.22
	Ckgj	0.05	0.56	0.12	0.88	<0.04

DTPA EXTRACTABLE METAL CONCENTRATIONS (ppm) IN SOILS

		Cd	Cu	Ni	Pb	Zn
WATERSHED 4						
Site 1	Ap	0.16	1.75	0.79	1.22	1.85
	A ₁	0.16	1.29	0.48	1.51	2.59
	Bg ₁	0.05	0.62	0.22	1.19	0.25
	Bg ₂	0.04	0.64	0.20	1.39	0.28
	Ckg	0.04	0.59	0.15	1.11	0.18
Site 2	Ap	0.12	0.77	0.26	1.08	0.86
	Bg	0.06	0.85	0.19	0.69	0.27
	Btg	0.05	0.41	0.08	0.71	0.15
	Ckg	<0.02	0.39	0.09	0.42	0.23
Site 3	Ap	0.10	0.77	0.28	0.68	1.00
	Ae	0.04	1.05	0.21	0.62	0.66
	Bt	0.04	0.89	0.21	0.75	2.25
	Ckg	0.03	0.44	0.12	0.62	0.67
Site 4	Ap	0.10	0.76	0.22	1.05	1.80
	Ae ₂	0.04	0.45	0.12	0.70	0.34
	Bt	0.05	0.86	0.15	1.20	0.60
	Ck	<0.02	0.39	0.11	0.72	0.36
WATERSHED 5						
Site 1	Ap	0.14	0.72	0.30	1.41	1.77
	Aeg	0.04	0.40	0.20	0.70	0.58
	Btg ₁	0.04	0.47	0.15	0.80	0.66
	Btg ₂	0.02	0.54	0.13	0.75	0.22
	Ckg	<0.02	0.43	0.08	0.67	0.30
Site 2	Ap	0.08	0.53	0.25	0.75	1.43
	Ae	0.06	0.60	0.16	0.44	0.50
	Bt	0.03	0.60	0.14	0.49	0.26
	Ck	0.02	0.92	0.07	0.32	0.22
Site 3	Ap	0.09	0.85	0.22	0.80	1.16
	Ae	0.05	0.55	0.06	0.98	0.15
	Btg	0.04	0.53	0.11	0.63	0.16
	Ckg	<0.02	0.28	0.06	0.55	0.16

DTPA EXTRACTABLE METAL CONCENTRATIONS (ppm) IN SOILS

		Cd	Cu	Ni	Pb	Zn
WATERSHED 5						
Site 4	Ap	0.15	1.05	0.38	1.96	2.42
	Btg1	0.04	0.43	0.09	0.46	0.30
	Btg2	0.05	0.62	0.12	0.57	0.36
	Ckg	<0.03	0.34	0.07	0.55	0.22
Site 5	Ap	0.09	0.43	0.18	1.07	0.87
	Ae	0.04	0.23	0.07	0.53	0.18
	Bt	0.06	0.86	0.14	0.75	0.50
	Ckg	<0.02	0.24	0.07	0.61	0.36
Site 6	Ap	0.09	0.41	0.16	1.12	1.07
	Ae	0.03	0.38	0.11	0.34	0.20
	IIBt	0.03	0.45	0.10	0.49	0.28
	IICk	0.02	0.44	0.05	0.50	0.31
	IIICk	<0.02	0.23	0.06	0.35	0.25
WATERSHED 10						
Site 1	Ap	0.06	0.85	0.47	1.48	0.44
	Bg	0.03	1.40	1.47	1.19	0.30
	Ckg	0.03	0.87	0.12	0.67	0.05
Site 2	Ap	0.09	0.83	0.81	0.99	1.98
	Bt	0.05	1.54	0.61	1.29	0.60
	Ckg	0.03	0.70	0.14	0.99	0.05

DTPA EXTRACTABLE METAL CONCENTRATIONS (ppm) IN SOILS

		Cd	Cu	Ni	Pb	Zn
WATERSHED 13						
Site 1	Ap	0.12	1.10	0.23	0.75	1.59
	Aeg	0.04	0.45	0.12	0.35	0.25
	Btg	0.05	0.93	0.21	0.86	0.34
	Ckg	0.05	0.75	0.11	0.86	0.17
Site 2	Ap	0.11	0.64	0.16	3.28	1.22
	Bm1	0.02	0.15	0.04	0.19	0.05
	Bm2	0.02	0.18	<0.04	<0.14	0.06
	Bg	0.04	0.45	0.04	0.52	0.14
	Ckg	0.11	0.46	0.06	0.28	0.22
Site 3	Ap	0.16	1.53	0.22	1.42	1.13
	Aeg	<0.02	0.35	0.05	0.36	0.07
	Beg	0.05	0.79	0.16	0.88	0.22
	Btg	0.06	1.00	0.28	1.04	0.27
	2 Ck	0.02	0.73	0.16	0.57	0.22

APPENDIX TABLE 9.

CORRELATION COEFFICIENTS FOR DTPA EXTRACTIONS OF Ap SOILS

	Cu	Ni	Pb	Zn
Clay	.54	.56	-.02	.14
Organic Matter	-.03	.14	-.34	.10
Al (total)	.37	.35	-.27	-.05
Fe (total)	-.01	.31	-.28	-.03
pH	.11	-.21	-.43	-.04
Cu (total)	.69			
Ni (total)		.54		
Pb (total)			.05	
Zn (total)				.48

$r = .37$ significant at .05

$r = .48$ significant at .01

APPENDIX TABLE 10.

ANALYSIS OF SOILS USED FOR THE EXTRACTION OF HUMIC ACIDS (HA) AND FULVIC ACIDS (FA)

	TOTAL C	ORGANIC C	TOTAL N	TOTAL S	pH	C/N RATIO	TOTAL ORGANIC MATTER	HUMIC ACID YIELD	FULVIC ACID YIELD	HA+FA YIELD %	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Zn
	g/kg SOIL						g/kg SOIL				mg/g SOIL		µg/g SOIL						
WATERSHED 1	21.1	20.8	2.2	4.0	6.9	9.9	35.8	13.1	5.7	52.5	61.0	23.3	0.7	35.8	25.0	265.0	26.5	24.5	117.5
WATERSHED 3	31.8	29.3	2.6	3.0	7.5	11.3	50.3	3.6	6.6	20.2	69.1	35.8	0.3	59.2	98.8	695.0	32.0	25.0	101.3
WATERSHED 4	27.6	26.9	2.5	3.7	7.1	10.6	46.3	11.2	5.9	36.9	60.0	27.5	0.4	26.4	16.6	830.0	18.7	24.5	89.5
WATERSHED 5	27.9	26.8	2.7	3.3	7.1	9.8	46.0	16.6	9.2	56.1	57.2	23.9	0.1W	50.0	21.3	700.0	15.8	24.0	88.6
WATERSHED 10	27.0	26.2	2.8	3.8	7.1	10.0	45.0	2.7	1.5	9.3	75.2	57.7	1.0	44.5	22.5	3718.0	16.0	31.5	115.2
WATERSHED 13	12.4	12.4	1.2	3.1	6.8	11.0	21.3	6.3	2.8	42.7	38.7	12.5	0.1W	23.8	16.0	158.0	10.5	23.3	51.5

APPENDIX TABLE 11

ULTIMATE ANALYSIS, FUNCTIONAL GROUP ANALYSIS AND TOTAL HEAVY METAL CONCENTRATIONS OF HUMIC ACIDS (HA) EXTRACTED FROM AGRICULTURAL SOILS

	YIELD g/kg SOIL	C %	H %	N %	S %	O %	ASH %	E4/ E6	TOTAL	TOTAL	PHENOLIC	Al	Fe	Cd	Cr	Cu	Ni	Pb	Zn
									ACIDITY	CARBOXYL	OH								
									meq/g HA			mg/g HA		µg/g HA					
WATERSHED 1	13.1	54.3	6.4	3.5	1.0	34.9	10.6	4.9	9.7	4.6	5.1	26.3	4.2	ND	40.0	107.7	13.5	ND	15.3
WATERSHED 3	3.6	47.9	6.5	5.0	0.6	39.8	14.1	4.4	9.6	3.0	6.6	45.8	20.8	ND	57.7	181.2	30.4	93.9	81.6
WATERSHED 4	14.9	54.1	5.3	2.8	1.2	36.7	6.9	4.1	9.3	5.7	3.6	ND	5.7	ND	75.7	106.9	15.9	1.5	64.3
WATERSHED 5	16.5	52.6	6.7	3.4	0.9	36.5	8.1	4.8	9.0	4.8	4.2	27.4	5.7	ND	38.7	82.0	11.7	ND	13.3
WATERSHED 10	2.7	52.2	6.0	4.0	0.9	37.0	16.6	3.5	ND	ND	ND	20.5	24.4	6.2	2778.7	279.4	476.0	402.2	119.4
WATERSHED 13	6.3	56.0	6.1	3.1	1.0	33.6	13.2	4.4	8.9	6.8	2.1	42.7	5.2	ND	54.7	78.8	29.3	3.5	31.0
AVERAGE WATER- SHED SOIL HA	9.5	52.9	6.2	3.6	0.9	36.4	11.5	4.5	9.3	5.0	4.3								
MEAN HA *		56.2	4.7	3.2	0.8	35.5		4.8	6.7	3.6	3.9								

* From Schnitzer (1977)

APPENDIX TABLE 12

ULTIMATE ANALYSIS, FUNCTIONAL GROUP ANALYSIS AND TOTAL HEAVY METAL CONCENTRATIONS OF FULVIC ACIDS (FA) EXTRACTED FROM AGRICULTURAL SOILS

	YIELD g/kg SOIL	C %	H %	N %	S %	O %	ASH	E ₄ / E ₆	TOTAL	TOTAL	PHENOLIC	Al	Fe	Cd	Cr	Cu	Ni	Pb	Zn
									ACIDITY	CARBOXYL	OH								
WATERSHED 1	5.7	45.0	6.8	3.7	1.7	42.8	22.0	4.8	14.7	7.6	7.1	17.9	4.7	ND	67.8	76.8	69.3	ND	87.5
WATERSHED 3	6.6	46.5	7.0	4.0	1.6	36.7	22.9	3.2	9.0	4.3	4.7	31.0	17.3	ND	59.2	94.8	87.7	100.9	96.1
WATERSHED 4	5.9	46.5	6.0	3.1	1.2	43.6	16.6	5.5	13.5	7.0	6.5	5.5	13.8	ND	925.6	59.7	103.9	2.8	39.0
WATERSHED 5	9.2	43.3	6.5	4.0	1.3	44.9	22.4	5.1	11.5	6.6	4.9	23.1	6.3	ND	226.5	101.4	98.7	ND	23.0
WATERSHED 10	1.6	41.7	6.2	3.4	1.2	47.5	20.3	3.4	ND	ND	ND	19.5	3.6	85.7	1280.9	592.0	134.1	891.0	165.0
WATERSHED 13	2.8	45.4	6.5	4.1	2.5	41.6	28.9	6.8	12.4	7.1	5.3	30.0	3.7	ND	2143.3	116.4	40.3	3.4	24.5
AVERAGE WATER- SHED SOIL FA	5.3	44.7	6.5	3.7	1.6	43.5	22.2	5.1	12.2	6.5	5.7								
MEAN FA *		45.7	5.4	2.1	1.9	44.8		9.6	10.3	8.2	3.0								

* from Schnitzer (1977)

APPENDIX TABLE 13
 WATERSHED 1 - BIG CREEK, ESSEX COUNTY

MEAN VALUES FOR TOTAL METAL CONCENTRATIONS IN SOIL REPLICATES
 n is the number of replicates

SITE 1		Cr ppm	Cu ppm	Mn ppm	Ni ppm	Pb ppm	Zn ppm	Al %	Fe %	C %	N %	
A HORIZON (n=5)	MEAN	55.5 ± 15.9	24.6 ± 1.0	275.8 ± 38.6	30.1 ± 2.5	23.9 ± 3.5	115.7 ± 11.0	6.63 ± 0.30	2.61 ± 0.16	2.10 ± 0.15	0.212 ± 0.012	
	SE	7.1	0.4	17.2	1.1	1.6	4.9	0.13	0.08	0.06	0.005	
	CV	28.6	4.1	14.0	8.3	14.6	9.5	4.5	7.3	7.1	5.6	
	B HORIZON (n=5)	MEAN	57.5 ± 10.0	33.0 ± 1.8	492.0 ± 55.4	47.4 ± 3.4	21.6 ± 2.7	131.7 ± 7.0	7.86 ± 0.54	3.62 ± 0.26	0.49 ± 0.09	0.078 ± 0.009
		SE	4.4	0.8	24.7	1.5	1.2	3.1	0.24	0.11	0.04	0.004
		CV	17.4	5.4	11.3	7.2	12.5	5.2	6.9	7.2	18.3	11.5
	C HORIZON (n=5)	MEAN	64.3 ± 18.5	34.0 ± 1.7	539.0 ± 110.5	49.8 ± 1.7	20.2 ± 2.7	114.2 ± 8.1	7.63 ± 1.07	3.63 ± 0.60	1.60 ± 0.28	0.006 ± 0.007
		SE	8.2	0.7	49.4	0.7	1.2	3.6	0.47	0.26	0.12	0.003
		CV	28.8	5.0	20.5	3.4	13.4	7.1	14.0	16.5	17.5	10.6
SITE 2												
A HORIZON (n=5)	MEAN	65.5 ± 5.1	20.0 ± 0.9	272.0 ± 19.9	22.6 ± 1.0	24.8 ± 3.3	117.0 ± 5.5	5.61 ± 0.39	2.28 ± 0.06	2.63 ± 0.20	0.249 ± 0.014	
	SE	2.2	0.4	8.8	0.4	1.4	2.4	0.17	0.02	0.08	0.006	
	CV	7.8	4.5	7.3	4.4	13.3	4.7	7.0	2.6	7.6	5.6	
B HORIZON (n=5)	MEAN	58.0 ± 8.2	24.9 ± 8.1	538.4 ± 113.2	44.4 ± 10.7	20.7 ± 4.0	94.7 ± 13.0	7.02 ± 0.80	3.21 ± 0.66	0.56 ± 0.09	0.071 ± 0.015	
	SE	3.7	3.6	50.6	4.7	1.8	5.8	0.35	0.29	0.04	0.006	
	CV	14.1	32.5	21.0	24.1	19.3	13.7	11.4	20.5	16.0	21.1	
C HORIZON (n=5)	MEAN	62.3 ± 11.5	32.3 ± 1.7	509.0 ± 83.2	47.1 ± 5.9	20.0 ± 4.2	96.5 ± 5.5	6.84 ± 0.53	3.21 ± 0.22	2.16 ± 0.41	0.064 ± 0.008	
	SE	5.1	0.7	37.2	2.6	1.8	2.4	0.23	0.09	0.18	0.003	
	CV	18.5	5.3	16.3	12.5	21.0	5.7	7.7	6.8	18.9	12.5	

SE - standard error
 CV - coefficient of variation

APP. TABLE 13 (cont'd)

WATERSHED 3 - LITTLE AUSABLE RIVER, HURON COUNTY

SITE 1		Cr ppm	Cu ppm	Mn ppm	Ni ppm	Pb ppm	Zn ppm	Al %	Fe %	C %	N %
A HORIZON											
(n=6)	MEAN	71.1 ± 34.9	27.4 ± 0.6	335.8 ± 9.2	29.5 ± 1.2	29.7 ± 0.5	92.1 ± 1.0	7.28 ± 0.50	2.77 ± 0.10	2.50 ± 0.07	0.14 ± 0.11
	SE	14.2	0.2	3.7	0.4	0.2	0.4	0.20	0.04	0.02	0.04
	CV	49.1	2.2	2.7	4.1	1.7	1.1	6.9	3.6	2.8	78.6
B HORIZON											
(n=6)	MEAN	79.6 ± 15.6	28.1 ± 0.7	357.5 ± 17.8	37.3 ± 1.8	27.0 ± 2.1	90.3 ± 1.5	7.12 ± 0.23	3.28 ± 0.22	1.13 ± 0.26	0.06 ± 0.01
	SE	6.3	0.2	7.5	0.7	0.8	0.6	0.09	0.08	0.10	0.01
	CV	19.6	2.5	5.0	4.8	7.8	1.7	3.2	6.7	23.0	16.7
C HORIZON											
(n=6)	MEAN	57.1 ± 1.9	22.2 ± 1.0	557.5 ± 59.4	16.0 ± 0.1	20.6 ± 0.7	61.8 ± 3.6	4.76 ± 0.29	2.49 ± 0.26	4.23 ± 0.59	0.03 ± 0.01
	SE	0.7	0.4	24.2	0.1	0.3	1.4	0.11	0.10	0.24	0.01
	CV	3.3	4.5	1.1	0.6	3.4	5.8	6.1	10.4	13.9	33.3
SITE 2											
A HORIZON											
(n=6)	MEAN	74.2 ± 2.0	26.7 ± 2.6	1076.7 ± 31.1	33.3 ± 0.8	23.1 ± 1.1	110.0 ± 0.6	7.14 ± 0.10	3.28 ± 0.03	3.81 ± 0.21	0.34 ± 0.02
	SE	0.9	1.0	12.6	0.3	0.5	0.2	0.04	0.01	0.08	0.01
	CV	2.7	9.7	2.9	2.4	4.8	0.5	1.4	0.9	5.5	5.8
B HORIZON											
(n=6)	MEAN	48.3 ± 18.3	25.8 ± 2.0	852.5 ± 57.2	39.6 ± 4.4	20.2 ± 1.1	103.3 ± 18.6	7.60 ± 0.70	3.64 ± 0.45	1.49 ± 0.32	0.10 ± 0.02
	SE	7.4	0.9	23.3	1.7	0.5	7.5	0.28	0.18	0.13	0.01
	CV	37.9	7.8	6.7	11.1	5.4	18.0	9.2	12.4	21.4	20.0
C HORIZON											
(n=6)	MEAN	54.4 ± 12.3	21.4 ± 0.7	532.5 ± 38.6	22.5 ± 1.2	13.8 ± 1.0	59.2 ± 2.0	4.47 ± 0.33	2.43 ± 0.23	5.34 ± 0.40	0.03 ± 0.01
	SE	5.0	0.2	15.7	0.5	0.4	0.9	0.13	0.09	0.16	0.01
	CV	22.6	3.3	7.2	5.3	7.2	3.4	7.4	9.5	7.4	33.3
SITE 3											
A HORIZON											
(n=6)	MEAN	82.3 ± 9.9	21.7 ± 1.4	816.3 ± 22.4	26.6 ± 2.1	26.7 ± 1.2	96.2 ± 3.9	6.21 ± 0.29	2.84 ± 0.02	3.49 ± 0.06	0.30 ± 0.01
	SE	4.0	0.5	9.1	0.8	0.4	1.5	0.11	0.01	0.02	0.01
	CV	12.0	6.5	2.7	7.9	4.5	4.1	4.7	0.7	1.7	3.3
B HORIZON											
(n=6)	MEAN	88.5 ± 12.9	30.7 ± 4.2	784.0 ± 192.7	30.9 ± 14.5	20.1 ± 2.5	87.7 ± 15.3	4.52 ± 1.41	6.56 ± 2.21	3.21 ± 1.99	0.07 ± 0.02
	SE	5.2	1.7	78.6	5.9	1.0	6.2	0.57	0.90	0.81	0.01
	CV	14.6	13.7	24.6	46.9	12.4	17.4	31.2	33.7	61.9	28.6
C HORIZON											
(n=6)	MEAN	43.0 ± 9.1	21.9 ± 0.3	450.5 ± 8.0	30.4 ± 17.4	13.6 ± 1.1	54.5 ± 2.3	4.27 ± 0.14	2.12 ± 0.09	6.12 ± 0.15	0.06 ± 0.02
	SE	3.7	0.1	3.2	7.1	0.4	0.9	0.05	0.03	0.06	0.01
	CV	21.2	1.4	1.8	57.2	8.1	4.2	3.2	4.2	2.4	33.3

APP. TABLE 13 (cont'd)

WATERSHED 4 - CANAGAGIGUE CREEK, WELLINGTON COUNTY

SITE 1	Cr ppm	Cu ppm	Mn ppm	Ni ppm	Pb ppm	Zn ppm	Al %	Fe %	C %	N %
A HORIZON										
MEAN	53.4 ± 15.2	20.3 ± 5.5	854.0 ± 89.8	23.4 ± 3.1	24.8 ± 4.6	94.2 ± 5.2	6.29 ± 0.31	2.94 ± 0.33	3.27 ± 0.17	0.324 ± 0.015
(n=5) SE	6.8	2.4	40.1	1.3	2.0	2.3	0.13	0.14	0.07	0.006
CV	28.5	27.1	10.5	13.2	18.5	5.5	4.9	11.2	5.1	4.6
B HORIZON										
MEAN	65.2 ± 18.7	26.2 ± 6.7	894.0 ± 23.8	34.1 ± 2.7	22.2 ± 1.3	97.7 ± 3.2	7.72 ± 0.53	3.80 ± 0.32	0.63 ± 0.25	0.063 ± 0.017
(n=5) SE	8.3	3.0	10.6	1.2	0.5	1.4	0.23	0.14	0.11	0.007
CV	28.7	25.6	2.7	7.9	5.9	3.3	7.2	8.4	39.6	26.9
C HORIZON										
MEAN	62.3 ± 13.9	21.7 ± 5.7	741.6 ± 137.6	29.8 ± 9.2	20.6 ± 7.0	76.0 ± 13.2	6.71 ± 1.42	3.21 ± 0.66	2.07 ± 1.34	0.040 ± 0.011
(n=5) SE	6.2	2.5	61.5	4.1	3.1	5.9	0.63	0.29	0.59	0.004
CV	22.3	26.3	18.6	30.9	34.0	17.4	21.2	20.6	64.7	27.5
SITE 2										
A HORIZON										
MEAN	48.5 ± 10.2	16.3 ± 5.1	768.0 ± 125.1	19.7 ± 2.3	23.4 ± 1.5	83.8 ± 9.3	5.92 ± 0.11	2.58 ± 0.14	2.57 ± 0.25	0.230 ± 0.010
(n=5) SE	4.6	2.2	55.9	1.0	0.6	4.1	0.04	0.06	0.11	0.004
CV	21.0	31.3	16.3	11.7	6.4	11.1	1.9	5.4	9.7	4.3
B HORIZON										
MEAN	50.8 ± 11.4	21.6 ± 4.9	622.5 ± 136.5	24.7 ± 5.0	19.1 ± 4.0	74.5 ± 17.9	6.04 ± 1.10	2.77 ± 0.50	0.81 ± 0.29	0.071 ± 0.014
(n=5) SE	5.0	2.1	61.0	2.2	1.7	8.0	0.49	0.22	0.13	0.006
CV	22.4	22.7	21.9	20.2	20.9	24.0	18.2	18.1	35.8	19.7
C HORIZON										
MEAN	45.0 ± 11.3	21.5 ± 3.3	583.0 ± 117.1	18.6 ± 3.5	17.7 ± 8.6	59.2 ± 6.2	4.80 ± 1.31	2.38 ± 0.55	4.70 ± 0.24	0.024 ± 0.007
(n=5) SE	5.0	1.4	52.6	1.5	3.8	2.7	0.58	0.24	0.11	0.003
CV	25.1	15.3	20.1	18.8	4.9	10.5	27.3	23.1	5.1	29.1
SITE 3										
A HORIZON										
MEAN	71.5 ± 8.5	23.4 ± 2.8	819.0 ± 62.4	24.5 ± 4.1	23.6 ± 2.2	104.8 ± 17.3	6.74 ± 0.34	3.07 ± 0.20	3.56 ± 0.71	0.348 ± 0.066
(n=5) SE	3.8	1.2	27.9	1.8	0.9	7.7	0.15	0.08	0.31	0.029
CV	11.9	12.0	7.6	16.7	9.3	16.5	5.0	6.5	19.9	18.9
B HORIZON										
MEAN	67.9 ± 10.4	22.9 ± 10.3	901.0 ± 55.7	27.6 ± 2.8	23.4 ± 1.8	103.2 ± 7.4	7.25 ± 0.87	3.39 ± 0.59	0.82 ± 0.14	0.091 ± 0.024
(n=5) SE	4.6	4.6	24.9	1.2	0.8	3.3	0.38	0.26	0.06	0.010
CV	15.3	45.0	6.2	10.1	7.7	7.2	12.0	17.4	17.0	26.3
C HORIZON										
MEAN	40.7 ± 14.7	20.7 ± 2.0	615.5 ± 89.9	21.9 ± 5.8	16.3 ± 3.6	64.1 ± 18.5	5.17 ± 1.04	2.52 ± 0.51	4.04 ± 0.78	0.027 ± 0.004
(n=5) SE	6.5	0.8	40.2	2.5	1.6	8.2	0.46	0.22	0.34	0.002
CV	36.1	9.7	14.6	26.5	22.1	28.9	20.1	20.2	19.3	14.8

APP. TABLE 13 (cont'd)

WATERSHED 5 - HOLIDAY CREEK, OXFORD COUNTY

SITE 1		Cr ppm	Cu ppm	Mn ppm	Ni ppm	Pb ppm	Zn ppm	Al %	Fe %	C %	N %
A HORIZON											
	MEAN	53.5 ± 5.1	15.7 ± 1.7	541.0 ± 58.4	18.3 ± 2.1	24.2 ± 3.6	139.0 ± 22.1	6.51 ± 0.27	2.83 ± 0.13	3.47 ± 0.36	0.343 ± 0.001
(n=5)	SE	2.2	0.7	26.1	0.9	1.6	9.8	0.12	0.05	0.16	0.001
	CV	9.5	10.8	10.8	11.5	14.9	15.9	4.1	4.6	10.3	0.2
B HORIZON											
	MEAN	52.7 ± 6.3	15.1 ± 3.5	469.5 ± 45.4	20.6 ± 0.8	19.0 ± 3.2	92.1 ± 8.9	6.66 ± 0.12	3.95 ± 0.85	0.75 ± 0.19	0.066 ± 0.017
(n=5)	SE	2.8	1.5	20.3	0.3	1.4	3.9	0.05	0.38	0.08	0.007
	CV	12.0	33.1	9.7	3.9	16.8	9.7	1.8	2.2	25.3	25.7
C HORIZON											
	MEAN	40.1 ± 5.3	18.6 ± 1.4	505.5 ± 24.1	17.1 ± 1.3	15.9 ± 4.2	57.3 ± 5.6	5.26 ± 0.39	2.42 ± 0.28	3.72 ± 0.49	0.022 ± 0.001
(n=5)	SE	2.3	0.6	10.7	0.5	1.8	2.5	0.17	0.12	0.21	0.001
	CV	13.2	7.5	4.7	7.6	2.6	9.8	7.4	11.6	13.1	4.5
SITE 2											
A HORIZON											
	MEAN	49.1 ± 8.8	18.6 ± 0.9	865.0 ± 85.3	17.3 ± 1.1	22.7 ± 1.7	80.3 ± 5.3	6.04 ± 0.21	2.57 ± 0.11	2.16 ± 0.22	0.225 ± 0.018
(n=5)	SE	3.3	0.4	38.1	0.4	0.7	2.3	0.09	0.04	0.09	0.080
	CV	17.9	4.8	9.9	6.4	7.5	6.6	3.5	4.3	10.1	8.0
B HORIZON											
	MEAN	41.5 ± 8.3	23.2 ± 2.6	821.0 ± 86.4	22.7 ± 2.2	20.0 ± 2.9	69.8 ± 4.2	6.73 ± 0.31	3.00 ± 0.17	0.62 ± 0.17	0.061 ± 0.020
(n=5)	SE	3.7	1.1	38.6	0.9	1.2	1.8	0.13	0.07	0.07	0.090
	CV	2.0	11.2	10.5	9.7	14.5	6.0	4.6	5.7	27.4	32.7
C HORIZON											
	MEAN	25.6 ± 5.6	19.5 ± 2.8	565.5 ± 21.7	17.8 ± 2.5	13.7 ± 3.0	51.3 ± 7.1	4.99 ± 0.27	2.07 ± 0.16	3.43 ± 0.17	0.208 ± 0.006
(n=5)	SE	2.5	1.2	9.7	1.1	1.3	3.1	0.12	0.07	0.07	0.002
	CV	21.9	14.4	3.8	14.0	21.9	13.8	5.4	7.7	4.9	2.8

APP. TABLE 13 (cont'd)

WATERSHED 10 - TWENTY MILE CREEK, LINCOLN COUNTY

SITE 1		Cr ppm	Cu ppm	Mn ppm	Ni ppm	Pb ppm	Zn ppm	Al %	Fe %	C %	N %
A HORIZON											
	MEAN	65.0 ± 5.0	19.0 ± 2.2	356.0 ± 17.5	24.2 ± 2.5	25.6 ± 1.2	92.0 ± 6.7	7.14 ± 0.20	3.48 ± 0.11	2.82 ± 0.83	0.18 ± 0.01
(n=6)	SE	2.0	0.8	7.1	1.0	0.04	2.7	0.08	0.04	0.33	0.01
	CV	7.7	11.6	4.9	10.3	4.7	7.3	2.8	3.2	29.4	5.6
B HORIZON											
	MEAN	83.5 ± 14.1	29.0 ± 5.5	605.0 ± 96.4	26.5 ± 5.8	23.6 ± 1.1	107.5 ± 10.9	8.43 ± 0.84	4.53 ± 0.87	0.99 ± 0.20	0.07 ± 0.01
(n=6)	SE	5.7	2.2	39.3	2.3	0.4	4.4	0.34	0.35	0.08	0.01
	CV	16.9	19.0	15.9	21.9	4.7	10.1	10.0	19.2	20.2	14.3
C HORIZON											
	MEAN	72.5 ± 20.2	30.0 ± 0.0	518.0 ± 9.7	21.0 ± 4.3	18.9 ± 1.1	93.5 ± 2.2	7.47 ± 0.07	3.88 ± 0.11	3.10 ± 0.14	0.04 ± 0.01
(n=6)	SE	8.2	---	3.9	1.7	0.4	0.9	0.02	0.04	0.05	0.01
	CV	27.9	0.0	1.9	20.4	5.8	2.4	0.9	2.8	4.5	25.0
SITE 2											
A HORIZON											
	MEAN	66.0 ± 6.5	15.5 ± 1.1	3491.0 ± 1068.1	24.6 ± 0.4	32.2 ± 3.4	147.5 ± 9.4	7.04 ± 0.44	5.71 ± 0.82	3.44 ± 0.37	0.31 ± 0.02
(n=6)	SE	2.6	0.4	435.9	0.1	1.3	3.8	0.17	0.33	0.15	0.01
	CV	9.8	7.1	30.6	1.6	10.6	6.4	6.3	14.4	10.7	6.5
B HORIZON											
	MEAN	85.5 ± 16.6	38.5 ± 2.2	733.0 ± 119.8	47.7 ± 1.3	24.3 ± 1.0	141.0 ± 7.4	8.39 ± 0.83	4.77 ± 0.11	0.52 ± 0.03	0.08 ± 0.01
(n=6)	SE	6.7	0.8	48.8	0.5	0.4	3.0	0.33	0.04	0.01	0.01
	CV	19.4	5.7	16.3	2.7	4.1	5.2	9.9	2.3	5.7	12.5
C HORIZON											
	MEAN	60.5 ± 16.6	30.0 ± 0.0	554.0 ± 23.0	32.2 ± 1.2	19.8 ± 0.8	88.0 ± 2.7	6.63 ± 0.45	3.44 ± 0.23	3.43 ± 0.12	0.03 ± 0.01
(n=6)	SE	6.7	---	9.3	0.4	0.3	1.1	0.18	0.09	0.04	0.01
	CV	27.4	0.0	4.2	3.7	4.0	3.1	6.8	6.7	3.4	33.3

APP. TABLE 13 (cont'd)

WATERSHED 10

SITES 1, 2, 3, 4 and 6	Cr ppm	Cu ppm	Mn ppm	Ni ppm	Pb ppm	Zn ppm	Al %	Fe %	C %	N %
A HORIZON										
MEAN	79.6 ± 16.9	20.8 ± 5.5	1305.4 ± 1258.4	20.3 ± 5.5	28.0 ± 3.1	112.2 ± 22.5	6.85 ± 0.81	4.16 ± 0.96	2.57 ± 0.66	0.22 ± 0.06
(n=5) SE	7.5	2.5	561.8	2.5	1.4	10.0	0.36	0.43	0.29	0.03
CV	21.2	26.4	96.4	27.1	11.1	20.1	11.8	23.1	25.6	27.3
B HORIZON										
MEAN	101.4 ± 15.5	34.5 ± 3.7	673.1 ± 63.5	32.0 ± 8.8	24.1 ± 2.5	112.7 ± 16.1	9.19 ± 0.80	4.93 ± 0.33	0.79 ± 0.19	0.08 ± 0.03
(n=5) SE	6.9	1.6	28.3	3.9	1.1	7.2	0.36	0.15	0.08	0.01
CV	15.3	10.7	9.4	27.5	10.4	14.3	8.7	6.7	24.0	37.5
C HORIZON										
MEAN	70.5 ± 12.4	31.7 ± 2.2	548.9 ± 28.1	23.0 ± 5.3	19.4 ± 2.5	86.6 ± 7.1	7.26 ± 0.44	3.74 ± 0.36	3.05 ± 0.37	0.06 ± 0.04
(n=5) SE	5.5	0.1	12.5	2.4	1.1	3.2	0.20	0.16	0.17	0.02
CV	17.6	6.9	5.1	23.0	12.9	8.2	6.1	9.6	12.1	66.7
SITES 2, 3, 4, 5 and 6										
A HORIZON										
MEAN	83.8 ± 14.9	22.1 ± 5.8	1398.7 ± 1185.6	18.9 ± 5.2	29.1 ± 3.1	118.9 ± 19.8	6.82 ± 0.80	4.23 ± 0.91	2.45 ± 0.65	0.22 ± 0.06
(n=5) SE										
CV	17.8	26.2	84.8	27.5	10.7	16.6	11.7	21.5	26.5	27.3
B HORIZON										
MEAN	103.1 ± 13.4	36.7 ± 2.7	707.4 ± 64.1	31.7 ± 9.1	23.7 ± 2.7	112.2 ± 16.3	9.29 ± 0.71	5.01 ± 0.25	0.71 ± 0.16	0.09 ± 0.03
(n=5) SE										
CV	13.0	7.4	9.1	28.7	11.4	14.5	7.6	5.0	22.5	33.3
C HORIZON										
MEAN	66.7 ± 14.3	33.6 ± 4.0	580.3 ± 57.4	22.0 ± 6.2	19.1 ± 2.7	84.0 ± 6.3	6.98 ± 0.65	3.71 ± 0.35	2.83 ± 0.59	0.07 ± 0.04
(n=5) SE										
CV	21.4	11.9	9.9	28.2	14.1	7.5	9.3	9.4	20.8	57.1

APP. TABLE 13 (cont'd)

WATERSHED #10

SITES 2, 3, 4 and 6	Cr ppm	Cu ppm	Mn ppm	Ni ppm	Pb ppm	Zn ppm	Al %	Fe %	C %	N %
A HORIZON										
(n=4) MEAN	83.2 ± 17.1	21.2 ± 6.3	1542.6 ± 1317.5	19.3 ± 5.8	28.6 ± 3.3	117.2 ± 22.4	6.73 ± 0.85	4.33 ± 1.00	2.50 ± 0.74	0.23 ± 0.07
SE	8.6	3.2	658.8	2.9	1.7	11.2	0.42	0.50	0.37	0.04
CV	20.6	29.7	85.4	30.1	11.5	19.1	12.6	23.1	29.6	30.4
B HORIZON										
(n=4) MEAN	105.8 ± 13.7	35.9 ± 2.4	690.1 ± 58.8	33.4 ± 9.5	24.2 ± 2.9	114.1 ± 18.3	9.38 ± 0.78	5.04 ± 0.28	0.74 ± 0.17	0.09 ± 0.03
SE	6.9	1.2	29.4	4.8	1.5	9.2	0.39	0.14	0.09	0.02
CV	12.9	6.7	8.5	28.4	12.0	16.0	8.3	5.6	23.0	33.3
C HORIZON										
(n=4) MEAN	70.0 ± 14.2	32.1 ± 2.3	556.6 ± 25.6	23.6 ± 6.0	19.6 ± 2.8	84.9 ± 6.9	7.20 ± 0.49	3.70 ± 0.40	3.03 ± 0.43	0.07 ± 0.05
SE	7.1	1.2	12.8	3.0	1.4	3.5	0.25	0.20	0.22	0.03
CV	20.3	7.2	4.6	25.4	14.3	8.1	6.8	10.8	14.2	71.4
SITES 1, 2, 3, 4, 5 and 6										
A HORIZON										
(n=6) MEAN	80.7 ± 15.4	21.6 ± 5.4	1224.9 ± 1142.7	19.8 ± 5.1	28.6 ± 3.1	114.4 ± 20.8	6.88 ± 0.73	4.10 ± 0.87	2.51 ± 0.60	0.22 ± 0.06
SE	6.3	2.2	466.4	2.1	1.3	8.5	0.30	0.36	0.24	0.02
CV	19.1	25.0	93.3	25.8	10.8	18.2	10.6	21.2	23.9	27.3
B HORIZON										
(n=6) MEAN	99.8 ± 14.4	35.4 ± 4.0	690.5 ± 71.0	30.9 ± 8.4	23.7 ± 2.4	111.4 ± 14.8	9.14 ± 0.72	4.93 ± 0.30	0.76 ± 0.18	0.08 ± 0.02
SE	5.9	1.6	29.0	3.4	1.0	6.0	0.29	0.12	0.07	0.01
CV	14.4	11.3	10.3	27.2	10.1	13.3	7.9	6.1	23.7	25.0
C HORIZON										
(n=6) MEAN	67.7 ± 13.0	33.0 ± 3.8	569.9 ± 57.3	21.9 ± 5.5	19.0 ± 2.2	85.6 ± 6.8	7.06 ± 0.62	3.74 ± 0.32	2.87 ± 0.54	0.06 ± 0.04
SE	5.3	1.6	23.4	2.2	0.9	2.8	0.25	0.13	0.22	0.02
CV	19.2	11.5	10.1	25.1	11.6	7.9	8.8	8.6	18.8	66.7

APP. TABLE 13 (cont'd)

WATERSHED 13 - HILLMAN CREEK, ESSEX COUNTY

SITE 1	Cr ppm	Cu ppm	Mn ppm	Ni ppm	Pb ppm	Zn ppm	Al %	Fe %	C %	N %
A HORIZON										
(n=5) MEAN	20.5 ± 1.1	13.8 ± 1.3	248.6 ± 14.0	13.3 ± 2.7	20.2 ± 2.0	57.8 ± 3.9	4.50 ± 0.27	1.34 ± 0.10	1.48 ± 0.16	0.112 ± 0.005
SE	0.4	0.5	6.2	1.2	0.8	1.7	0.12	0.04	0.07	0.002
CV	5.4	9.4	5.6	20.3	9.9	6.7	6.0	7.5	10.8	4.4
B HORIZON										
(n=5) MEAN	24.2 ± 2.3	25.0 ± 3.2	597.5 ± 150.4	27.0 ± 5.1	17.1 ± 3.0	76.1 ± 1.0	5.39 ± 0.41	2.56 ± 0.35	0.57 ± 0.18	0.033 ± 0.004
SE	1.0	1.4	67.2	2.2	1.3	0.4	0.18	0.15	0.08	0.002
CV	9.5	12.8	25.2	18.9	17.5	1.3	7.6	13.7	31.5	12.1
C HORIZON										
(n=5) MEAN	34.2 ± 8.1	22.1 ± 2.3	409.7 ± 59.7	27.1 ± 4.2	14.7 ± 1.8	66.4 ± 6.1	4.67 ± 0.49	2.04 ± 0.32	2.22 ± 0.86	0.022 ± 0.006
SE	3.6	1.0	26.6	1.8	0.8	2.7	0.21	0.14	0.38	0.002
CV	23.8	10.4	14.6	15.5	12.2	9.2	10.5	15.7	38.7	27.2
SITE 2										
A HORIZON										
(n=5) MEAN	32.2 ± 4.1	11.2 ± 2.5	219.3 ± 25.0	13.9 ± 3.2	23.5 ± 2.2	59.8 ± 6.4	4.25 ± 0.32	1.41 ± 0.18	1.43 ± 0.27	0.115 ± 0.020
SE	1.8	1.1	11.8	1.4	0.9	2.8	0.14	0.08	0.12	0.008
CV	12.7	22.3	11.4	23.0	9.4	10.7	7.5	12.8	18.8	17.3
B HORIZON										
(n=5) MEAN	19.3 ± 6.0	8.8 ± 1.1	259.3 ± 9.7	16.1 ± 3.3	10.6 ± 1.4	40.2 ± 9.1	4.58 ± 0.39	1.58 ± 0.13	0.51 ± 0.23	0.028 ± 0.015
SE	2.6	0.4	4.3	1.4	0.6	4.0	0.17	0.05	0.10	0.006
CV	31.1	12.5	3.7	20.5	13.2	22.7	8.5	8.2	45.0	53.5
C HORIZON										
(n=5) MEAN	20.6 ± 1.5	17.2 ± 1.9	420.2 ± 55.8	17.9 ± 4.3	11.9 ± 1.2	56.5 ± 4.0	3.90 ± 0.48	1.63 ± 0.21	2.35 ± 0.37	0.013 ± 0.003
SE	2.6	0.8	24.9	1.9	0.5	1.7	0.21	0.09	0.16	0.001
CV	7.3	11.0	13.3	24.0	10.1	7.1	12.3	12.9	15.7	23.0

APP. TABLE 13 (cont'd)

WATERSHED 13 - HILLMAN CREEK, ESSEX COUNTY

SITE 3		Cu ppm	Cu ppm	Mn ppm	Ni ppm	Pb ppm	Zn ppm	Al %	Fe %	C %	N %
A HORIZON											
(n=5)	MEAN	20.5 ± 8.4	13.6 ± 0.5	309.3 ± 89.4	13.9 ± 3.9	16.1 ± 1.0	51.6 ± 5.4	4.22 ± 0.20	1.42 ± 0.14	1.00 ± 0.13	0.083 ± 0.017
	SE	3.8	0.2	39.9	1.7	0.4	2.4	0.10	0.06	0.05	0.007
	CV	41.0	3.7	28.9	28.1	6.2	10.5	4.7	9.9	13.0	20.4
B HORIZON											
(n=5)	MEAN	38.9 ± 8.8	29.9 ± 1.1	505.5 ± 27.9	29.9 ± 4.7	16.6 ± 1.2	74.1 ± 6.0	6.13 ± 0.51	2.85 ± 0.13	0.29 ± 0.08	0.028 ± 0.006
	SE	3.9	0.5	12.5	2.1	0.5	2.7	0.22	0.05	0.03	0.002
	CV	22.6	3.7	5.5	15.7	7.2	8.1	8.3	4.6	27.5	21.4
C HORIZON											
(n=5)	MEAN	33.3 ± 2.8	23.8 ± 4.1	517.0 ± 51.2	25.6 ± 3.4	13.1 ± 1.2	63.8 ± 2.8	4.97 ± 0.86	2.35 ± 0.36	2.58 ± 0.81	0.028 ± 0.009
	SE	1.3	1.8	22.9	1.5	0.5	1.3	0.38	0.16	0.36	0.003
	CV	8.4	17.2	9.9	13.3	9.2	4.4	17.3	15.3	31.4	32.1
SITE 4											
A HORIZON											
(n=4)	MEAN	19.3 ± 2.9	9.0 ± 0.9	294.8 ± 4.4	16.1 ± 0.3	17.8 ± 0.6	49.8 ± 3.3	4.11 ± 0.27	1.27 ± 0.15	0.91 ± 0.09	0.063 ± 0.014
	SE	1.5	0.5	2.2	0.2	0.3	1.7	0.13	0.08	0.04	0.007
	CV	15.0	10.0	1.5	1.9	3.4	6.6	6.6	11.8	9.8	22.2
B HORIZON											
(n=4)	MEAN	22.6 ± 1.9	22.8 ± 3.9	411.1 ± 78.9	27.5 ± 2.1	12.8 ± 1.6	69.3 ± 4.3	5.19 ± 0.28	2.47 ± 0.46	0.35 ± 0.06	0.023 ± 0.003
	SE	1.0	2.0	39.5	1.1	0.8	2.2	0.14	0.23	0.03	0.001
	CV	8.4	17.1	19.2	7.6	12.5	6.2	5.4	18.6	17.1	13.0
C HORIZON											
(n=4)	MEAN	26.0 ± 3.1	13.4 ± 1.5	373.3 ± 25.2	21.1 ± 1.7	10.9 ± 0.9	53.4 ± 8.7	4.65 ± 0.15	1.51 ± 0.15	1.25 ± 0.54	0.016 ± 0.003
	SE	1.6	0.8	12.6	0.8	0.5	4.4	0.08	0.08	0.27	0.001
	CV	11.9	11.2	6.8	8.1	8.3	16.3	3.2	9.9	43.2	18.8

APPENDIX TABLE 14.

TRACE METALS IN FERTILIZERS USED IN ESSEX COUNTY (1975)

		Cd	Co	Cr	Cu	Ni	Pb	Zn	Fe
Monoammonium phosphate 12.5-50-0	Mean	5.7	4	66	2.9	39	<3	69	11,808
	SE mean (2)	0.3	2	20	0.3	9	--	6	537
	SE difference	0.5	2	23	0.9	13	--	7	972
Diammonium phosphate 18-46-0	Mean	5.6	4	68	2.6	37	<3	71	11,192
	SE mean (2)	0.2	1	14	0.3	9	--	3	930
	SE difference	1.4	1	20	0.8	12	--	7	1,315
Superphosphate 0-20-0	Mean	2.1	4	39	2.4	23	<3	42	5,713
	SE mean (2)	0.2	2	6	0.5	4	--	5	445
	SE difference	0.3	3	8	0.7	6	--	7	629
Triple Super- phosphate 0-46-0	Mean	9.3	5	92	3.1	36	3	108	10,809
	SE mean (2)	1.2	2	17	0.2	4	--	9	185
	SE difference	1.7	3	24	0.3	5	--	13	261
Urea 46-0-0	Mean	<0.1	<1	<3	<0.4	<1	<3	<1	<3
	SE mean (2)	--	1	--	0.3	1	--	--	-----
	SE difference	--	1	--	0.4	1	--	--	-----
Ammonium nitrate 34-0-0	Mean	<0.2	<1	<5	<0.3	7	<3	<3	180
	SE mean (2)	--	-	--	----	1	--	--	72
	SE difference	--	-	--	----	1	--	--	102
Potash 0-0-60	Mean	<0.1	2	<3	<0.6	4	3	<1	362
	SE mean (2)	--	0.5	-	----	1	-	--	71
	SE difference	--	1	-	----	2	-	--	101
Potassium sulphate 0-0-50	Mean	<0.2	1	<3	<0.5	5	<3	<3	543
	SE mean (2)	----	0	-	----	0.5	--	--	98
	SE difference	----	0	-	----	0.7	--	--	139
Dolomite	Mean	<0.1	<1	<3	<0.2	5	<3	<2	119
	SE mean (2)	----	-	-	----	0.8	--	--	34
	SE difference	----	-	-	----	1	--	--	49

APPENDIX TABLE 15

TOTAL HEAVY METALS IN BOTTOM SEDIMENTS

WATERSHED 1 - BIG CREEK, ESSEX COUNTY

	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppb	Mn ppm	Ni ppm	Pb ppm	Se ppm	Zn ppm	Al %	Fe %	C %	C _{org} %	N %	S %	P ppm	pH	CLAY %	ORGANIC MATTER %	CARBONATES %
030675	9.4	1.3	64.0	24.5	34	650.0	36.5	18.5	0.66	107.5	5.72	2.48	3.63	1.26	0.09	0.63	295	7.75	27.7	1.1	17.7
290376	2.1	0.4T	55.0	27.5	38	665.0	45.5	22.0	0.62	98.5	5.45	2.78	2.35	0.37	0.08	0.33	359	7.40	18.9	1.4	13.8
250576	14.0	2.3	85.0	35.0	77	1140.0	39.0	30.5	0.71	120.0	6.13	3.15	3.91	1.56	ND	ND	442	7.10	16.0	1.2	16.7
250576	15.0	1.3	40.0	35.0	-	885.0	34.0	27.0	0.76	130.0	5.15	2.78	2.54	1.12	ND	ND	472	7.10	14.8	1.2	8.9
260776	9.9	0.5T	80.0	35.0	50	550.0	23.0	22.5	0.68	125.0	6.40	3.45	3.26	1.75	ND	ND	491	6.60	35.6	1.5	15.0
051176	11.0	1.3	48.0	28.5	35	535.0	45.0	20.0	0.68	120.5	4.05	3.58	3.53	1.07	ND	ND	496	7.00	ND	ND	ND
AVERAGE	10.2	1.2	62.0	30.9	47	737.5	37.2	23.4	0.69	117.0	5.48	3.04	3.20	1.19	0.08	0.48	426	7.15	22.6	1.3	14.4
MCE 4-11-75	4.2	0.5	2.5	14.0	20		29.0	7.5		46.0								7.85			

WATERSHED 3 - LITTLE AUSABLE RIVER, HURON COUNTY

APP. TABLE 15 (cont'd)

	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppb	Mn ppm	Ni ppm	Pb ppm	Se ppm	Zn ppm	Al %	Fe %	C %	Corg %	N %	S %	P ppm	pH	CLAY %	ORGANIC MATTER %	CARBONATES %
100675	2.2	1.0	18.5	12.5	32	475.0	13.8	24.0	0.15	55.0	3.80	1.60	6.37	4.58	0.05	0.43	371	7.68	22.1	1.1	45.1
080676	3.1	0.2W	50.0	25.0	28	590.0	19.0	18.5	0.31	80.0	4.08	1.78	6.27	1.19	ND	ND	656	6.60	9.7	1.1	70.3
080676	3.2	0.2W	35.0	25.0	15	625.0	16.5	16.0	0.32	80.0	4.10	1.75	4.92	1.19	ND	ND	704	6.60	14.2	2.2	36.9
190776	3.7	0.1W	40.0	20.0	67	560.0	19.5	11.0	0.64	71.0	3.50	1.78	6.47	1.26	ND	ND	1052	6.90	12.2	1.5	44.2
190776	3.2	0.1W	40.0	20.0	58	725.0	20.5	13.5	0.35	80.5	3.00	1.78	7.29	2.11	ND	ND	681	6.90	16.1	3.0	49.5
141076	3.2	0.8	43.5	15.0	43	630.0	18.0	14.5	0.49	63.0	2.38	1.92	8.77	1.47	ND	ND	776	7.20	ND	ND	ND
141076	2.1	0.8	25.5	10.0	19	365.0	11.5	22.0	0.23	39.0	1.30	1.04	5.23	0.45	ND	ND	297	7.20	ND	ND	ND
AVERAGE	3.0	●	36.1	18.2	37	567.1	17.0	17.1	0.36	66.9	3.17	1.66	6.47	1.75	0.05	0.43	648	7.00	14.9	1.8	49.2

MOE 6-11-75 1.9 <0.5 28.0 8.5 20 9.0 3.5 31.0 7.11

● Cannot Average

WATERSHED 4 - CANAGAGIQUE CREEK, WELLINGTON COUNTY

APP. TABLE 15 (cont'd)

	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppb	Mn ppm	Ni ppm	Pb ppm	Se ppm	Zn ppm	Al %	Fe %	C %	C _{org} %	N %	S %	P ppm	pH	CLAY %	ORGANIC MATTER %	CARBONATES %
280575	2.2	0.1W	31.5	7.5	34	550.0	10.3	13.5	0.19	38.5	5.22	1.53	2.45	2.30	0.07	0.46	304	8.08	9.8	1.4	4.4
010676	3.3	0.8	20.0	15.0	12	700.0	16.5	20.0	0.16	70.0	4.70	1.98	4.65	0.81	ND	ND	673	7.50	10.9	1.7	16.6
010676	3.4	0.8	50.0	20.0	18	800.0	20.0	21.0	0.20	90.0	4.88	2.23	4.75	1.08	ND	ND	559	7.70	7.0	1.3	16.4
120776	3.4	0.1W	50.0	15.0	42	755.0	17.5	25.0	0.22	52.0	5.00	2.45	4.59	1.52	ND	ND	482	7.40	6.5	0.9	16.5
120776	2.8	0.1W	35.0	20.0	48	585.0	16.5	20.0	0.15	67.0	4.50	1.78	4.16	0.73	ND	ND	758	7.40	9.7	1.2	16.0
071076	3.5	0.8	47.0	15.0	-	775.0	18.5	19.5	0.28	83.0	3.13	2.38	4.70	1.23	ND	ND	711	7.00	ND	ND	ND
AVERAGE	3.1	*	38.9	15.4	31	694.2	16.6	19.8	0.20	66.8	4.57	2.06	4.22	1.28	0.07	0.47	581	7.50	8.8	1.3	14.0

MOE 2-12-75 2.9 <0.3 15.0 4.5 <20 7.5 1.5 23.0 N.D.

* CANNOT AVERAGE

WATERSHED 5 - HOLIDAY CREEK, OXFORD COUNTY

APP. TABLE 15 (cont'd)

	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppb	Mn ppm	Ni ppm	Pb ppm	Se ppm	Zn ppm	Al %	Fe %	C %	Co _{org} %	N %	S %	P ppm	pH	CLAY %	ORGANIC MATTER %	CARBONATES %
100675	3.6	0.5	45.5	15.0	77	750.0	15.0	25.0	0.50	73.0	5.00	2.03	5.58	3.62	0.33	0.31	733	7.43	15.2	7.0	54.5
030676	4.4	0.8	50.0	20.0	28	770.0	15.0	21.0	0.37	95.0	5.33	2.38	5.80	1.93	ND	ND	ND	7.10	ND	3.2	14.4
030676	3.9	0.1W	25.0	15.0	8	635.0	15.0	12.0	0.18	55.0	3.88	1.70	4.66	1.87	ND	ND	402	7.00	11.3	2.2	10.5
030676	2.6	0.2W	45.0	20.0	42	765.0	16.5	16.0	0.38	85.0	5.08	2.20	4.68	0.44	ND	ND	818	7.00	2.7	0.9	21.9
250876	ND	0.1W	47.5	15.0	-	760.0	12.5	24.0	0.35	92.0	3.05	2.29	3.98	1.26	ND	ND	ND	7.30	12.8	3.0	20.4
051076	4.2	1.0	40.0	13.5	-	645.0	10.5	69.5	0.35	61.0	2.52	1.79	5.12	1.43	ND	ND	645	7.10	9.0	2.6	27.7
051076	4.5	0.8	42.0	12.5	-	605.0	13.5	67.0	0.29	65.0	2.72	1.87	4.81	1.36	ND	ND	724	7.10	4.9	1.2	25.8
AVERAGE	3.9	*	42.1	15.9	39	704.3	14.0	33.5	0.35	75.1	3.94	2.04	5.29	1.70	0.33	0.31	664	7.15	9.3	2.9	25.0

MOE 5-11-75 1.9 <0.3 13.0 7.2 20 8.5 5.0 57.0 7.31

* CANNOT AVERAGE

WATERSHED 10 - TWENTY MILE CREEK, LINCOLN COUNTY

APP. TABLE 15 (cont'd)

	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppb	Mn ppm	Ni ppm	Pb ppm	Se ppm	Zn ppm	Al %	Fe %	C %	C _{org} %	N %	S %	P ppm	pH	CLAY %	ORGANIC MATTER %	CARBONATES %
280575	3.9	0.9	59.0	24.0	40	900.0	27.0	56.0	0.15	700.0	5.64	2.59	3.93	0.14	0.08	0.37	571	7.35	27.0	1.2	26.5
020676	5.6	1.3	30.0	35.0	38	840.0	26.5	62.0	0.13	350.0	5.63	3.48	3.04	0.56	ND	ND	670	7.10	25.4	1.3	25.2
140776	5.0	0.5T	30.0	30.0	33	870.0	18.5	64.0	0.14	325.0	5.60	3.28	3.53	0.63	ND	ND	648	6.90	24.3	1.0	26.8
121076	5.3	1.0	35.0	24.5	48	770.0	31.5	32.0	0.25	230.0	4.02	3.63	2.50	1.21	ND	ND	783	6.80	ND	ND	ND
AVERAGE	5.0	0.9	38.7	28.4	40	845.0	25.9	53.5	0.17	401.3	5.22	3.25	3.25	0.64	0.08	0.37	668	7.05	25.6	1.2	26.2
MOE 25-1-76	1.2	<0.3	12.0	12.0	20		8.0	21.0		110.0								7.90			
23-2-76	4.9	0.4	26.0	20.0	40		19.0	36.0		240.0								6.70			
15-6-76	3.4	0.7	14.0	23.0	20		12.0	< 3.0		50.0								7.10			

WATERSHED 13 - HILLMAN CREEK, ESSEX COUNTY

APP. TABLE 15 (cont'd)

	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppb	Mn ppm	Ni ppm	Pb ppm	Se ppm	Zn ppm	Al %	Fe %	C %	C _{org} %	N %	S %	P ppm	pH	CLAY %	ORGANIC MATTER %	CARBONATES %	
030675	3.2	0.1W	11.0	6.6	25	250.0	7.5	11.5	0.17	29.5	3.75	1.00	1.10	0.47	0.04	0.27	234	7.72	6.0	0.8	3.6	
290376	3.9	0.1W	7.5	9.0	24	287.5	16.5	15.0	0.16	40.5	3.93	1.28	1.85	0.35	0.07	0.18	357	7.30	11.8	2.0	5.3	
290376	4.7	0.1W	12.5	10.0	15	317.0	17.5	14.0	0.18	49.0	4.10	1.25	1.31	0.60	0.16	ND	406	7.30	10.0	1.5	4.3	
290376	8.5	0.1W	65.0	25.0	40	525.0	22.5	24.0	0.35	165.0	4.80	2.03	2.82	1.67	ND	ND	711	7.25	9.2	2.5	5.8	
290376	6.8	0.1W	65.0	25.0	44	500.0	20.0	20.5	0.41	70.0	3.70	1.60	2.73	1.40	ND	ND	612	7.20	6.1	1.6	2.8	
270576	7.4	0.8	15.0	25.0	32	445.0	20.0	27.0	0.26	100.0	4.85	2.15	3.13	1.50	ND	ND	700	7.10	10.2	1.3	21.8	
270776	1.6	0.1W	20.0	20.0	24	555.0	14.5	21.0	0.42	91.5	4.50	2.08	2.75	1.72	ND	ND	739	7.10	4.5	1.2	3.2	
270776	8.1	0.1W	2.5T	10.0	-	285.5	10.5	15.0	0.11	35.0	3.75	1.13	1.26	0.30	ND	ND	279	7.10	1.7	0.2	4.8	
041176	9.7	1.2	43.5	27.5	-	595.0	34.0	26.5	0.70	150.5	3.43	3.13	2.86	1.56	ND	ND	1041	7.30	ND	ND	ND	
AVERAGE	6.0	*	26.9	14.8	29	417.8	18.1	19.4	0.31	81.2	4.09	1.74	2.20	1.06	0.09	0.22	564	7.25	7.4	1.4	6.5	
MOE 4-11-75	2.3	<0.5	<2.5	13.0	20		20.0	5.0		38.0												N.D.
		* CANNOT AVERAGE																				

APPENDIX TABLE 16.

CORRELATION COEFFICIENTS FOR BOTTOM SEDIMENTS

	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn	C	C _{org}	Al	Fe	Mn	P
BOTTOM SEDIMENTS (INDIVIDUAL SAMPLES n = 39)															
CLAY	.19	*	.34	.24	.21	.51	.28	.26	.53	.03	.09	.48	.61	.29	-.38
ORGANIC MATTER	-.12	*	.14	-.10	.38	-.15	-.03	.17	-.10	.36	.49	-.11	-.04	.16	.09
CARBONATES	-.31	*	.12	-.11	.34	-.03	.14	.07	.10	.79	.38	-.19	.05	.24	.09
Al	.34	*	.43	.27	.23	.58	.02	.29	.42	-.23	-.09	-	.72	.45	-.37
Fe	.32	*	.58	.24	.33	.63	.46	.42	.52	.06	-.08	.72	-	.74	-.22
Mn	.17	*	.59	.05	.41	.49	.41	.34	.46	.40	.03	.45	.74	-	.05
BOTTOM SEDIMENTS (AVERAGE SAMPLES n = 6)															
CLAY	-.36	*	.56	.96	.77	.79	.60	.27	.76	-.15	-.51	.63	.88	.69	-.27
ORGANIC MATTER	.67	*	-.03	-.44	.08	-.53	.01	.04	-.38	.59	.72	-.54	-.40	-.04	.98
CARBONATES	.14	*	-.07	.01	.23	-.24	.06	-.09	.06	.85	.50	-.56	-.18	.11	-.26
Al	-.32	*	.61	.77	.49	.80	.47	.24	.56	-.67	-.74	-	.90	.64	-.29
Fe	-.42	*	.62	.92	.71	.80	.71	.21	.77	-.43	-.68	.90	-	.81	-.20
Mn	.03	•	.58	.66	.65	.43	.72	-.02	.63	.06	-.31	.64	.81	-	.99

r = .26 significant at .1
r = .30 significant at .05
r = .39 significant at .01
r = .49 significant at .001

r = .62 significant at .1
r = .71 significant at .05
r = .83 significant at .01
r = .93 significant at .001

APPENDIX TABLE 17.

DTPA EXTRACTABLE METAL CONCENTRATIONS (ppm)
IN BOTTOM SEDIMENTS

	Gd	Cu	Ni	Pb	Zn
WATERSHED 1					
290376	0.20	2.02	0.78	1.27	1.27
250576	0.26	2.10	0.79	1.47	1.02
250576	0.26	3.23	0.99	2.03	1.41
151176	0.20	4.15	0.52	1.49	2.17
AVERAGE	0.23	2.88	0.77	1.57	1.47
WATERSHED 3					
080676	0.13	2.07	0.52	1.18	2.11
080676	0.09	1.85	0.32	0.89	1.21
190776	0.11	2.70	0.45	1.59	2.26
190776	0.11	1.64	0.45	1.10	3.28
141076	0.06	3.87	0.37	1.75	3.60
141076	0.04	1.14	0.41	0.29	1.32
AVERAGE	0.09	2.21	0.42	1.13	2.30

DTPA EXTRACTABLE METAL CONCENTRATIONS (ppm)
IN BOTTOM SEDIMENTS

	Cd	Cu	Ni	Pb	Zn
WATERSHED 4					
280575	0.06	0.68	0.20	0.75	0.48
010676	0.06	0.56	0.13	0.87	0.18
010676	0.07	1.33	0.30	1.61	0.56
120776	0.05	0.81	0.30	0.62	0.56
120776	0.07	1.62	0.36	1.17	1.05
071076	0.05	1.63	0.08	0.81	1.36
AVERAGE	0.06	1.11	0.23	0.97	0.70
WATERSHED 5					
030675	0.14	3.25	0.52	6.79	3.23
030675	0.04	0.43	0.17	0.52	0.93
030676	0.14	2.66	0.51	2.31	2.80
250876	0.05	1.30	0.08	1.40	2.21
051076	0.11	0.81	0.22	0.70	2.49
AVERAGE	0.10	1.69	0.30	2.34	2.33

DTPA EXTRACTABLE METAL CONCENTRATIONS (ppm)
IN BOTTOM SEDIMENTS

	Cd	Cu	Ni	Pb	Zn
WATERSHED 10					
020676	0.11	4.31	0.37	17.11	12.96
140776	0.18	6.54	0.48	18.04	18.10
121076	0.21	7.41	0.62	9.37	13.20
AVERAGE	0.17	6.09	0.49	14.84	14.75
WATERSHED 13					
290376	0.06	0.45	0.13	0.53	0.98
290376	0.09	0.74	0.18	0.93	0.92
290376	0.19	3.01	0.63	2.14	2.70
290376	0.18	1.96	0.69	2.48	22.49
270576	0.16	1.41	0.27	1.76	2.37
130676	0.12	1.95	0.34	2.10	2.07
270776	0.05	0.45	0.20	0.63	0.74
270776	0.32	6.86	1.31	3.24	3.01
270776	0.25	2.93	0.36	2.17	3.47
041176	0.12	5.49	0.20	3.12	6.70
AVERAGE	0.15	2.53	0.43	2.34	4.55

APPENDIX TABLE 18.

CORRELATION COEFFICIENTS FOR DTPA EXTRACTIONS OF BOTTOM SEDIMENTS

	Cu	Ni	Pb	Zn
Clay	.08	.18	.41	.33
Organic Matter	-.31	-.19	-.12	-.14
Al (total)	.10	.32	.36	.19
pH	.61	.28	.57	.42
Cu (total)	-.18			
Ni (total)		.25		
Pb (total)			-.03	
Zn (total)				-.27

$r = .33$ significant at .05

$r = .42$ significant at .01

APPENDIX TABLE 19

ANALYSIS OF BOTTOM SEDIMENTS USED FOR THE EXTRACTION OF HUMIC ACIDS AND FULVIC ACIDS

	TOTAL C	ORGANIC C	TOTAL N	TOTAL S	pH	C/N RATIO	TOTAL ORGANIC MATTER	HUMIC ACID	FULVIC ACID	HA+FA YIELD %	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Zn
	g/kg SEDIMENT						g/kg				mg/g SEDIMENT		µg/g SEDIMENT						
AG 1	23.5	3.7	0.8	3.3	7.1	4.6	6.3	0.9	1.9	44.4	58.8	10.4	1.5	26.0	25.5	650.0	39.5	20.0	95.0
AG 3	57.7	3.7	0.5	4.3	6.6	7.4	6.3	2.8	1.8	73.0	40.8	17.8	0.1W	50.0	25.0	590.0	19.0	18.5	80.0
AG 4	47.5	2.8	0.7	4.6	7.6	4.0	4.8	1.4	1.4	58.3	42.8	22.3	0.1W	50.0	20.0	800.0	20.0	21.0	90.0
AG 5	47.0	5.8	3.3	3.1	7.1	1.8	9.9	2.5	2.2	47.5	46.0	20.4	0.1W	37.5	17.5	702.0	15.0	16.5	75.0
AG 10	33.4	2.4	0.8	3.7	7.1	3.0	4.1	1.2	1.0	53.7	56.3	34.8	0.1W	30.0	35.0	840.0	26.5	62.0	350.0
AG 13	18.5	3.5	0.7	1.8	7.1	5.0	6.0	2.9	1.8	78.3	44.8	14.8	0.1W	10.0	15.0	350.0	16.5	16.5	55.0

APPENDIX TABLE 20

ULTIMATE ANALYSIS, FUNCTIONAL GROUP ANALYSIS AND TOTAL METAL CONCENTRATIONS OF HUMIC ACIDS (HA) EXTRACTED FROM BOTTOM SEDIMENTS

	YIELD g/kg SEDIMENT	C %	H %	N %	S %	O %	ASH %	E4/E6	TOTAL ACIDITY	TOTAL CARBOXYL	PHENOLIC OH	Al	Fe	Cd	Cr	Cu	Ni	Pb	Zn
									meq /g HA			mg/g HA		µg/g HA					
AG 1	0.9	52.5	6.8	4.1	0.5	36.1	6.3	3.8	7.8	4.4	3.4	55.4	9.0	1.8	22.8	384.2	58.8	18.0	96.0
AG 3	2.8	55.8	6.7	5.5	1.9	29.8	2.3	3.8	7.2	2.8	4.4	32.4	21.5	0.1W	88.4	132.2	35.6	7.6	49.3
AG 4	1.4	55.1	6.7	5.6	1.9	30.6	4.1	4.3	6.6	2.8	3.8	39.3	25.1	0.1W	42.3	150.2	22.7	27.0	63.8
AG 5	2.5	55.7	6.3	4.9	1.8	31.1	1.8	3.8	7.2	2.8	4.4	27.0	16.7	0.1W	54.2	171.0	33.8	91.9	72.1
AG 10	1.2	56.3	7.1	6.0	6.2	24.2	1.5	3.5	5.0	2.0	3.0	40.0	13.2	0.7	27.5	1048.8	81.2	248.3	165.7
AG 13	2.9	56.8	6.3	6.3	1.8	28.6	1.8	3.7	8.0	4.2	3.8	15.0	3.2	1.3	45.4	233.5	45.5	18.8	354.5
AVERAGE SEDIMENT HA		56.0	6.7	5.7	2.7	28.9	2.3	3.8	6.8	2.9	3.9	34.9	14.8	0.6	46.8	353.3	46.3	68.6	133.6
IDEAL MEAN HA*		56.2	4.7	3.2	0.8	35.5		4.8	6.7	3.6	3.9								

* from Schnitzer (1977)

APPENDIX TABLE 21

ULTIMATE ANALYSIS, FUNCTIONAL GROUP ANALYSIS AND TOTAL METAL CONCENTRATIONS OF FULVIC ACIDS (FA) EXTRACTED FROM BOTTOM SEDIMENTS

	YIELD g/kg SEDIMENT	C %	H %	N %	S %	O %	ASH %	E4/E6	TOTAL ACIDITY	TOTAL CARBOXYL	PHENOLIC OH	Al	Fe	Cd	Cr	Cu	Ni	Pb	Zn
									meq /g FA			mg/g FA		µg/g FA					
AG 1	1.9	37.4	5.1	4.5	1.5	51.5	41.8	4.17	11.9	4.7	7.2	*	*	3.0	37.0	1034.8	*	47.0	1169.6
AG 3	1.8	38.2	6.7	4.5	0.9	49.7	12.6	4.46	8.3	2.7	5.6	8.4	4.7	2.0	31.5	1365.0	81.0	117.5	250.0
AG 4	1.4	37.9	6.1	4.3	0.9	50.8	13.3	4.59	7.4	2.0	5.4	8.4	2.4	2.0	37.0	1700.0	135.0	155.0	1400.0
AG 5	2.2	39.2	5.7	4.3	1.1	49.7	7.6	4.87	6.9	2.3	4.6	2.7	7.7	2.5	25.5	1500.0	90.0	235.0	1050.0
AG 10	1.0	38.5	6.4	4.8	2.9	47.4	18.7	3.39	9.2	2.5	6.7	22.6	0.4	5.7	18.2	1482.3	142.5	980.6	416.2
AG 13	1.8	39.8	6.4	4.2	1.1	48.5	30.7	4.84	8.8	2.8	6.0	*	*	3.7	17.9	684.2	*	36.8	678.9
AVERAGE SEDIMENT FA		38.7	6.3	4.4	1.3	49.6	20.8	4.4	8.1	2.5	5.6	10.5	3.8	3.1	27.8	1294.4	112.1	262.0	827.5
IDEAL FA*		45.7	5.4	2.1	1.9	44.8		9.6	10.3	8.2	3.0								

* From Schnitzer (1977)

FORMS OF COPPER IN BOTTOM SEDIMENTS

APPENDIX TABLE 22

	TOTAL ppm	WATER SOLUBLE %	EXCHANGEABLE %	CARBONATE BOUND %	MANGANESE OXIDE BOUND %	ORGANICALLY BOUND %	IRON OXIDE BOUND %	CRYSTALLINE %	RECOVERED %
AG-1	35.0	-	0.6	8.6	17.2	10.8	25.8	36.9	116
AG-3	25.0	-	1.5	6.6	2.2	8.3	37.4	44.0	91
AG-4	11.5	-	2.0	19.9	23.9	27.9	-	26.3	109
AG-5	11.0	-	1.7	6.4	19.2	21.4	-	51.3	106
AG-10	35.0	-	0.7	14.0	7.6	2.3	23.4	24.6	122
AG-13	19.5	-	1.3	7.8	20.8	22.1	24.7	23.4	99

APP. TABLE 22 (cont'd)

FORMS OF LEAD IN BOTTOM SEDIMENTS

	TOTAL ppm	WATER SOLUBLE %	EXCHANGEABLE %	CARBONATE BOUND %	MANGANESE OXIDE BOUND %	ORGANICALLY BOUND %	IRON OXIDE BOUND %	CRYSTALLINE %	RECOVERED %
AG-1	26.5	-	0.7	26.7	21.0	3.8	-	47.7	98
AG-3	14.0	-	1.9	11.1	22.2	4.1	-	60.7	96
AG-4	19.5	-	1.3	20.1	21.5	4.5	-	52.6	96
AG-5	12.0	-	2.4	23.8	19.1	7.1	-	47.6	88
AG-10	52.5	-	1.0	39.4	24.7	0.7	-	35.2	101
AG-13	19.0	-	1.5	10.2	38.3	9.0	-	40.9	103

APP. TABLE 22 (cont'd)

FORMS OF NICKEL IN BOTTOM SEDIMENTS

	TOTAL ppm	WATER SOLUBLE %	EXCHANGEABLE %	CARBONATE BOUND %	MANGANESE OXIDE BOUND %	ORGANICALLY BOUND %	IRON OXIDE BOUND %	CRYSTALLINE %	RECOVERED %
AG-1	45.5	-	-	6.5	-	14.7	21.0	57.9	110
AG-3	20.5	-	-	2.8	-	-	28.0	69.2	130
AG-4	13.0	-	1.6	6.0	-	32.8	-	59.6	97
AG-5	14.5	-	-	-	-	13.4	-	86.6	84
AG-10	26.0	-	0.8	4.2	-	1.3	25.1	68.6	115
AG-13	21.0	-	1.1	-	-	23.4	32.4	43.2	90

APP. TABLE 22 (cont'd)

FORMS OF ZINC IN BOTTOM SEDIMENTS

	TOTAL ppm	WATER SOLUBLE %	EXCHANGEABLE %	CARBONATE BOUND %	MANGANESE OXIDE BOUND %	ORGANICALLY BOUND %	IRON OXIDE BOUND %	CRYSTALLINE %	RECOVERED %
AG-1	112.0	0.1	0.3	5.6	10.5	10.8	19.3	53.4	115
AG-3	65.0	0.3	0.4	10.3	5.6	1.6	14.1	67.6	122
AG-4	47.0	0.2	0.7	6.9	9.2	18.3	12.0	52.7	93
AG-5	44.5	0.2	0.7	9.9	10.5	15.8	6.6	56.3	102
AG-10	225.0	0.1	0.1	11.2	20.0	15.3	34.3	19.0	122
AG-13	72.0	0.2	0.7	16.8	14.4	23.0	14.4	45.6	87

APPENDIX TABLE 23

The fate of Cadmium added to soils and sediments from Big Creek and Canagagigue Creek Watersheds. Soils and sediments were incubated for 10 weeks. Control values are for soils and sediments incubated with no cadmium added. Single additions are only 5 ppm Cd and combination additions are also 100 ppm Cu, 100 ppm Pb, 100 ppm Ni and 250 ppm Zn. Incubated values (ppm) are after subtraction of control values and percentages (%) are of added cadmium.

	WATER SOLUBLE		EXCHANGEABLE		CARBONATE BOUND		MANGANESE OXIDE BOUND		ORGANICALLY BOUND		IRON OXIDE BOUND		CRYSTALLINE	
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
<u>BIG CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	0.1	20.0	0.2	40.0	-	-	-	-	-	-	0.2	40.0
SINGLE ADDITION	-	-	4.3	84.3	0.8	15.7	-	-	-	-	-	-	-	-
COMBINATION ADDITION	0.6	12.2	3.2	65.3	1.1	22.4	-	-	-	-	-	-	-	-
<u>BIG CREEK WATERSHED - SEDIMENT</u>														
CONTROL	-	-	0.1	16.7	0.3	50.0	-	-	-	-	-	-	0.2	33.3
SINGLE ADDITION	-	-	3.0	57.7	2.2	42.3	-	-	-	-	-	-	-	-
COMBINATION ADDITION	-	-	1.5	29.4	3.6	70.6	-	-	-	-	-	-	-	-
<u>CANAGAGIGUE CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	-	-	0.1	25.0	-	-	-	-	-	-	0.3	75.0
SINGLE ADDITION	-	-	2.4	45.3	2.9	54.7	-	-	-	-	-	-	-	-
COMBINATION ADDITION	0.1	2.0	2.5	49.0	2.5	49.0	-	-	-	-	-	-	-	-
<u>CANAGAGIGUE CREEK WATERSHED - SEDIMENT</u>														
CONTROL	-	-	-	-	-	-	-	-	-	-	-	-	0.3	100.0
SINGLE ADDITION	-	-	2.7	50.9	2.6	49.1	-	-	-	-	-	-	-	-
COMBINATION ADDITION	0.1	1.9	2.4	45.3	2.8	52.8	-	-	-	-	-	-	-	-

APP. TABLE 23 (cont'd)

The fate of Copper added to soils and sediments from Fig Creek and Canagagigue Creek Watersheds. Soils and sediments were incubated for 10 weeks. Control values are for soils and sediments incubated with no copper added. Single additions are only 100 ppm Cu and combination additions are also 100 ppm Ni, 100 ppm Pb, 5 ppm Cd and 250 ppm Zn. Incubated values (ppm) are after subtraction of control values and percentages (%) are of added copper.

	WATER SOLUBLE		EXCHANGEABLE		CARBONATE BOUND		MANGANESE OXIDE BOUND		ORGANICALLY BOUND		IRON OXIDE BOUND		CRYSTALLINE	
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
<u>BIG CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	0.2	0.7	-	-	5.2	21.4	3.0	12.8	7.7	32.0	8.0	33.0
SINGLE ADDITION	0.1	0.1	0.6	0.6	39.3	40.5	12.8	13.2	26.0	26.8	13.4	13.8	4.9	5.0
COMBINATION ADDITION	0.1	0.1	1.8	1.8	39.8	39.8	15.8	15.8	34.9	34.9	4.2	4.2	3.3	3.3
<u>BIG CREEK WATERSHED - SEDIMENT</u>														
CONTROL	-	-	0.2	0.8	3.3	11.1	5.0	16.5	4.1	15.2	9.3	30.8	7.7	25.3
SINGLE ADDITION	-	-	0.5	0.5	79.2	78.7	0.7	0.7	6.7	6.7	6.1	6.1	7.4	7.4
COMBINATION ADDITION	-	-	-	-	58.0	57.6	2.0	2.0	22.5	22.3	8.7	8.7	9.5	9.5
<u>CANAGAGIGUE CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	0.1	0.6	-	-	3.8	17.4	2.1	9.6	7.2	33.1	8.5	39.2
SINGLE ADDITION	-	-	0.5	0.5	36.9	36.9	12.1	12.1	41.4	41.4	2.7	2.7	6.5	6.5
COMBINATION ADDITION	-	-	0.2	0.2	20.8	20.6	7.4	7.4	57.0	56.4	12.5	12.3	3.1	3.1
<u>CANAGAGIGUE CREEK WATERSHED - SEDIMENT</u>														
CONTROL	-	-	0.2	1.8	1.8	16.9	2.4	22.7	2.4	22.7	-	-	3.9	35.9
SINGLE ADDITION	-	-	0.6	0.6	70.8	69.8	-	-	7.8	7.6	19.6	19.2	3.5	3.4
COMBINATION ADDITION	0.3	0.3	0.5	0.5	56.9	55.5	-	-	20.9	20.4	15.1	14.7	8.9	8.7

APP. TABLE 23 (cont'd)

The fate of Copper added to soils and sediments from Big Creek and Canagagigue Creek Watersheds. Soils and sediments were incubated for 10 weeks. Control values are for soils and sediments incubated with no copper added. Single additions are only 250 ppm Cu and combination additions are also 250 ppm Ni, 250 ppm Pb, 5 ppm Cd and 250 ppm Zn. Incubated values (ppm) are after subtraction of control values and percentages (%) are of added copper.

	WATER SOLUBLE		EXCHANGEABLE		CARBONATE BOUND		MANGANESE OXIDE BOUND		ORGANICALLY BOUND		IRON OXIDE BOUND		CRYSTALLINE	
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
<u>BIG CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	0.2	0.7	-	-	5.2	21.4	3.0	12.8	7.7	32.0	8.0	33.0
SINGLE ADDITION	0.7	0.3	1.4	0.6	99.9	40.1	40.8	16.4	56.9	22.8	35.0	14.0	14.7	5.9
MULTIPLE ADDITION	4.5	1.8	10.9	4.4	102.4	41.1	42.1	16.9	69.4	27.9	13.5	5.4	6.2	2.5
<u>BIG CREEK WATERSHED - SEDIMENT</u>														
CONTROL	-	-	0.2	0.8	3.3	11.1	5.0	16.5	4.1	15.2	9.3	30.8	7.7	25.3
SINGLE ADDITION	0.6	0.2	0.7	0.3	185.9	74.4	5.3	2.1	32.4	13.0	14.8	5.9	10.2	4.1
MULTIPLE ADDITION	0.2	0.1	0.4	0.2	169.6	67.7	13.4	5.3	39.4	15.7	18.3	7.3	9.4	3.7
<u>CANAGAGIGUE CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	0.1	0.6	-	-	3.8	17.4	2.1	9.6	7.2	33.1	8.5	39.2
SINGLE ADDITION	-	-	0.7	0.3	97.0	38.7	63.8	25.5	65.9	26.3	23.2	9.3	-	-
MULTIPLE ADDITION	1.2	0.5	1.1	0.4	135.4	54.3	27.2	10.9	64.9	26.0	10.0	4.0	9.5	3.8
<u>CANAGAGIGUE CREEK WATERSHED - SEDIMENT</u>														
CONTROL	-	-	0.2	1.8	1.8	16.9	2.4	22.7	2.4	22.7	-	-	3.9	35.9
SINGLE ADDITION	-	-	1.2	0.5	206.6	82.1	-	-	10.8	4.3	29.5	11.7	3.5	1.4
MULTIPLE ADDITION	-	-	1.6	0.6	114.0	45.4	23.2	9.2	81.1	32.3	25.7	10.2	5.5	2.2

APP. TABLE 23 (cont'd)

The fate of Lead, added to soils and sediments from Big Creek and Canagagigue Creek Watersheds. Soils and sediments were incubated for 10 weeks. Control values are for soils and sediments incubated with no lead added. Single additions are only 100 ppm Pb and combination additions are 100 ppm lead plus 100 ppm Ni, 100 ppm Cu, 5 ppm Cd and 250 ppm Zn. Incubated values (ppm) are after subtraction of control values, and percentages (%) are of added lead.

	WATER SOLUBLE		EXCHANGEABLE		CARBONATE BOUND		MANGANESE OXIDE BOUND		ORGANICALLY BOUND		IRON OXIDE BOUND		CRYSTALLINE	
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
<u>BIG CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	0.4	1.4	-	-	12.4	41.2	3.0	10.0	6.0	20.0	8.3	27.5
SINGLE ADDITION	0.3	0.3	-	-	8.6	8.5	0.7	0.7	49.4	48.7	42.4	41.8	-	-
COMBINATION ADDITION	0.1	0.1	6.9	6.8	13.0	12.8	17.6	17.3	56.2	55.3	-	-	7.9	7.8
<u>BIG CREEK WATERSHED - SEDIMENT</u>														
CONTROL	-	-	0.6	2.5	6.4	27.2	7.0	30.0	1.5	6.6	-	-	7.9	33.8
SINGLE ADDITION	-	-	-	-	36.1	43.1	-	-	11.7	14.0	36.0	43.0	-	-
COMBINATION ADDITION	0.1	0.1	0.7	0.7	45.8	47.9	3.4	3.6	29.3	30.6	2.2	2.3	14.2	14.8
<u>CANAGAGIGUE CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	-	-	-	-	10.3	33.8	3.1	10.2	4.3	14.2	12.8	41.8
SINGLE ADDITION	-	-	0.1	0.1	11.1	10.6	-	-	44.9	42.8	48.9	46.6	-	-
COMBINATION ADDITION	0.1	0.1	1.3	1.1	13.5	11.7	6.4	5.6	81.8	71.0	6.2	5.4	6.0	5.2
<u>CANAGAGIGUE CREEK WATERSHED- SEDIMENT</u>														
CONTROL	-	-	0.3	2.1	3.7	21.0	3.3	18.6	1.2	7.0	-	-	9.3	51.3
SINGLE ADDITION	0.3	0.5	-	-	0.7	1.1	-	-	5.8	9.4	44.1	71.2	11.0	17.8
COMBINATION ADDITION	0.4	0.4	1.9	1.9	49.7	50.1	1.2	1.2	24.3	24.5	-	-	21.7	21.9

APP. TABLE 23 (cont'd)

The fate of Lead added to soils and sediments from Big Creek and Canagagigue Creek Watersheds. Soils and sediments were incubated for 10 weeks. Control values are for soils and sediments incubated with no lead added. Single additions are only 250 ppm Pb and combination additions are also 250 ppm Ni, 250 ppm Cu, 5 ppm Cd and 250 ppm Zn. Incubated values (ppm) are after subtraction of control values and percentages (%) are of added lead.

	WATER SOLUBLE		EXCHANGEABLE		CARBONATE BOUND		MANGANESE OXIDE BOUND		ORGANICALLY BOUND		IRON OXIDE BOUND		CRYSTALLINE	
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
<u>BIG CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	0.4	1.4	-	-	12.4	41.2	3.0	10.0	6.0	20.0	8.3	27.5
SINGLE ADDITION	-	-	1.0	0.4	22.3	8.8	49.4	19.6	92.3	36.5	87.6	34.7	-	-
COMBINATION ADDITION	1.2	0.5	60.3	23.9	31.5	12.5	51.6	20.4	103.8	41.1	4.0	1.6	-	-
<u>BIG CREEK WATERSHED - SEDIMENT</u>														
CONTROL	-	-	0.6	2.5	6.4	27.2	7.0	30.0	1.5	6.6	-	-	7.9	33.8
SINGLE ADDITION	-	-	-	-	112.8	45.1	-	-	42.0	16.8	89.4	35.8	5.8	2.3
COMBINATION ADDITION	0.4	0.2	1.3	0.5	167.6	66.8	23.5	9.4	50.1	20.0	8.1	3.2	-	-
<u>CANAGAGIGUE CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	-	-	-	-	10.3	33.8	3.1	10.2	4.3	14.2	12.8	41.8
SINGLE ADDITION	-	-	0.3	0.1	32.2	12.8	27.9	11.1	100.0	39.8	90.8	36.1	-	-
COMBINATION ADDITION	0.8	0.3	3.6	1.4	111.8	44.7	32.6	13.0	92.0	36.8	5.6	2.2	3.8	1.5
<u>CANAGAGIGUE CREEK WATERSHED - SEDIMENT</u>														
CONTROL	-	-	0.3	2.1	3.7	21.0	3.3	18.6	1.2	7.0	-	-	9.3	51.3
SINGLE ADDITION	1.7	0.7	0.4	0.2	128.8	50.4	6.1	2.4	19.1	7.5	96.5	37.7	3.2	1.3
COMBINATION ADDITION	-	-	2.8	1.1	84.7	33.9	30.1	12.0	109.5	43.8	14.0	5.6	8.9	3.6

APP. TABLE 23 (cont'd)

The fate of Nickel added to soils and sediments from Big Creek and Canagagigue Creek Watersheds. Soils and sediments were incubated for 10 weeks. Control values are for soils and sediments incubated with no nickel added. Single additions are only 100 ppm Ni and combination additions are also 100 ppm Cu, 100 ppm Pb, 5 ppm Cd and 250 ppm Zn. Incubated values (ppm) are after subtraction of control values and percentages (%) are of added nickel.

	WATER SOLUBLE		EXCHANGEABLE		CARBONATE BOUND		MANGANESE OXIDE BOUND		ORGANICALLY BOUND		IRON OXIDE BOUND		CRYSTALLINE	
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
<u>BIG CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	-	-	0.3	1.6	-	-	3.4	16.8	4.9	24.7	11.4	56.9
SINGLE ADDITION	0.4	0.4	13.7	13.7	27.9	27.9	11.3	11.3	30.2	30.2	6.7	6.7	10.0	10.0
MULTIPLE ADDITION	7.2	7.2	29.6	29.6	35.1	35.1	11.0	11.0	9.8	9.8	2.3	2.3	4.9	4.9
<u>BIG CREEK WATERSHED - SEDIMENT</u>														
CONTROL	-	-	0.5	1.3	2.5	6.5	0.5	1.2	7.2	18.5	8.8	22.6	19.4	50.1
SINGLE ADDITION	-	-	0.3	0.3	39.4	39.4	6.9	6.9	37.9	37.9	12.6	12.6	2.8	2.8
MULTIPLE ADDITION	-	-	1.4	1.4	45.9	45.9	13.7	13.7	17.2	17.2	8.8	12.6	12.8	2.8
<u>CANAGAGIGUE CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	-	-	-	-	-	-	2.6	10.8	7.2	30.2	14.0	58.8
SINGLE ADDITION	-	-	1.1	1.1	21.0	21.0	12.6	12.6	63.1	63.1	5.4	5.4	-	-
MULTIPLE ADDITION	0.2	0.2	3.0	3.0	37.9	37.9	23.5	23.5	28.7	28.7	2.6	2.6	4.2	4.2
<u>CANAGAGIGUE CREEK WATERSHED - SEDIMENT</u>														
CONTROL	-	-	0.2	1.5	-	-	-	-	3.5	25.9	-	-	9.8	72.6
SINGLE ADDITION	0.8	0.8	4.7	4.7	29.5	29.5	4.5	4.5	10.7	10.7	48.7	48.7	1.2	1.2
MULTIPLE ADDITION	2.0	2.0	6.6	6.6	52.9	52.9	10.4	10.4	8.4	8.4	9.9	9.9	9.7	9.7

APP. TABLE 23 (cont'd)

The fate of Nickel added to soils and sediments from Big Creek and Canagagigue Creek Watersheds. Soils and sediments were incubated for 10 weeks. Control values are for soils and sediments incubated with no nickel added. Single additions are only 250 ppm Ni and combination additions are also 250 ppm Cu, 250 ppm Pb, 5 ppm Cd and 250 ppm Zn. Incubated values (ppm) are after subtraction of control values and percentages (%) are of added nickel.

	WATER SOLUBLE		EXCHANGEABLE		CARBONATE BOUND		MANGANESE OXIDE BOUND		ORGANICALLY BOUND		IRON OXIDE BOUND		CRYSTALLINE	
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
<u>BIG CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	-	-	0.3	1.6	-	-	3.4	16.8	4.9	24.7	11.4	56.9
SINGLE ADDITION	4.6	2.1	46.4	20.8	50.5	22.6	27.8	12.5	63.6	28.5	16.2	7.3	14.0	6.3
COMBINATION ADDITION	43.2	17.2	88.6	35.3	66.9	26.7	19.2	7.7	18.2	7.2	4.8	1.9	9.9	3.9
<u>BIG CREEK WATERSHED - SEDIMENT</u>														
CONTROL	-	-	0.5	1.3	2.5	6.5	0.5	1.2	7.2	18.5	8.8	22.6	19.4	50.1
SINGLE ADDITION	-	-	1.8	0.7	66.8	26.7	13.4	5.4	139.5	55.8	23.8	9.5	4.9	2.0
COMBINATION ADDITION	2.3	0.9	13.7	5.5	123.1	49.3	27.2	10.9	55.2	22.1	18.6	7.5	9.5	3.8
<u>CANAGAGIGUE CREEK WATERSHED - SOIL</u>														
CONTROL	-	-	-	-	-	-	-	-	2.6	10.8	7.2	30.2	14.0	58.8
SINGLE ADDITION	0.3	0.1	4.4	1.8	45.5	18.2	28.7	11.5	145.3	58.1	25.9	10.3	0.2	0.1
MULTIPLE ADDITION	7.1	2.8	34.8	13.9	120.2	47.9	37.8	15.1	40.7	16.2	9.2	3.7	1.1	0.4
<u>CANAGAGIGUE CREEK WATERSHED - SEDIMENT</u>														
CONTROL	-	-	0.2	1.5	-	-	-	-	3.5	25.9	-	-	9.8	72.6
SINGLE ADDITION	1.1	0.4	19.8	7.9	63.8	25.4	24.0	9.5	27.1	10.8	115.7	46.0	-	-
MULTIPLE ADDITION	5.8	2.3	26.2	10.5	101.2	40.4	36.1	14.4	52.6	21.0	19.8	7.9	8.6	3.4

APP. TABLE 23 (cont'd)

The fate of Zinc added to soils and sediments from Big Creek and Canagagigue Creek Watersheds. Soils and sediments were incubated for 10 weeks. Control values are for soils and sediments incubated with no zinc added. Single additions are only 250 ppm Zn and combination additions are also 250 ppm Cu, 250 ppm Ni, 250 ppm Pb and 5 ppm Cd. Incubated values (ppm) are after subtraction of control values and percentages (%) are of added zinc.

	WATER SOLUBLE		EXCHANGEABLE		CARBONATE BOUND		MANGANESE OXIDE BOUND		ORGANICALLY BOUND		IRON OXIDE BOUND		CRYSTALLINE	
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
<u>BIG CREEK WATERSHED - SOIL</u>														
CONTROL	0.1	0.1	0.2	0.4	5.2	8.4	5.2	8.4	7.0	11.2	13.0	21.0	31.5	50.2
SINGLE ADDITION	1.1	0.4	33.4	13.4	117.8	47.1	18.0	7.2	7.0	2.8	61.5	24.6	11.0	4.4
COMBINATION ADDITION	23.6	9.4	46.5	18.6	69.6	27.8	13.0	5.2	39.9	16.0	24.9	10.0	32.2	12.9
<u>BIG CREEK WATERSHED - SEDIMENT</u>														
CONTROL	0.1	0.1	0.4	0.4	5.5	5.8	9.8	10.3	14.9	15.6	20.0	21.0	44.7	46.9
SINGLE ADDITION	-	-	0.6	0.2	161.5	61.9	8.0	3.1	4.8	1.8	82.5	31.6	3.7	1.4
COMBINATION ADDITION	0.6	0.3	0.4	0.2	119.0	52.1	20.2	8.8	42.6	18.7	30.2	13.2	15.3	6.7
<u>CANAGAGIGUE CREEK WATERSHED - SOIL</u>														
CONTROL	0.1	0.1	0.3	0.3	3.5	3.8	6.1	6.6	6.3	6.8	14.9	16.0	62.0	66.6
SINGLE ADDITION	1.3	0.5	3.8	1.4	180.3	64.2	35.9	12.8	5.9	2.1	53.6	19.1	-	-
COMBINATION ADDITION	2.4	1.0	5.6	2.2	121.0	48.3	33.6	13.4	61.7	24.6	20.2	8.0	6.5	2.6
<u>CANAGAGIGUE CREEK WATERSHED - SEDIMENT</u>														
CONTROL	0.1	0.4	0.2	0.7	2.5	7.0	2.8	7.7	5.8	16.1	5.0	13.8	19.5	54.4
SINGLE ADDITION	1.0	0.4	6.5	2.5	197.8	75.7	3.4	1.3	-	-	52.5	20.0	-	-
COMBINATION ADDITION	2.4	1.0	5.4	2.1	118.0	47.1	20.4	8.1	29.3	11.7	31.3	12.0	43.7	17.5

CONCENTRATION OF TOTAL METALS AND NUTRIENTS IN STREAMWATER COLLECTED FROM AGRICULTURAL WATERSHEDS.
 RESULTS ARE BASED ON DRIED MATERIAL. THE PARTICULATE FRACTION WAS THAT SAMPLE >.45u AND THE DISSOLVED <.45u.

APPENDIX TABLE 24

YIELD mg/l	ASH %	TOTAL C %	ORGANIC C %	INORG. C %	TOTAL N %	TOTAL S %	Al %	Fe %	Cd %	Cr	Cu	Mn	Ni	Pb	Se	Zn	←-----μg/g-----→									
																	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn		
TOTAL																										
290376-1	493.5	65.1	4.2	0.5	3.7	0.6	3.9	1.8	6.2	3.5	12.5	120.0	60.0	97.0	7.5	2.87	45.0									
250576-1	421.4	75.4	3.7	1.3	2.4	0.3	9.9	0.2	8.8	0.5	16.5	51.9	26.9	36.4	16.5	1.41	27.9									
260776-1	514.3	70.8	5.3	2.5	2.8	0.4	5.0	1.7	0.8	0.1W	30.0	107.0	286.0	74.0	13.5	1.10	49.5									
051176-1	856.6	76.4	2.4	1.2	1.2	0.2	7.5	0.3	0.2	0.3T	13.0	118.0	32.0	77.0	11.5	0.50	16.5									
DISSOLVED																										
290376-1	428.5	61.3	3.4	0.5	2.9	0.5	5.8	0.1	<0.1	0.8	11.0	105.0	5.0	82.5	2.5	3.20	10.0									
250576-1	426.8	69.0	3.5	1.6	1.9	0.1	8.5	<0.1	<0.1	0.1W	17.8	149.1	7.9	59.2	15.3	1.48	19.3									
260776-1	448.7	59.7	5.1	2.3	2.8	0.4	5.9	0.1	<0.1	0.1W	5.0	207.0	14.0	50.0	9.0	1.20	14.5									
051176-1	789.8	73.9	2.6	1.2	1.4	0.3	7.2	<0.1	<0.1	0.1W	14.5	125.0	8.0	52.0	11.5	0.45	12.0									
PARTICULATE																										
290376-1	76.2	87.9	3.1	1.6	1.5	0.2	0.3	-	-	6.3	31.7	90.4	425.0	56.1	54.3	0.88	289.3									
250576-1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-									
260776-1	10.7	94.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-									
051176-1	70.0	80.4	4.64	-	-	0.27	2.10	-	-	1.1	-	55.0	811.6	47.7	130.8	-	146.2									

APP. TABLE 24 (cont'd)

	YIELD mg/l	ASH %	TOTAL C %	ORGANIC C %	INORG. C %	TOTAL N %	TOTAL S %	Al %	Fe %	←-----μg/g-----→							
										Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
TOTAL																	
050476-3	169.2	55.2	6.6	0.6	6.0	1.0	2.2	-	-	1.9	20.0	405.0	34.3	-	10.3	0.21	47.0
250476-3 E	627.4	72.2	5.1	1.7	3.4	1.6	1.0	6.1	2.6	1.8	58.3	40.1	510.2	51.0	27.7	0.71	94.4
080676-3	272.1	60.5	8.1	1.1	7.0	0.8	3.0	<0.1	0.3	0.1W	11.7	161.5	11.7	31.7	31.2	1.51	15.6
190776-3	425.0	49.2	6.6	1.2	5.4	2.0	2.0	0.1	<0.1	0.1W	10.0	71.0	18.0	56.0	30.0	0.86	38.0
141076-3	240.1	56.2	7.7	1.2	6.5	0.8	3.0	1.0	<0.1	1.8	8.7	68.2	13.8	38.3	7.7	0.84	11.8
DISSOLVED																	
050476-3	158.8	50.3	6.6	0.4	6.2	1.2	2.1	0.2	0.1	0.8	15.0	365.0	46.5	230.0	9.0	0.71	22.0
250476-3 E	103.8	60.0	8.2	1.5	6.7	0.2	1.2	0.6	0.7	0.1W	29.5	166.1	43.8	68.0	15.9	0.65	35.5
080676-3	264.5	59.1	8.0	1.1	6.9	0.9	3.2	0.1	<0.1	-	15.0	175.0	25.0	1375.0	6.0	1.37	25.0
190776-3	396.9	51.2	4.3	1.0	3.3	1.6	1.6	<0.1	<0.1	0.5T	18.5	90.0	14.5	31.0	22.5	0.93	45.0
141076-3	190.1	56.9	7.8	1.4	6.4	1.3	3.2	<0.1	<0.1	2.7	14.1	865.0	12.1	352.8	22.7	0.86	25.7
PARTICULATE																	
050476-3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
250476-3 E	466.6	85.6	4.8	2.2	2.6	1.1	0.2	3.6	0.8	-	80.0	40.0	650.0	47.5	27.5	0.58	155.0
080676-3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
190776-3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
141076-3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

APP. TABLE 24 (cont'd)

	YIELD mg/l	ASH %	TOTAL C %	ORGANIC C %	INORG. C %	TOTAL N %	TOTAL S %	Al %	Fe %	←----- μg/g -----→							
										Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
TOTAL																	
260376-4	436.5	69.9	5.2	1.2	4.0	0.5	0.8	4.9	2.9	0.1W	28.0	195.0	575.0	102.0	22.5	0.60	105.0
010676-4	252.2	40.8	10.2	1.4	8.8	1.3	2.3	0.1	0.1	0.1W	6.6	130.4	29.6	90.9	13.2	0.66	19.1
120776-4	433.1	56.5	9.5	2.2	7.3	0.6	2.2	0.8	0.4	0.1W	5.0	327.0	270.0	72.5	10.0	0.40	29.0
071076-4	215.0	58.0	9.7	1.9	7.8	0.5	2.4	0.1	<0.1	1.3	24.2	376.2	103.5	136.4	10.1	0.31	23.2
DISSOLVED																	
260376-4	132.9	57.6	8.8	1.2	7.8	1.3	2.5	-	-	0.1W	6.7	1003.8	17.7	421.6	5.0	0.13	30.1
010676-4	258.2	41.5	10.2	1.6	8.6	1.2	1.8	<0.1	<0.1	0.1W	10.7	103.6	14.6	52.3	14.1	0.42	18.0
120776-4	370.8	53.0	10.4	2.3	8.1	0.7	1.4	<0.1	<0.1	0.5T	5.0	138.0	13.5	57.5	9.0	0.43	27.0
071076-4	204.7	53.2	9.5	2.0	7.5	0.8	1.8	<0.1	<0.1	1.2	17.1	360.4	40.0	334.9	52.8	0.31	28.0
PARTICULATE																	
260376-4	342.9	87.2	3.7	2.1	1.6	0.2	0.4	7.1	4.0	0.1W	55.0	37.0	850.0	29.0	32.5	0.48	135.0
010676-4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
120776-4	-	-	-	-	-	-	-	2.1	2.6	0.3T	54.7	16.0	826.7	16.7	33.3	-	59.3
071076-4	11.6	87.0	10.6	-	-	1.0	0.5	3.7	3.7	7.8	105.3	50.7	2457.0	23.4	113.1	-	230.1

APP. TABLE 24 (cont'd)

	YIELD	ASH	TOTAL C	ORGANIC C	INORG. C	TOTAL N	TOTAL S	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
	mg/l	%	%	%	%	%	%	%	%	←----- μg/g -----→							
TOTAL																	
310376-5	386.0	54.5	1.6	1.5	0.1	1.7	1.9	6.4	1.2	0.1W	7.3	97.6	48.2	42.7	8.5	0.28	23.8
250476-5 E	314.6	51.9	9.7	3.7	6.0	1.8	2.0	1.5	0.8	0.1W	24.2	293.2	276.0	98.7	14.0	0.82	54.5
030676-5	283.5	53.6	9.2	2.7	6.5	1.0	2.5	<0.1	<0.1	1.0	15.5	37.5	12.5	15.0	5.0	0.35	14.5
150776-5 E	324.6	56.3	6.4	1.8	4.6	2.1	1.1	0.5	0.3	0.5T	10.0	180.0	93.0	64.0	20.0	0.65	30.0
210776-5 E	277.8	48.6	8.8	3.7	5.1	2.1	1.7	1.2	0.7	0.5T	17.5	240.0	143.0	24.0	17.5	0.80	44.5
280876-5	309.1	42.2	3.6	1.1	2.5	1.1	1.8	0.1	<0.1	0.5T	20.0	730.0	14.0	5.0	16.0	0.43	19.0
051076-5	330.5	53.0	8.8	1.2	7.6	0.9	2.1	0.1	<0.1	2.6	16.1	207.5	11.6	160.6	8.4	0.27	16.1
DISSOLVED																	
310376-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
250476-5 E	189.0	43.5	9.2	2.2	7.0	0.6	2.5	<0.1	<0.1	0.1W	16.6	127.3	80.6	61.5	12.9	0.44	18.9
030676-5	242.0	54.8	8.9	2.4	6.5	1.4	2.0	<0.1	<0.1	0.1W	15.0	156.0	11.0	65.0	41.5	0.32	14.0
150776-5 E	312.7	45.4	7.0	2.3	4.7	2.2	1.6	0.2	0.1	0.1W	210.0	20.5	34.0	8.0	30.0	0.69	33.0
210776-5 E	229.5	44.3	8.2	2.7	5.5	2.2	1.5	0.5	0.3	1.5T	16.0	195.0	46.0	8.0	15.0	0.87	34.5
280876-5	277.7	52.9	5.5	1.8	3.7	1.3	2.6	<0.1	<0.1	1.5T	<2.5	330.0	13.5	5.0	20.0	0.43	37.5
051076-5	319.8	55.3	7.3	1.5	5.8	0.8	2.1	<0.1	<0.1	2.5	11.6	531.6	10.1	108.6	21.7	0.24	36.9
PARTICULATE																	
310376-5	1.8	58.2	9.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-
250476-5 E	45.6	76.3	9.7	-	-	2.7	0.4	5.3	2.8	-	70.0	90.0	525.0	75.0	58.5	0.73	192.3
030676-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
150776-5 E	16.2	70.2	7.3	-	-	0.9	0.3	5.9	3.8	0.1W	122.0	118.5	755.9	37.8	63.6	-	242.2
210776-5 E	33.5	75.2	6.8	-	-	0.9	0.3	6.2	4.0	0.1W	97.4	71.0	1146.9	33.0	23.1	-	203.8
280876-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

APP. TABLE 24 (cont'd)

	YIELD	ASH	TOTAL	ORGANIC	INORG.	TOTAL	TOTAL	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
	mg/l	%	C	C	C	N	S	%	%	←-----µg/g-----→							
			%	%	%	%	%										
TOTAL																	
100376-10	384.0	74.6	4.6	2.0	2.6	0.4	4.6	3.8	2.8	1.5	46.0	235.0	215.0	205.0	11.5	0.47	115.0
250476-10 E	669.9	85.8	2.9	2.4	0.5	1.5	1.2	9.0	4.4	1.3	39.5	184.2	413.0	168.4	70.4	0.49	153.9
020676-10	1290.6	80.9	2.1	1.1	1.0	-	12.9	0.1	0.1	0.1W	12.7	59.0	83.2	19.2	3.5	0.07	10.7
140776-10	2125.0	69.9	1.0	0.9	0.1	0.2	12.9	0.2	3.3	0.1W	11.5	45.0	62.5	16.5	5.0	0.11	18.0
121076-10	1532.2	77.6	2.9	1.2	1.7	0.4	12.9	0.4	0.1	0.8	10.0	42.0	215.0	22.5	9.0	0.09	16.5
DISSOLVED																	
100376-10	248.9	58.8	5.9	3.6	2.3	0.3	7.8	0.6	0.3	1.3	33.5	240.0	38.0	-	7.5	0.55	60.0
250476-10 E	183.0	71.3	5.0	3.7	1.3	1.8	3.5	4.9	2.3	1.6	64.0	173.2	141.6	180.0	148.0	0.98	110.4
020676-10	1286.9	81.9	2.3	1.2	1.1	-	4.7	<0.1	<0.1	0.1W	19.3	61.7	11.6	33.4	147.8	0.04	10.3
140776-10	2083.9	66.1	1.3	0.9	0.4	0.3	12.8	<0.1	<0.1	0.5T	10.0	25.0	5.0	10.0	11.0	0.06	7.0
121076-10	1450.0	76.3	1.8	0.9	0.9	0.4	13.5	0.2	<0.1	1.4	9.0	21.0	5.0	10.0	6.5	0.06	5.5
PARTICULATE																	
100376-10	114.5	89.2	1.8	1.1	0.7	0.1	0.2	-	-	3.5	76.9	67.3	480.7	45.2	37.5	0.26	201.9
250476-10 E	515.0	90.6	1.6	1.4	0.2	0.3	0.1	10.3	5.1	0.1W	65.0	235.0	540.0	44.0	55.0	0.26	189.5
020676-10	35.7	78.9	5.1	-	-	0.5	0.2	7.2	4.9	0.1W	187.2	57.7	778.4	48.4	20.3	0.16	500.8
140776-10	59.0	78.9	4.83	-	-	0.7	0.4	6.4	3.9	0.4T	39.0	45.1	2272.6	33.8	121.4	0.18	364.2
121076-10	74.8	81.9	3.7	-	-	0.8	0.9	4.7	4.3	1.4	76.7	24.3	3641.6	31.3	378.2	0.07	270.2

APP. TABLE 24 (cont'd)

	YIELD mg/l	ASH %	TOTAL C %	ORGANIC C %	INORG. C %	TOTAL N %	TOTAL S %	Al %	Fe %	Cd	Cr	←-----µg/g-----→					
												Cu	Mn	Ni	Pb	Se	Zn
TOTAL																	
290376-13	575.2	66.9	3.2	0.5	2.7	1.0	2.4	0.4	0.2	0.1W	12.5	65.0	149.5	88.0	11.0	1.02	39.0
270576-13	433.8	52.3	5.1	0.8	4.3	0.9	7.1	<0.1	<0.1	0.1W	7.0	127.3	18.0	41.3	9.3	0.78	16.3
270776-13	510.3	57.0	4.4	1.1	3.3	0.8	6.7	0.2	0.1	2.50	6.5	60.0	1045.0	26.5	5.0	0.72	16.5
041176-13	403.5	76.1	3.5	1.3	2.2	1.0	7.2	0.3	0.3	0.5	21.8	93.7	102.9	46.0	16.7	0.53	24.1
DISSOLVED																	
290376-13	511.8	50.0	3.9	0.9	3.0	1.2	6.3	<0.1	<0.1	0.1W	16.5	195.0	27.0	29.0	11.0	1.51	17.5
270576-13	396.0	73.5	4.1	0.9	3.2	0.1	7.5	<0.1	<0.1	0.1W	14.3	161.0	7.9	51.2	50.2	1.02	17.2
270776-13	464.7	60.5	5.0	1.4	3.6	0.6	7.2	-	<0.1	0.1W	2.5	60.0	9.5	22.0	7.5	0.61	15.0
041176-13	403.4	74.2	4.3	1.0	3.3	1.0	7.5	<0.1	<0.1	0.1W	14.5	125.0	8.0	52.0	11.5	0.57	12.0
PARTICULATE																	
290376-13	5.8	88.0	0.3	-	-	0.1	-	-	-	-	-	-	-	-	-	-	-
270576-13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
270776-13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
041176-13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

CONCENTRATIONS OF TOTAL METALS AND NUTRIENTS IN STREAM WATER. THE DATA OF TABLE 26 ARE EXPRESSED ON A PER LITRE BASIS.
THE PARTICULATE FRACTION IS THAT SAMPLE >.45 μ AND THE DISSOLVED <.45 μ .

APPENDIX TABLE 25

	YIELD mg/l	ASH %	SOLIDS mg/l	TOTAL C mg/l	ORGANIC C mg/l	INORG. C mg/l	TOTAL N mg/l	TOTAL S mg/l	Al mg/l	Fe mg/l	←----- μ g/l-----→							
											Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
<u>290376-1</u>																		
TOTAL	493.5	65.1	321.4	20.8	2.7	18.1	3.0	19.1	9.0	30.7	1.7	6.2	59.2	29.6	47.9	3.7	1.4	22.2
PARTICULATE	76.2	87.9	67.0	2.4	1.2	1.2	0.2	0.2	-	-	0.5	2.4	6.9	32.4	4.3	4.1	0.1	22.0
DISSOLVED	428.5	61.3	262.7	14.7	2.1	12.6	2.2	25.0	0.3	0.2	0.3	4.7	45.0	2.1	35.4	1.1	1.3	4.3
<u>250576-1</u>																		
TOTAL	421.4	75.4	317.7	15.6	5.5	10.1	1.3	41.7	0.8	37.2	0.2	7.0	21.9	11.3	15.3	6.9	0.6	11.8
PARTICULATE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DISSOLVED	426.8	69.0	294.5	14.9	6.8	8.1	0.4	36.3	0.1	0.2	0.1W	7.6	63.9	3.4	25.3	6.5	0.6	8.2
<u>260776-1</u>																		
TOTAL	514.3	70.8	364.1	27.3	12.9	14.4	2.1	25.7	9.0	4.1	0.1W	15.4	55.0	147.0	38.0	6.9	0.6	25.5
PARTICULATE	10.7	94.9	10.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DISSOLVED	448.7	59.7	267.9	24.9	10.3	14.6	1.8	26.5	0.4	0.2	0.1W	2.2	92.9	6.3	22.4	4.0	0.5	6.5
<u>051176-1</u>																		
TOTAL	856.6	76.4	654.4	20.6	10.3	10.3	1.7	64.2	2.6	1.7	0.3	11.1	101.1	27.4	65.9	9.9	0.4	14.1
PARTICULATE	70.0	80.4	56.3	3.2	-	-	<0.1	1.5	-	-	0.1	-	3.9	56.8	3.3	9.2	-	10.2
DISSOLVED	789.8	73.9	583.7	20.5	9.5	11.0	2.4	56.6	<0.1	<0.1	<0.1	11.5	98.7	6.3	41.1	9.1	0.4	9.5

APP. TABLE 25 (cont'd)

	YIELD	ASH	SOLIDS	TOTAL	ORGANIC	INORG.	TOTAL	TOTAL	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
	mg/l	%	mg/l	C	C	C	N	S	mg/l	mg/l	←----- μg/l ----->							
				mg/l	mg/l	mg/l	mg/l	mg/l										
<u>050476-3</u>																		
TOTAL	169.2	55.2	93.4	11.1	1.0	10.1	1.7	3.7	-	-	0.3	3.4	68.5	5.8	-	1.7	0.1	8.0
PARTICULATE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DISSOLVED	158.8	50.3	80.3	10.5	0.6	9.9	1.9	3.4	0.5	0.3	0.1	4.9	120.1	15.3	75.7	3.0	0.1	7.2
<u>250476-3E</u>																		
TOTAL	627.4	72.2	452.9	32.0	10.7	21.3	10.1	6.1	38.2	16.5	1.1	36.6	25.2	321.0	32.0	17.4	0.4	59.2
PARTICULATE	466.6	85.8	400.2	22.4	10.2	12.2	5.3	1.0	16.8	3.7	-	37.3	18.7	303.3	22.2	12.8	0.3	72.3
DISSOLVED	103.8	60.0	62.2	8.5	1.6	6.9	2.1	1.3	0.6	0.8	0.1W	3.1	17.2	4.5	7.1	1.7	0.1	3.7
<u>080676-3</u>																		
TOTAL	272.1	60.5	164.7	22.0	3.0	19.0	2.3	8.2	0.1	0.8	0.1W	3.2	43.9	3.2	8.6	8.5	0.4	4.2
PARTICULATE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DISSOLVED	264.5	59.1	156.3	21.2	2.9	18.3	2.3	8.4	0.3	<0.2	-	4.0	46.3	6.6	363.7	1.6	0.4	6.6
<u>190776-3</u>																		
TOTAL	425.0	49.2	209.1	28.1	5.1	23.0	8.5	8.5	0.4	0.2	0.1W	4.2	30.4	7.6	23.8	12.8	0.4	16.2
PARTICULATE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DISSOLVED	396.9	51.2	203.2	17.1	4.0	13.1	6.3	6.3	0.2	0.1	0.2T	7.3	35.7	5.8	12.3	8.9	0.4	17.8
<u>141076-3</u>																		
TOTAL	240.1	56.2	134.9	18.5	2.9	15.6	1.9	7.2	2.4	<0.1	0.4	2.1	16.4	3.3	9.2	1.8	0.2	2.8
PARTICULATE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DISSOLVED	190.1	56.9	108.2	14.8	2.7	12.1	2.5	6.1	<0.1	<0.1	0.5	2.7	16.4	2.3	67.1	4.3	0.2	4.9

APP. TABLE 25 (cont'd)

	YIELD	ASH	SOLIDS	TOTAL C	ORGANIC C	INORG. C	TOTAL N	TOTAL S	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
	mg/l	%	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	←----- μg/l -----→						
<u>260376-4</u>																		
TOTAL	436.8	69.9	305.5	22.7	5.4	17.3	2.3	3.6	21.4	12.6	0.1W	12.2	85.2	251.2	44.6	9.8	0.3	45.9
PARTICULATE	342.9	87.2	299.0	12.7	7.1	5.6	0.8	1.2	24.2	13.6	0.1W	18.9	12.7	291.5	9.9	11.1	0.2	46.3
DISSOLVED	127.8	57.6	73.6	11.2	1.6	9.6	1.6	3.2	-	-	-	0.9	128.3	2.3	53.9	0.6	0.1	3.8
<u>010676-4</u>																		
TOTAL	252.2	40.8	102.9	25.8	3.7	22.1	3.3	5.7	0.2	0.2	0.1W	1.7	32.9	7.5	22.9	3.3	0.2	4.8
PARTICULATE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DISSOLVED	258.2	41.5	107.2	26.4	4.2	22.2	3.2	4.6	0.1	0.1	0.1W	2.8	26.7	3.8	13.5	3.6	0.1	4.6
<u>120776-4</u>																		
TOTAL	433.1	56.5	244.7	41.1	9.5	31.6	2.6	9.3	3.6	1.7	0.1W	2.2	141.6	116.9	31.4	4.3	0.2	12.6
PARTICULATE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DISSOLVED	370.8	53.0	196.5	38.6	8.5	30.1	2.6	5.2	0.2	0.1	0.2T	1.9	51.2	5.0	21.3	3.4	0.2	10.0
<u>071076-4</u>																		
TOTAL	215.0	58.0	124.7	20.8	4.1	16.7	1.1	5.2	<0.1	<0.1	0.3	5.2	80.9	22.3	29.3	2.2	0.1	5.0
PARTICULATE	11.6	87.0	10.0	1.2	-	-	0.1	0.1	-	-	-	-	-	-	-	-	-	-
DISSOLVED	204.7	53.2	108.9	19.4	4.1	15.3	1.6	3.7	<0.1	<0.1	0.3	3.5	73.8	8.2	68.6	10.8	0.1	23.2

APP. TABLE 25 (cont'd)

	YIELD	ASH	SOLIDS	TOTAL C	ORGANIC C	INORG. C	TOTAL N	TOTAL S	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn	
	mg/l	%	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	←-----	-----→	μg/l	-----	-----	-----	-----	-----	
<u>310376-5</u>																			
TOTAL	386.0	54.5	210.4	6.0	5.8	0.2	6.6	7.3	24.6	5.6	0.1W	2.8	37.7	18.6	16.5	3.3	0.1	9.2	
PARTICULATE	1.8	58.2	1.0	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
DISSOLVED	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
<u>250476-5 E</u>																			
TOTAL	314.6	51.9	163.3	30.5	11.6	18.9	5.7	6.3	4.8	2.5	0.1W	7.6	92.2	86.8	31.1	4.4	0.3	17.1	
PARTICULATE	45.6	76.3	34.5	4.4	-	-	1.2	0.2	2.4	1.3	-	3.2	4.1	23.9	3.4	2.7	0.1	8.8	
DISSOLVED	189.0	43.5	82.2	18.4	4.1	14.3	1.1	4.7	0.1	0.1	<0.1	3.1	24.1	15.2	11.6	2.4	0.1	3.5	
<u>030676-5</u>																			
TOTAL	283.5	53.6	152.0	26.1	10.4	15.7	2.9	7.0	0.1	0.1	0.3	4.4	10.6	3.5	4.3	1.4	0.1	4.1	
PARTICULATE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
DISSOLVED	242.0	54.8	132.7	21.5	9.9	10.6	3.5	4.9	0.1	0.1	0.1W	3.6	37.8	2.7	15.7	10.0	0.1	3.4	
<u>150776-5 E</u>																			
TOTAL	324.6	56.3	182.7	20.8	5.8	15.0	6.9	3.4	1.6	0.8	0.2T	3.2	58.4	30.2	20.8	6.5	0.2	9.7	
PARTICULATE	16.2	70.2	11.4	0.1	-	-	<0.1	<0.1	1.0	0.6	0.1W	2.0	2.0	12.2	0.6	1.0	-	3.9	
DISSOLVED	312.7	45.4	142.0	21.9	7.2	14.7	7.0	5.1	0.6	0.3	0.1W	65.6	6.4	10.6	2.5	9.3	0.2	10.3	
<u>210776-5 E</u>																			
TOTAL	277.8	48.6	135.0	24.4	10.3	14.1	5.8	3.0	3.2	1.9	0.1T	4.9	66.7	39.7	6.7	4.9	0.2	12.4	
PARTICULATE	33.5	75.2	25.2	2.3	-	-	0.3	<0.1	2.1	1.3	0.1W	3.3	2.4	38.4	1.1	0.8	-	6.8	
DISSOLVED	229.5	44.3	101.7	18.8	6.2	12.6	5.1	3.5	1.1	0.6	0.3T	3.6	44.8	10.5	1.8	3.4	0.2	7.9	
<u>280876-5</u>																			
TOTAL	309.1	42.2	130.4	11.1	3.4	7.7	3.4	5.6	0.2	0.1	0.5%	6.2	225.6	4.3	1.5	4.9	0.1	5.9	
PARTICULATE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
DISSOLVED	277.7	58.9	163.5	15.3	5.0	10.3	3.5	7.1	0.1	0.1	0.4T	<0.6	91.6	3.7	1.4	5.5	0.1	10.4	
<u>051076-5</u>																			
TOTAL	330.5	53.0	175.2	29.1	4.0	25.1	3.0	6.9	<0.1	<0.1	0.9	5.3	68.6	3.8	53.1	2.8	0.1	5.3	
PARTICULATE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
DISSOLVED	319.8	55.3	176.8	23.3	4.7	18.6	2.6	6.7	<0.1	<0.1	0.8	3.7	170.0	3.2	34.7	6.9	0.1	11.8	

APP. TABLE 25 (cont'd)

	YIELD	ASH	SOLIDS	TOTAL C	ORGANIC C	INORG. C	TOTAL N	TOTAL S	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
	mg/l	%	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l
<u>100376-10</u>																		
TOTAL	384.0	74.6	286.5	17.7	7.7	10.0	1.5	17.7	14.6	10.8	0.6	17.7	90.2	82.6	78.7	4.4	0.2	44.2
PARTICULATE	135.1	89.2	120.5	2.4	1.5	0.9	0.1	0.2	-	-	0.4	10.3	9.1	64.9	6.1	5.1	0.1	27.3
DISSOLVED	248.9	58.8	146.3	14.7	9.0	5.7	0.7	19.4	1.5	0.8	0.3	8.3	59.7	9.5	-	1.8	0.1	14.9
<u>250476-10 E</u>																		
TOTAL	669.9	85.8	574.7	19.4	16.0	3.4	10.0	8.0	60.3	29.5	0.9	26.4	123.4	276.7	112.8	47.2	0.3	104.0
PARTICULATE	486.9	90.6	441.1	7.8	6.8	1.0	1.5	0.5	50.2	24.8	0.1W	31.6	114.4	262.9	21.4	26.8	0.1	92.3
DISSOLVED	183.0	71.3	130.4	9.2	6.8	2.3	3.4	6.4	9.0	4.1	0.3	11.7	31.7	26.0	32.9	27.1	0.2	20.2
<u>020676-10</u>																		
TOTAL	1290.6	80.9	1043.6	26.5	14.2	12.3	-	166.0	1.2	0.6	0.1W	16.4	76.1	107.4	24.8	4.5	0.1	13.8
PARTICULATE	3.7	86.8	3.1	0.2	-	-	-	-	0.3	0.2	0.1W	0.7	0.2	22.8	0.2	0.1	-	1.8
DISSOLVED	1286.9	81.9	1054.2	29.3	15.3	14.0	-	60.5	0.3	0.4	0.1W	24.8	79.4	14.9	43.0	1.9	0.1	13.2
<u>140776-10</u>																		
TOTAL	2125.0	69.9	1485.4	20.4	19.1	1.3	4.7	273.3	3.8	69.7	0.1W	24.4	95.6	132.8	35.0	10.6	0.2	38.3
PARTICULATE	59.0	78.9	46.6	2.8	-	-	0.4	0.3	3.8	2.3	0.1T	2.3	2.7	134.0	2.0	7.2	0.1	21.5
DISSOLVED	2083.9	66.1	1377.5	27.5	18.7	8.8	5.2	266.5	0.3	0.2	1.0T	20.8	52.1	10.4	20.9	22.9	0.1	14.6
<u>121076-10</u>																		
TOTAL	1532.2	77.6	1189.0	44.4	18.4	26.0	6.1	197.6	6.2	1.5	1.2	15.3	64.4	329.4	34.5	13.8	0.1	25.3
PARTICULATE	74.8	81.9	61.3	2.8	-	-	0.6	0.7	3.5	3.2	0.1	5.7	1.8	272.4	2.3	28.3	0.1	20.2
DISSOLVED	1450.0	76.3	1106.4	26.1	13.1	13.1	5.8	195.8	2.9	<0.1	2.0	13.1	30.5	7.3	14.5	9.4	0.1	8.0

APP. TABLE 25 (cont'd)

	YIELD	ASH	SOLIDS	TOTAL	ORGANIC	INORG.	TOTAL	TOTAL	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
	mg/l	%	mg/l	C	C	C	N	S	mg/l	mg/l	←-----µg/l-----→							
				mg/l	mg/l	mg/l	mg/l	mg/l										
<u>290376-13</u>																		
TOTAL	575.2	66.9	342.6	16.2	2.8	13.4	5.7	13.8	2.3	1.2	0.1W	13.0	33.3	76.5	45.0	5.6	0.5	20.0
PARTICULATE	63.4	88.0	55.7	0.2	-	-	0.1	-	-	-	-	-	-	-	-	-	-	-
DISSOLVED	511.8	50.0	287.6	20.0	5.0	15.0	6.1	32.2	0.4	0.4	0.1W	17.1	112.2	15.5	16.7	6.3	0.7	10.1
<u>270576-13</u>																		
TOTAL	433.8	63.5	275.5	22.1	3.3	18.8	3.9	32.5	0.2	0.2	0.1W	3.0	55.2	7.8	17.9	4.0	0.3	7.1
PARTICULATE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DISSOLVED	396.0	62.3	246.7	16.0	3.4	12.6	0.1	29.5	0.1	0.1	0.1W	5.7	63.8	3.1	20.3	19.9	0.4	17.6
<u>270776-13</u>																		
TOTAL	510.3	57.0	290.9	22.4	5.4	17.0	4.3	34.1	1.0	0.5	1.3	3.3	30.6	533.3	13.5	2.6	0.4	8.4
PARTICULATE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DISSOLVED	464.7	60.5	281.1	23.4	5.7	17.7	2.6	33.4	-	0.1	0.1W	1.1	27.9	4.4	10.2	3.5	0.3	7.0
<u>041176-13</u>																		
TOTAL	403.5	76.1	307.1	14.1	5.2	8.9	4.0	29.1	1.2	1.2	0.2	8.8	37.8	41.5	18.6	6.7	0.2	9.7
PARTICULATE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DISSOLVED	403.4	74.2	299.3	17.3	4.0	13.3	4.0	30.2	<0.1	<0.1	<0.1	5.9	50.4	3.2	21.0	4.6	0.2	4.8

APPENDIX TABLE 26

CORRELATION COEFFICIENTS FOR SUSPENDED SEDIMENTS (ALL WATERSHEDS COMBINED)

	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
<u>PARTICULATE</u>										
Yield	.33	-.03	-.32	-.30	.39	-.33	.01	-.22	.30	-.50
Total C	.04	.21	.16	.32	-.23	.18	.03	-.04	-.18	-.02
Organic C	.23	.15	-.48	-.02	-.50	.74	-.34	-.58	.43	-.51
Inorganic C	-.30	-.40	-.11	.04	-.75	.39	.05	-.66	.61	-.22
Total N	.08	.06	-.22	.06	-.08	.04	.51	.06	.19	-.16
Total S	-.11	.23	.17	-.15	-.53	.87	-.34	.90	-.22	.02
Total Al	-	.89	-.66	.24	.43	.05	-.19	-.04	-.35	.08
Total Fe	.89	-	-.43	.39	.21	.39	-.41	.25	-.67	.27
<u>DISSOLVED</u>										
Yield	-.15	-.18	-.12	-.37	-.35	-.23	.10	-.26	-.42	.38
Total C	-.05	-.02	.08	.06	.36	.25	.30	-.16	-.18	.19
Organic C	.59	.58	.23	.31	-.009	.59	-.15	.31	-.17	.68
Inorganic C	-.25	-.21	.008	-.05	.40	.06	.37	-.28	-.14	-.02
Total N	.31	.26	.25	.45	.15	.36	.08	.05	.001	.43
Total S	-.09	-.13	-.08	-.20	-.32	-.32	-.21	-.13	.02	-.35
Total Al	-	.99	.27	.24	-.04	.83	.004	.63	-.07	.84
Total Fe	.99	-	.24	.22	-.06	.82	-.008	.61	.07	.83
<u>TOTAL</u>										
Yield	-.01	.17	-.18	-.16	-.38	.05	-.21	-.12	-.28	-.09
Total C	-.31	-.37	.07	.17	.26	-.10	.16	-.05	.06	-.12
Organic C	.21	-.11	-.20	.23	.14	.15	.20	.21	-.14	.34
Inorganic C	-.42	-.38	.14	.12	.25	-.16	.12	-.13	.11	-.22
Total N	-.07	-.17	.08	.07	.31	-.07	.25	-.10	-.17	-.07
Total S	-.36	.22	-.15	-.29	-.41	-.06	-.33	-.37	-.16	-.37
Total Al	-	.37	.12	.43	-.06	.37	.40	.61	-.07	.82
Total Fe	-	.37	.12	.43	-.06	.37	.40	.61	-.07	.82

r = .36 significant at .05

r = .46 significant at .01

APPENDIX TABLE 27

CORRELATION COEFFICIENTS FOR THE TOTAL SUSPENDED SEDIMENTS COLLECTED IN EACH WATERSHED

	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn	
<u>TOTAL</u>											
<u>WATERSHED 1</u>											
Yield	-.36	-.73	-.29	-.31	.56	-.22	.32	-.25	-.61	-.65	
Total C	.78	.06	.11	.78	-.01	.82	.11	.04	.38	.95	r = .81 significant at .05
Organic C	.12	-.50	-.76	.95	-.11	.85	-.28	.57	-.59	.30	r = .91 significant at .01
Inorganic C	.80	.47	.74	.14	.08	.27	.35	-.41	.91	.86	
Total N	.85	.34	.85	.01	.31	.21	.58	-.63	.93	.81	
Total S	-.94	.34	-.59	-.21	-.81	-.49	-.90	.80	-.53	-.73	
Total Al	-	-.15	.54	.41	.56	.63	.70	-.59	.61	.92	
Total Fe	-.15	-	.43	-.38	-.69	-.50	-.44	.19	.61	.06	
<u>WATERSHED 3</u>											
Yield	.84	.87	-.03	.77	-.68	.85	.76	.62	.08	.77	
Total C	-.77	-.77	-.41	-.86	.13	-.84	-.25	-.18	.56	-.97	
Organic C	.81	.80	-.01	.62	-.89	.75	.85	.49	.33	.50	r = .75 significant at .05
Inorganic C	-.88	-.87	-.34	-.90	.36	-.91	-.44	-.29	.38	-.95	r = .87 significant at .01
Total N	.32	.35	-.28	.33	-.40	.38	.64	.54	-.18	.56	
Total S	-.78	-.80	-.28	-.86	.18	-.85	-.32	-.33	.45	-.98	
Total Al	-	.98	.45	.95	-.48	.98	.43	.22	-.13	.84	
Total Fe	.98	-	.32	.96	-.44	.99	.37	-.04	.86	.46	
<u>WATERSHED 4</u>											
Yield	.94	.87	-.73	-.60	-.003	-.09	.10	.06	-.33	.02	
Total C	-.87	-.65	.44	.84	.33	.44	.23	.05	.59	.35	r = .81 significant at .05
Organic C	-.50	-.17	-.02	.996	.55	.73	.48	-.06	.63	.64	r = .91 significant at .01
Inorganic C	-.94	-.78	.56	.73	.23	.31	.13	.09	.53	.22	
Total N	.17	.36	-.68	-.15	.68	.47	.73	.90	.57	.56	
Total S	.04	-.04	.34	.40	-.40	-.14	-.44	-.91	-.40	-.23	
Total Al	-	.91	-.66	-.48	-.14	-.14	-.04	-.26	-.49	-.07	
Total Fe	.91	-	-.90	-.14	.27	.29	.35	-.06	-.10	.35	

APP. TABLE 27 (cont'd)

CORRELATION COEFFICIENTS FOR THE TOTAL SUSPENDED SEDIMENTS COLLECTED IN EACH WATERSHED (cont'd)

	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn	
<u>TOTAL</u>											
<u>WATERSHED 5</u>											
Yield	.78	.53	-.09	-.60	-.17	-.15	.29	-.21	-.47	-.19	
Total C	-.64	-.34	.38	.56	-.28	.41	.38	-.05	.44	.36	r = .67 significant at .05
Organic C	-.08	.34	-.38	.47	-.27	.78	-.13	.16	.78	.79	r = .80 significant at .01
Inorganic C	-.75	-.56	.63	.48	-.23	.17	.53	-.13	.21	.09	
Total N	.33	.62	-.65	-.19	-.18	.65	-.16	.69	.75	.75	
Total S	-.02	-.12	.33	.31	-.21	-.20	.04	-.88	-.44	-.30	
Total Al	-	.88	-.46	-.54	-.32	.07	-.11	-.23	-.21	.10	
Total Fe	.88	-	-.61	-.24	-.30	.51	-.06	.03	.25	.55	
<u>WATERSHED 10</u>											
Yield	-.71	-.28	-.85	-.90	-.91	-.66	-.90	-.49	-.85	-.82	
Total C	.43	.05	.88	.77	.80	.51	.80	.18	.69	.61	r = .75 significant at .05
Organic C	.95	.61	.89	.92	.90	.90	.92	.82	.96	.98	r = .87 significant at .01
Inorganic C	-.05	-.33	.59	.42	.48	.10	.45	-.29	.29	.17	
Total N	.94	.67	.65	.60	.54	.95	.61	.98	.73	.83	
Total S	-.96	-.73	-.85	-.94	-.91	-.85	-.94	-.81	-.98	-.999	
Total Al	-	.74	.74	.80	.76	.92	.80	.95	.89	.96	
Total Fe	.74	-	.43	.64	.59	.49	.62	.66	.73	.75	
<u>WATERSHED 13</u>											
Yield	.53	-.27	.15	-.39	-.73	.33	.59	-.47	.86	.63	
Total C	-.98	-.78	.21	-.70	.59	.16	-.69	-.56	-.17	-.85	r = .81 significant at .05
Organic C	-.26	.32	.47	.42	.06	.31	-.75	.26	-.97	-.60	r = .91 significant at .01
Inorganic C	-.84	-.88	.02	-.84	.55	.03	-.37	-.63	.22	-.58	
Total N	.67	.82	-.82	.78	.14	-.81	.75	.88	.12	.74	
Total S	-.76	-.11	.32	.01	.52	.16	-.92	.01	-.87	-.92	
Total Al	-	.67	-.22	.58	-.64	-.15	.45	.34	.92	-.39	
Total Fe	.67	-	-.39	.99	-.08	-.46	.38	.93	-.36	.50	

APPENDIX TABLE 28

CORRELATION COEFFICIENTS FOR THE DISSOLVED FRACTION OF THE SUSPENDED SEDIMENTS COLLECTED IN EACH WATERSHED

	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn	
<u>DISSOLVED</u>											
<u>WATERSHED 1</u>											
Yield	-	-	-.36	.25	-.28	-.08	-.43	.23	-.67	-.33	
Total C	-	-	-.16	-.78	.87	.80	-.25	-.12	.07	.24	
Organic C	-	-	-.80	-.38	.97	.95	-.83	.54	-.61	.61	r = .81 significant at .05
Inorganic C	-	-	.60	-.73	.25	.17	.50	-.73	.73	-.28	
Total N	-	-	.68	-.74	-.12	-.03	.47	-.95	.51	-.88	r = .91 significant at .01
Total S	-	-	-.55	.87	-.10	-.19	-.32	.88	-.43	.77	
Total Al	-	1.0	-	-	-	-	-	-	-	-	
Total Fe	1.0	-	-	-	-	-	-	-	-	-	
<u>WATERSHED 3</u>											
Yield	-.67	-.59	-.13	-.37	-.45	-.69	.11	.28	.53	.56	
Total C	.41	.42	.10	.18	.10	.31	.45	-.40	.07	-.63	r = .75 significant at .05
Organic C	.38	.54	.17	.50	-.79	-.36	.01	.47	.04	.31	r = .87 significant at .01
Inorganic C	.34	.30	.06	.05	.34	.45	.49	-.57	.07	-.79	
Total N	-.88	-.88	.44	-.77	-.14	-.63	-.09	.35	.20	.10	
Total S	-.69	-.65	.49	-.79	-.12	-.48	.74	-.22	.65	.67	
Total Al	-	.98	-.38	.93	.14	.68	-.40	-.04	-.60	.19	
Total Fe	.98	-	-.37	.96	-.05	.54	-.35	.05	-.50	.29	
<u>WATERSHED 4</u>											
Yield	.72	.72	.07	-.33	-.82	-.38	-.87	-.17	.88	-.33	
Total C	.85	.85	.02	-.14	-.95	-.34	-.97	-.08	.99	-.63	
Organic C	.80	.80	.61	.10	-.74	.19	-.54	.36	.74	.002	r = .81 significant at .05
Inorganic C	.28	-.28	-.70	-.39	-.52	-.76	-.80	-.58	.58	-.87	
Total N	-.68	-.68	-.74	-.16	.57	-.35	.31	-.46	-.55	-.23	r = .91 significant at .01
Total S	-.91	-.91	-.38	-.04	.92	.03	.79	-.20	-.93	.35	
Total Al	-	1.0	.48	.39	-.96	.20	-.72	.46	.92	-.54	
Total Fe	1.0	-	.48	.39	-.96	.20	-.72	.46	.92	-.54	

APP. TABLE 28 (cont'd)

CORRELATION COEFFICIENTS FOR THE DISSOLVED FRACTION OF THE SUSPENDED SEDIMENTS COLLECTED IN EACH WATERSHED (cont'd)

	Al	Fe	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn	
<u>DISSOLVED</u>											
<u>WATERSHED 5</u>											
Yield	-.19	-.31	.45	.46	.40	-.72	.07	.32	-.17	.64	
Total C	.13	.18	-.47	-.18	-.37	.54	.41	.07	.002	-.80	r = .67 significant at .05
Organic C	.68	.62	-.58	.21	-.78	.43	-.52	.12	.74	-.40	
Inorganic C	-.10	-.01	-.32	-.28	-.14	.46	.65	.04	-.26	-.77	r = .80 significant at .01
Total N	.72	.57	-.16	.57	-.50	-.12	-.74	.23	.82	.30	
Total S	-.73	-.60	.05	-.52	.35	.05	.26	-.25	-.67	-.16	
Total Al	-	.97	.16	.07	-.23	.25	-.51	-.32	.88	.31	
Total Fe	.97	-	.26	-.18	-.09	.24	-.40	-.39	.77	.26	
<u>WATERSHED 10</u>											
Yield	-.66	-.65	-.63	-.86	-.92	-.75	-.54	-.34	-.87	-.87	
Total C	.55	.55	.58	.79	.99	.66	.40	.17	.85	.84	r = .75 significant at .05
Organic C	.70	.70	.62	.87	.96	.79	.55	.24	.94	.93	
Inorganic C	.17	.16	.42	.48	.91	.30	.02	-.01	.54	.53	r = .87 significant at .01
Total N	.98	.98	.67	.86	.39	.95	.93	.44	.86	.86	
Total S	-.62	-.63	.05	-.78	-.58	-.68	-.67	-.87	-.63	-.67	
Total Al	-	.999	.59	.93	.48	.99	.97	.57	.90	.91	
Total Fe	.999	-	.59	.93	.48	.99	.97	.59	.90	.91	
<u>WATERSHED 13</u>											
Yield	-.25	-	-	-.10	.18	.87	-.85	-.60	.60	.45	
Total C	-.94	-	-	-.97	-.99	-.53	-.47	-.39	-.75	-.41	
Organic C	-.98	-	-	-.98	-.94	-.35	-.63	-.49	-.62	-.31	
Inorganic C	-.87	-	-	-.93	-.99	-.68	-.29	-.27	-.85	-.49	r = .81 significant at .05
Total N	.17	-	-	.28	.22	.66	-.30	-.81	.25	-.27	r = .91 significant at .01
Total S	-.09	-	-	-.24	-.50	-.98	.63	.43	-.81	-.55	
Total Al	-	1.0	-	.99	.87	.26	.72	.41	.48	.11	
Total Fe	1.0	-	-	-	-	-	-	-	-	-	

TABLE 29 .

PERCENTAGE OF TOTAL METAL BOUND BY
SOIL AND SEDIMENT HA's AND FA's

	Cr	Cu	Ni	Pb	Zn
SOIL HA + FA					
AG 1	3.1	8.4(12.8)*	3.0(16.8)*	ND(10.0)*	0.4(11.2)*
AG 3	1.2	1.4	2.2	4.4	1.0
AG 4	27.7	12.4(9.6)*	6.1(10.8)*	ND(10.2)*	0.6(6.8)*
AG 5	5.2	10.5	6.3	ND	0.6
AG 10	41.8	10.9	10.6	9.1	0.6
AG 13	26.4	5.0	2.7	0.4	0.4
SEDIMENT HA + FA					
AG 1	0.4	9.6(15.2)*	0.3(18.5)*	0.5(6.6)*	2.3(15.6)*
AG 3	0.6	12.4	1.5	1.6	0.9
AG 4	0.4	18.5(22.7)*	1.5(25.9)*	1.5(7.0)*	4.5(16.1)*
AG 5	0.6	19.4	2.0	4.4	3.5
AG 10	0.3	14.3	1.6	2.4	0.4
AG 13	2.0	14.7	0.6	0.6	3.9

ND - not determined

* percentage organically bound from Appendix Table 27.



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