

**AGRICULTURAL SOURCES, TRANSPORT and  
STORAGE OF METALS: COPPER, ZINC, CADMIUM  
and LEAD LEVELS in WATERS of SELECTED  
SOUTHERN ONTARIO AGRICULTURAL WATERSHEDS**

Technical Report on Project 9B

to

Agricultural Watershed Studies

Task Group C (Canadian Section), International  
Reference Group on Great Lakes Pollution from Land  
Use Activities, International Joint Commission

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## **DISCLAIMER**

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## SUMMARY

The objective of project 9 was to determine and assess the relationship between concentrations of selected heavy metals in stream waters, suspended sediments, bottom sediments and soils within selected agricultural watersheds, draining into the lower Great Lakes, with the aim of elucidating sources, and storage and transport mechanisms of these elements. In support of these goals, the main objective of the investigation reported here, was to obtain reliable analytical information regarding concentrations of Cu, Zn, Cd and Pb in waters and suspended sediments from the six watersheds: AG1 (Big Creek), AG3 (Upper Little Ausable River), AG4 (Canagagigue), AG5 (Holiday Creek, tributary of Middle Thames River), AG10 (North Creek, tributary of Twenty Mile Creek), and AG13 (west branch of Hillman Creek).

The very low concentrations ( $\mu\text{g/L}$  and sub  $\mu\text{g/L}$ ) at which these trace elements are normally found in natural waters necessitated careful execution of sampling and analysis. Central to the attainment of accurate data was attention to contamination-prevention, data quality control, and the participation of several laboratories using different analytical approaches to sample treatment and measurement. Procedures centering on sub-boiling evaporation/flame atomic spectrometry, solvent extraction/flame atomic spectrometry, and direct analysis by electrothermal atomization spectrometry and differential pulse anodic stripping voltammetry were applied to water samples, and atomic absorption and optical emission spectrometry were applied to suspended sediments and related solid samples. Considering the different laboratories and methodologies, subsampling steps, and low trace element levels, good agreement of analytical results was realized for a large number of samples. The outcome of these extensive experimental deliberations was a body of data from which were extracted fairly reliable estimates of total, dissolved and suspended sediment-contributed trace element concentrations.

For the 11-21 samplings, during 1976 (including four during the Spring of 1977) of streams draining the six watersheds, ranges of concentrations ( $\mu\text{g/L}$ ) of elements in dissolved form (that fraction passing through  $0.45 \mu\text{m}$  filters) were found to be 0.5-18.5 for Cu, 0.1-11.4 for Zn, 0.00-0.57 for Cd, and 0.0-13.1 for Pb, with median concentrations  $\pm$

standard errors of  $2.0 \pm 1.8$ ,  $3.1 \pm 2.7$ ,  $0.07 \pm 0.06$ , and  $0.1 \pm 0.2$  for Cu, Zn, Cd and Pb respectively. Suspended sediments (concentration range 2-19,000 mg/L, median 20 mg/L, defined as that fraction of stream water components retained on 0.45  $\mu\text{m}$  filters) contributed ( $\mu\text{g/L}$ ) 0.3-437 of Cu, 1.3-2,850 of Zn, 0.00-11.4 of Cd, and 0.3-399 of Pb with corresponding median concentrations  $\pm$  standard errors of  $4.3 \pm 0.5$ ,  $9.1 \pm 2.6$ ,  $0.09 \pm 0.06$  and  $3.1 \pm 1.1$  for Cu, Zn, Cd and Pb respectively. Ranges of total element concentrations and (medians  $\pm$  standard errors) ( $\mu\text{g/L}$ ) in stream waters were: Cu, 2.2-445 ( $3.9 \pm 2.6$ ); Zn, 4.3-2,500 ( $17.2 \pm 4.9$ ); Cd, 0.03-13.4 ( $0.08 \pm 0.02$ ); Pb, 0.9-433 ( $3.7 \pm 1.0$ ) .

Levels of these elements in dissolved form were generally found to be independent of suspended sediment concentration over the range 10-19,000 mg/L, but levels contributed by the suspended sediment were proportional to the sediment load of the stream. For Cu and Zn, the proportion of the total element concentration, associated with particulate stream material, increased with suspended sediment concentration over the range *ca* 0-100 mg/L and thereafter remained constant at *ca* 80-90%. In waters with low suspended sediment levels, below *ca* 20 mg/L, the majority of Cu and Zn is transported in dissolved form, whereas the suspended sediment accounts for most of the transport of these trace elements at higher particulate loads. The very low levels of Cd and Pb in natural waters, coupled with the experimental difficulties associated with their measurement, preclude firm conclusions regarding these elements.

Trace element concentrations in water samples, determined by acid leaching or solvent extraction treatment of the aqueous sample, without complete dissolution of the suspended sediment, approached total concentration values determined by complete destruction of particulate matter when suspended sediment levels were low, but were more deviant at higher suspended sediment loads. The former, however, were always lower than total levels, but were generally reasonable estimates of total concentrations.

The nature of the suspended sediment seemed to depend on its concentration in the water. Both solubility and amount of trace element leached-out by acid increased with decreasing suspended sediment load, suggesting a change in the physical and chemical character of the particulate material with its concentration in the stream. There was also a

hint that the concentration of Cu and perhaps other trace elements in the particulate material, increased with decreasing suspended sediment load.

It is difficult to meaningfully compare trace element levels in each of the six watershed streams because of the paucity of data, and an insufficient number of sampling periods. As dissolved levels were, however, fairly invariable, pooling these results over all watersheds gives the following information regarding mean, median, and 95% range concentrations ( $\mu\text{g/L}$ ): Cu, 2.2, 2.0, 0-4.6; Zn, 3.6, 3.1, 0-10.3; Cd, 0.12, 0.07, 0-0.50; Pb, 0.3, 0.1, 0-1.5. If there is no change in the watersheds, this information predicts that, for example, the most likely concentration of dissolved Cu to be encountered in a sample of stream water from any of these six watersheds is in the vicinity of 2  $\mu\text{g/L}$ , and 95% of all samples will fall within the range ca 0-5  $\mu\text{g/L}$ . From relations between total trace metal levels and suspended sediment concentrations, one can also estimate total concentrations of these trace elements knowing only the suspended sediment content of the stream.

In samples with low (< 20 mg/L) suspended sediment levels (one half of those investigated), most of the Cu and Zn were found and transported in the dissolved state. As the dominant mode of transport, at least for Cu and Zn, seems closely related to the particulate concentration in the waters, the most important mechanism for removing large amounts of element from the watersheds over the course of a year may be sediment transport. Detailed concentration, stream flow and integrated suspended sediment concentration information is required for accurate calculations of loadings. Although much information has been gleaned from a rather small body of data, much more valuable and interesting information regarding storage and transport mechanisms and loadings, can be obtained with only moderate effort from a continued small scale study of these six agricultural watersheds. Very sparse data is available on the behavior of the toxic elements Cd and Pb, and particular attention should be devoted to them.



## INTRODUCTION STUDY OBJECTIVES

The primary objective of project 9 was to determine and assess the relationship between concentrations of selected heavy metals in stream waters, suspended sediments, bottom sediments, and soils within selected agricultural watersheds draining into the lower Great Lakes, with the aim of elucidating storage and transport mechanisms. In support of the goals of project 9, the objectives of the investigation reported here were:

- (1) To assess, develop and adapt analytical methodology for the determination of trace and ultratrace levels of copper, zinc, cadmium and lead in water and suspended sediment samples.
- (2) To obtain reliable analytical information regarding concentrations of these metals in waters and suspended sediments from six watersheds selected by PLUARG for intensive study.
- (3) To assess relationships between metal concentrations in dissolved and particulate forms and to elucidate metal transport and storage mechanisms.

All of these goals relate to the overall objective of PLUARG in the agricultural watershed surveys, task C, activity 1 (International Reference Group on Pollution of the Great Lakes from Land Use Activities (Land Drainage Reference Group) 1974): "to obtain data on the inputs of pollutants into the Great Lakes Drainage System which have their origin in the complex land use activities known as agriculture", and to the detailed objectives:

### Phase II (Detailed Studies Program)

- (1) To determine the effects of the soil, land use and associated practices on ambient concentrations and loading rates of selected pollutants from agriculture.
- (2) To derive information on the mechanics of transport and storage of these pollutants within the selected agricultural watersheds.

- (3) To develop relationships so that the information derived can be utilized in a predictive sense and extrapolated to other areas.

A number of heavy metals, including Cu, Zn, Cd and Pb have been designated by PLUARG for surveillance.

## STUDY APPROACH

Water samples from the six agricultural watersheds AG1, 3, 4, 5, 10 and 13 were collected and processed by investigators in projects 8 and 9 of the Agricultural Watershed Studies, Task C, PLUARG, according to the protocol specified by the author. Most samples were collected at the same time as water and bottom sediment samples provided to other investigators in this and related projects. One half of the water samples were field-filtered, and unfiltered and filtered natural water samples, suspended sediments and processed and unprocessed control distilled water samples, all acid-preserved, were shipped to the author's laboratory in Ottawa. The very low, ultratrace concentrations ( $\mu\text{g/L}$  and sub  $\mu\text{g/L}$ ) at which these elements are normally found in natural waters necessitated careful execution of sampling and analysis. Efforts were concentrated on these aspects of the project particularly on analysis, the facet most easily controlled by the author, the premise being that valid analytical data are pre-requisites for sound conclusions and decisions. This approach served also to, hopefully, produce compatible data for comparison with other investigations as specified by PLUARG. Central to the attainment of accurate data was attention to contamination-prevention, data quality control, and the participation of several laboratories using different analytical approaches to sample treatment and measurement. Reasonably reliable experimental data were obtained regarding total, dissolved and suspended sediment-contributed concentrations of Cu, Zn, Cd and Pb. Relationships among these trace element concentrations and suspended sediment levels were established, information was gleaned regarding the physical and chemical nature of the suspended sediment, and conclusions were formulated regarding the mode of storage and transport of these trace elements in stream waters. It was expected that the analytical data would be useful to other objectives of project 9 dealing with relationship between trace element levels in water components and bottom sediments and adjacent soils, and

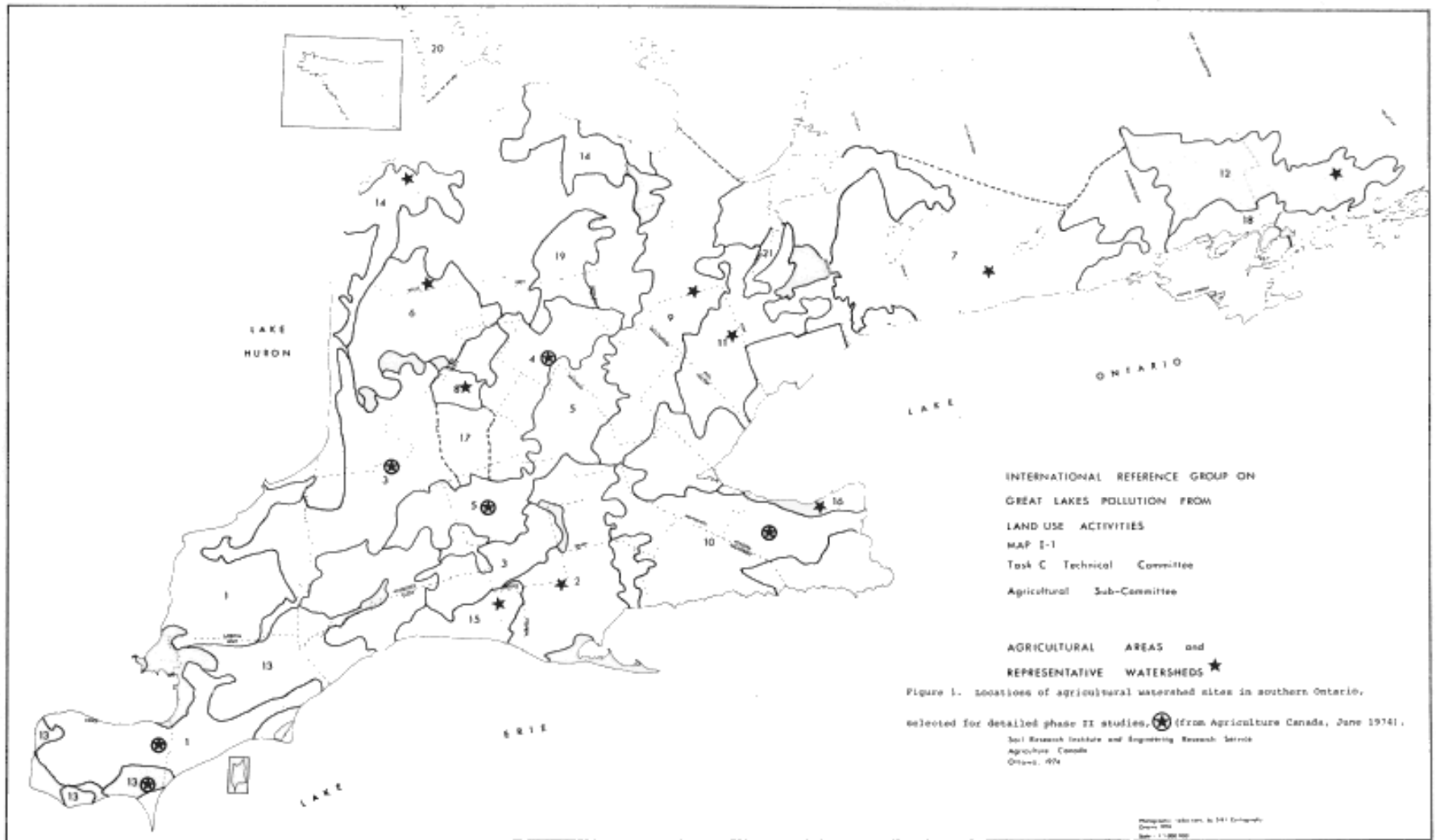
correlations of mineralogy, clay content and organic matter content of suspended sediment, bottom sediment and soil with respective metal concentrations. As much information was generated by the investigation described in this report, it was mutually decided among the project leaders in project 9, that two separate reports would be issued, one by Whitby, MacLean, Schnitzer and Gaynor (1978), referred to as project 9A, another by Ihnat (this report), designated project 9B.

## WATERSHED LOCATIONS

Agricultural areas and the six representative agricultural watershed chosen by PLUARG for intensive study are located on the map of southern Ontario depicted in figure 1. More detailed maps of locations and watershed boundaries may be found in Frank and Ripley (1977). Brief descriptions of the watersheds are given in Table 1; detailed documentation regarding descriptions of the agricultural areas and the small representative watersheds, including climatic zones, soil types and potential for pollutant transfer to water systems, agricultural land use inventory, and fertilizer use is available in other reports (Agriculture Canada 1974, 1975; Frank and Ripley, 1977).

Table 1. Description of Agricultural Watersheds selected for detailed studies

Code	Name of drainage basin	Location (county)	Area(km) <sup>2</sup>	Major soil type	Major land use activity (1974)
AG1	Big Creek	Essex	51.8	clay	soybeans, small grains, corn
AG3	Upper Little Ausable River	Huron	54.1	clay, loam	corn, small grains, forage and pasture, soybeans
AG4	Canagagigue Creek	Wellington	18.9	clay, loam	small grains, forage and pasture, corn
AG5	Holiday Creek, tributary of Middle Thames River	Oxford	29.5	silt, loam	corn, forage and pasture, small grains
AG10	Twenty Mile Creek, North Creek Branch	Lincoln	29.8	clay	forage and pasture, small grains, corn
AG13	Hillman Creek, West Branch	Essex	20.7	sandy loam	corn, small grains, horticultural





## DATA COLLECTION METHODS

### SAMPLING SITES AND SAMPLE COLLECTION

Stream water sampling sites, one in each watershed for all sampling during 1976 and 1977, were selected near the outlet sites of the streams from the watersheds and were usually on the upstream side of the bridges traversing the streams, at the gauging stations. Locations of the sampling sites are listed in Table 2. Drainage systems of each of the six watersheds and map locations of the water study sites are depicted in Figures 2-7. The sampling sites for water samples for this project are fairly well identical to the sites from which water and bottom sediment samples were taken for projects 9A (Whitby *et al.*, 1978) and 8 (Wall, 1978). Detailed descriptions of the sites and surrounding areas and exact locations of water (and therefore suspended sediment) and bottom sediment sampling sites were provided by K.L. LaHay. Parameters determined at the collection sites during sampling included stream velocity, width and depth, water temperature and pH, and dissolved O<sub>2</sub> and CO<sub>2</sub>. Details of collection and parameter measurements are available from G. Wall. Attempts were made to collect water samples during low and high flow conditions and several "event" samples were collected.

For estimation of trace metals at the µg/L levels, positive or negative contamination of the sample during sampling, handling, sample treatment and determination is a problem of continual concern, and care was exercised at each of the many steps of the sampling and analytical procedures. All glass and plastic ware used in collection and analysis, which came in contact with the water samples (with the exception of membrane filters used in the field) were acid cleaned prior to use. This was accomplished by contacting the item with 1 M reagent grade HNO<sub>3</sub> for at least 24 hr, and thoroughly rinsing with distilled or deionized water. Containers for storage of water samples were left filled with deionized water until required in the field; they were then drained, recapped and shipped to the samplers in Guelph. Containers for collection and storage of water samples were typically 1 L white, linear polyethylene, (LPE), narrow neck bottles with polypropylene (PP) screw closures without liners, providing for leak-proof sealing (Nalge Co., Rochester, N.Y.). Those which were not new, were first washed with detergent prior to acid treatment.

Water samples were collected using either a US DH-48 hand-held sampler fitted with a ca 450 ml glass bottle (earlier sampling), or an electric-powered peristaltic pump with tygon tubing (later sampling). Efforts were made to provide for vertical and lateral

integration of streams to give representative samples. This was accomplished where possible, by making a number of transects across the stream. Unfiltered water samples were collected by filling stream water-rinsed containers, directly from the DH-48 sampler, three or four transfers of *ca* 300 ml each being required, or from a 20 L carboy used as a temporary storage vessel. Contents of the latter vessel were agitated prior to dispensing, to redisperse suspended sediment. Two acids, reagent grade  $\text{HNO}_3$ , and  $\text{HCl}$  were used for sample preservation, with 2 ml of the 1:1 acid being dispensed into the 1 L sample immediately after collection. Quadruplicate unfiltered water samples were usually collected, one half acidified with each preserving acid. Hydrochloric acid was the necessary matrix for analyses by anodic stripping voltammetry. Samples collected in 1977 were shipped unacidified; acid was added to one half of the samples in Ottawa.

Field-filtered samples were prepared as follows: Four Sartorius polycarbonate 250 ml capacity filtering apparatuses (no. SM 16510) were assembled in tandem and fitted with Sartorius 47 mm diameter, 0.45  $\mu\text{m}$  pore size cellulose acetate membrane filters (no. SM 11106.047). The collection vessels were rinsed with the filtered water samples, 1 L of filtered water was collected by the application of vacuum with a hand pump, poured into a rinsed (filtered water) polyethylene bottle and acidified with  $\text{HNO}_3$ . This procedure was repeated with new membrane filters, and the collected filtrates were acidified with  $\text{HCl}$ . Membrane filters were removed and placed (in pairs with sediment sides in contact) in polyethylene-lined bags.

Duplicate 1 L volumes of distilled water were similarly filtered, and two other 1 L aliquots of distilled water were poured from the storage vessel into collection bottles to provide respectively, filtered and unfiltered quality control blanks in order to monitor the collection-filtration-storage procedure. Water and suspended sediment samples were placed in cold storage (*ca* 4°C) at the samplers laboratory in Guelph, and were shipped unrefrigerated, shortly thereafter to the analytical laboratory at the Chemistry and Biology Research Institute (CBRI), in Ottawa, where they were again stored at *ca* 4°C until analyzed. Typically, each sampling provided a total of 8-10 1-L samples: two-four unfiltered natural water samples one or two each preserved with  $\text{HNO}_3$  and  $\text{HCl}$ , one filtered natural water sample preserved with  $\text{HNO}_3$ , one filtered natural water sample preserved with  $\text{HCl}$ , two unfiltered and two filtered distilled water samples, one of each preserved with  $\text{kNO}_3$  and  $\text{HCl}$ , eight membrane filters containing suspended sediment from the duplicate filtering of natural water, and eight membrane filters from the duplicate filtering of distilled water. In addition, seven blind replicate natural and distilled water samples were sent to the Ottawa

laboratory as part of the quality procedure requested by PLUARG. Samples of the two acids used for field preservation, added to aliquots of pure deionized water supplied by the analytical laboratory at CBRI, and samples of the cellulose acetate filters used in the field were also forwarded to Ottawa for determination of contamination levels. A total of 140 natural water samples, 100 distilled water control samples, and 30 suspended sediment-on-filter samples (120 filters) were received for analysis. The bulk of these represented sampling during 1976; several were obtained during the 1977 spring run-off. The few samples collected in 1975 were used for preliminary analyses.

## CHEMICAL ANALYSIS

Of all the steps taken to insure analytical data of some reliability, most important to this study was the involvement of three other laboratories using several independently different analytical methods. Methodologies used for water and sediment sample analysis, and cooperating principal investigators are listed in Table 3. Descriptions of these analytical approaches and other facets of the experimental work are given below.

### Experimental Procedures in C.B.R.I. Laboratory

#### Subsampling of Water and Suspended Sediment Samples

Some time after receipt from the field, water samples were subsampled in the author's laboratory to provide aliquots of identical samples for analysis by the four laboratories participating in water analysis (Ihnat, Stoepler, Berman and Gaynor). Samples were removed from cold storage, shaken to redistribute settled sediment, and suitable portions were poured into 60-200 ml clean, LPE bottles after rinsing with sample solutions. Five hundred + ml of each sample was retained, usually in the original container, for analysis in the author's laboratory; the other subsamples were shipped to the three other laboratories. One half of the natural water samples and 15% of the distilled water control samples were subsampled.

Suspended sediment and residue samples were generally divided into two groups for analysis. Those samples with weights of 10's of mg were retained by the author for analysis by acid digestion/flame atomic spectrometry, whereas samples containing only several mg of material were forwarded to Russell and Tymchuk at NRC for analysis by optical emission spectrography. Occasional subsampling was done on high weight samples to permit analysis of identical samples by both laboratories.

## Reagents and Solutions

All reagents used were reagent grade or better. Deionized water was used throughout and was prepared by passing tap water through a train of four columns in the sequence: adsorber cartridge (no. 1506-10), universal ion exchange cartridge (no. 1506-20), and two research ion exchange cartridges (no. 1506-30) (Cole Parmer, Chicago, Illinois). The conductivity of freshly deionized water, as measured with a Radiometer conductivity meter was at the theoretical limit of  $0.055 \mu\text{mho cm}^{-1}$ ; the water was stored in a 20 L polyethylene container. Acids used for sample processing and other procedures were of the highest purity available (Ultrex  $\text{HNO}_3$  from J.T. Baker, Chemical Co., Phillipsburg, N.J., double distilled  $\text{HNO}_3$  and  $\text{HClO}_4$  from G. Frederick Smith, Chemical Co., Columbus, Ohio, and high purity HF prepared by sub-boiling evaporation, courtesy of NRC, Ottawa).

Cu, Zn and Cd metals and  $\text{Pb}(\text{NO}_3)_2$  were used as sources of the elements for standard solutions. The metals were dissolved in conc.  $\text{HNO}_3$  and the salt in water to prepare 1000  $\mu\text{g/ml}$  stock solutions *ca* 0.1 M with respect to  $\text{HNO}_3$ . Composite working solutions were prepared containing equal concentrations of each of the four elements. Standard solutions on which atomic absorption readings were made had 0, 50, 100, 200, 500 and 1000  $\text{ng/ml}$  of each element in an acid matrix matching that of the samples. Quality control standard solutions containing the four elements at levels of 500 and 600  $\text{ng/ml}$  in 0.2 M  $\text{HNO}_3$ , designated Q1 and Q2 respectively, were prepared and 1 L of each was used throughout this work (17 months), to monitor spectrometer performance and other facets of the analytical procedure.

A stock solution of 100-fold concentrated synthetic natural water was prepared from  $\text{CaCO}_3$ ,  $\text{MgSO}_4$ , NaCl, HCl and deionized water, to contain three of the most common inorganic cations found in fresh natural waters at levels of *ca* 10,000 mg Ca/L, 2000 mg Mg/L and 1000 mg Na/L. The stock solution was diluted with water as required (the solid in the stock was dispersed prior to removal of aliquot and dissolved completely upon dilution). A 100-fold diluted solution simulating a natural water sample had a pH of *ca* 2.5, about the value for acid-preserved samples of real natural water samples.

Two synthetic natural water quality control solutions were prepared by diluting 200 ml of the 100-fold concentrated stock solution + 100 ml conc.  $\text{HNO}_3$  to 1 L. One, denoted

AA with no other additions, was a 20-fold concentrated blank synthetic water sample in 1.6 M HNO<sub>3</sub>, the second, denoted BB was spiked with the four elements to contain an added 100 ng/ml of each. These samples, simulating the typical 20-fold concentrated natural water sample, were used in conjunction with Q1 and Q2 to monitor data quality.

EPA quality control samples for trace metal analyses (US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Quality Assurance Branch, Cincinnati, Ohio, courtesy of Mr. J.A. Winter) containing a mixture of trace elements in a nitric acid solution were obtained and used for validation of analytical procedures. Two different ampoules of each of the three concentrates, nos. 1-575, 2-575, 3-575 containing Cu, Zn, Cd and Pb at three different concentrations were used. Twenty ml of each concentrate together with 1 ml conc. HNO<sub>3</sub> were separately diluted to 2 L and stored in LPE bottles until analyzed; final HNO<sub>3</sub> concentration was 0.016 M as for all water samples.

#### Evaporation/Flame Atomic Absorption Spectrometry

Nitric acid- and HCl-preserved unfiltered and filtered natural water and distilled water control samples were heat-concentrated by a factor of 10-50 usually 20- or 50-fold. Typically, 500 ml of sample was measured into a 600 ml teflon beaker (polytetrafluoroethylene, PTFE, Bel-Art Products, Pequannock, N.J.) followed by the addition of 2 ml or 0.5 ml of HNO<sub>3</sub> for reduction to 25 ml (20x) or 10 ml (50x) respectively. The sample volume was reduced by sub-boiling evaporation for ca 15 hr in a clean micro-environment, to less than 25 or 10 ml, transferred (inclusive of residue) to a volumetric flask and made up to volume with water. The apparatus used for heat concentration was after the design of Thiers (1957). Samples were placed on a tray on a large hot plate and covered with 2 L pyrex beakers fitted with side arms at the bottom to permit the introduction of 0.45 µm-filtered air. Heat was applied above by 250 W infra-red lamps and from below, as required, by the hot plate.

The PTFE beakers were cleaned by contacting with hot 1:1 HNO<sub>3</sub> for 24 hr, rinsing with water, and thereafter rinsing with water before each use. Occasionally, these containers were recleaned by rinsing with 1:5 high purity HNO<sub>3</sub>. Volumetric flasks separately dedicated to measurement/dispensing of deionized water, filtered natural water and other clean samples, and unfiltered natural water samples were used to minimize cross-contamination. Samples processed included the natural water and distilled water

quality control samples, deionized water for estimation of reagent blanks, EPA quality control solutions, and deionized water, synthetic natural water and selected natural water samples spiked with different levels of Cu, Zn, Cd and Pb to test recoveries. Deionized water and related aliquots were acidified in the beakers with 2.5 and 1 ml conc. HNO<sub>3</sub> for reduction to 25 ml and 10 ml respectively, to give the same 1.6 M HNO<sub>3</sub> concentration in the final solutions as for natural water samples. One reagent blank was run with each set of 5-7 samples, on a rotating basis among the eight beakers used for reduction. One fifth of the natural water samples were analyzed in duplicate for Cu and Zn; 5% were analyzed in duplicate for Cd and Pb. Some samples such as the EPA solutions were also analyzed for the four elements by direct aspiration-FAAS without preconcentration, as were several water samples to determine Zn. Standard solutions were prepared to be identical to sample solutions in respect of the type and concentration of bulk acids.

The atomic absorption spectrometer used was a Varian Techtron (Varian Techtron Pty. Ltd., N. Springvale, Victoria, Australia) Model AA5 equipped with an R446 photomultiplier tube, an IM6D amplifier with a digital read-out, and a BC6 background corrector module. Air/acetylene flames were supported on a single slot (100 x 0.5 mm) AB51 burner head; solutions were aspirated into the flame at *ca* 5 ml/min through either a fixed or variable nebulizer. Air was introduced at a flow rate of *ca* 10 L/min (20°C and 1 atm) and the flow rate of acetylene was 0.3 L/min for Cu, Zn and Cd, and 1.2 L/min for Pb. Radiation from single element hollow cathode lamps (Varian Techtron, and Cathodeon Ltd. Cambridge, England) operated at 2mA(Cu), 5mA(Zn) and 3mA (Cd and Pb) was directed through the flames at a height of 5 mm above the top of the burner head. Entrance and exit slits on the monochromator were optimized at 50, 100, 150 and 300 µm for Cu, Zn, Cd and Pb respectively, corresponding to respective spectral band passes of 0.2, 0.3, 0.5 and 1.0 nm. Absorbances were measured at wavelengths for Cu, Zn, Cd and Pb of 324.8, 213.9, 228.8 & 217.0 nm respectively, and read on the digital read-out meter using a scale expansion of 10x and typically a 10 sec integration period. All readings were corrected for non-atomic absorbance by simultaneous use of a H<sub>2</sub> hollow cathode lamp (Varian Techtron) operated at a current to match emission intensities of the analyte lamps.

In a typical atomic spectrometric determination, six composite standard solutions containing 0-1000 ng/ml of each of the four elements, and quality control samples Q1, Q2, AA, and BB were run for one of the elements, followed by up to 10 sample solutions. Water was aspirated and read in between every solution to get instrumental zero readings. This

sequence was repeated with other sets of sample solutions until a total of up to 50 samples had been run. Instrumental parameters were then reoptimized with respect to maximum absorbance of check solutions and the entire measurement procedure was repeated to give duplicate FAAS determinations. This procedure was repeated for each of the three remaining elements. For calculating concentrations, standard solution absorbances measured with respect to water, and corrected for mean absorbance of acid reagent blanks, were plotted on large graphs against standard solution concentrations. Concentrations of Cu, Zn, Cd and Pb in the sample and quality control solutions were either read from the calibration curves, or calculated from the slopes of the linear portions of the curves. Application of appropriate concentration factors and correction for processing reagent blanks, gave concentrations in the original sample; no corrections were made for undissolved solid residue in the heat-concentrated solutions.

A small number of unfiltered natural water samples were also subjected to a more rigorous acid treatment procedure involving  $\text{HClO}_4$ . In this procedure, 500 ml of the sample +2 ml conc.  $\text{HNO}_3$  was evaporated as described above, to ca 100 ml and transferred to a tared 250 ml PTFE beaker. Further reduction of volume to 10-15 ml was effected, in the open, on a hot plate, 5 ml conc.  $\text{HNO}_3$  + 10 ml 70%  $\text{HClO}_4$  were introduced, the beaker was covered with a PTFE cover, and contents were refluxed for 1 hr. Heating was continued with cover displaced slightly to permit evaporation, until the volume of  $\text{HClO}_4$  was reduced to < 2.5 ml, the beaker and cover were weighed to 0.01g and condensed acid on the cover was rinsed into the beaker. Based on the estimated weight of  $\text{HClO}_4$  remaining (calculated from the weight of the contents and the total solids content of the sample), 70%  $\text{HClO}_4$  was added to provide a total of 2.5 ml of acid, and the liquid contents were transferred to a 25 ml volumetric flask and made to volume. Reagent blanks were similarly processed, and Cu, Zn, Cd and Pb in all solutions were determined by flame atomic spectrometry.

#### Analysis of Suspended Sediments and Residues by Acid Digestion/Flame Atomic Absorption Spectrometry

Suspended sediment samples received from the field and prepared in this laboratory, and solid material remaining after evaporation of acidified water samples, were analyzed by acid dissolution/flame atomic spectrometry. The suspended sediments-on-filters received from the field were dried at 70°C, weighed and scraped off with a teflon coated spatula into glass vials.

Upon completion of spectrometric analysis of the supernatant liquid phases of heat-concentrated solutions, those with visible solid residues were vacuum-filtered through 0.4  $\mu\text{m}$ , 47 mm diameter Nuclepore membrane filters (no. N040 Nuclepore Corp., Pleasanton, CA) supported on a Sartorius polycarbonate SM 16510 filter holder without the use of the silicone gasket or funnel. Solid material thus collected from unfiltered natural water samples, represented acid-leached suspended sediment, and is denoted residue, to distinguish it from bona-fide suspended sediment. Upon drying at *ca* 70°C under infrared lamps, the filters plus contents were weighed and residues were transferred to glass vials. Occasionally, solutions with trace quantities of residue were filtered through smaller filter sections cut from the 47 mm filters, permitting lower detection capability. In general, the estimated detection limit, based on three times the standard deviation of the weights of blank filters, was about 0.5 mg.

Suspended sediments in water samples collected in the Spring of 1977 were isolated in this laboratory by filtration of the unacidified samples through acid-cleaned 0.4  $\mu\text{m}$  Nuclepore membrane filters supported on Sartorius filter holders (with silicone gaskets and funnels). There was an unavoidable time lag between sample collection and processing. That this did not result in any serious effect is evident from the data presented in Fig. 31, page 116. The holders were cleaned disassembled by contacting with 1 M  $\text{HNO}_3$ . Filters were cleaned by inserting 4-5 together into a filter holder, filtering through, 200 ml 1 M  $\text{HNO}_3$  to fill pores with acid, and soaking in 1 M  $\text{HNO}_3$  for two days. They were then rinsed with water, by filtration, to remove acid from the pores, and soaked in water until used. The filtration procedure for natural water samples was as follows: Three filter holders were connected in series and to a water aspirator pump, and each was fitted with a clean filter. Each filter was rinsed, by filtration, with 250 ml water and then in turn with the same 50 ml aliquot of natural water sample (agitated to redisperse settled sediment). The remainder of the 1 L sample was then filtered in three equal portions through the three filters, the filtrates were pooled and acidified with 1 ml of conc.  $\text{HNO}_3$ . In cases where filtration slowed considerably due to clogging of pores, new filters were inserted to complete the filtration; 1 ½ to 3 hrs. and 3-6 filters were required for each of the four samples. Filters plus contents were dried at *ca* 70°C, and suspended sediment concentrations in the waters were computed from the weights of dry sediments and total volume of water filtered. Tests with four different sediments showed that drying at 70°C gave weights within 2-3% compared with drying at 110°C.

In a typical elemental analysis scheme, 3-30 mg (occasionally < 1 mg) of dry suspended sediment or residue was weighed into a tared 30 ml PTFE beaker fitted with a cover, and refluxed with 2 ml conc. HNO<sub>3</sub> + 2 ml 70% HClO<sub>4</sub> for 2 hrs. at 210°C. The cover was removed, the volume of the solution was reduced to < 1 ml and the contents were refluxed twice for 30 min. each, with two 0.5 ml portions of HF to completely dissolve the sample. The solution was reduced to near-dryness, cooled, beaker + contents were weighed to 0.001 g, and 70% HClO<sub>4</sub> was added to give a total weight of 0.340 g 70% HClO<sub>4</sub>. The solution was transferred to a graduated 15 ml polyethylene centrifuge tube and made to 2 ml; final HClO<sub>4</sub> concentration was 1.2 M. A reagent blank was run with every five samples, and a number of samples were analyzed in duplicate to calculate precision and detection limits. Several USGS rock samples were also processed to get estimates of accuracy.

For determination of element levels by flame atomic absorption spectrometry, instrumental parameters and procedures were similar to those described above except that solution aspiration rate was reduced to *ca* 3 ml/min to accommodate measurement with small volumes of solution available. Read-out of absorbance was on either a strip chart recorder (Hitachi Model 056, Perkin-Elmer Corp., Norwalk, CT) with B or C damping, or on a digital read-out meter with 3-10 sec integration period, and scale expansions of 10-50x. Measurements were made first for Cd using the most concentrated solutions (2 ml volume). The sample solution was then diluted with 1.2 M HClO<sub>4</sub> by a factor of two in the graduated tube, for measurement of Cu and Pb, followed by an additional 10-fold dilution for determination of Zn. This sequence of measurement and dilution was adopted to read the element at the lowest expected concentration in the most concentration solution, to have sufficient volume for the other elements, and to bring absorbance readings on scale. Dilutions with respect to the initial volume were 1, 2, 2, and 20 for Cd, Cu and Pb and Zn respectively.

#### Experimental Procedures for Analysis of Water Samples in Cooperating Laboratories

Brief descriptions of methodologies followed by cooperating laboratories are provided here, based on information and publications communicated to the author.

Perkin-Elmer Heated Graphite Atomizer/Atomic Absorption Spectrometry  
- M. Stoeppler

Electrothermal atomization measurements for Cu, Cd and Pb were carried out with a Perkin-Elmer AS-1 Auto Sampling System operated with a PE 400 atomic absorption spectrometer and an HGA 74 graphite furnace (Stoeppler *et al.* 1976). Fifty  $\mu\text{l}$  aliquots of  $\text{HNO}_3$ -preserved samples were taken, analyzed against calibration graphs of the elements in acidic aqueous solution, and occasionally using the technique of standard additions. Only the clear supernatant of unfiltered natural water samples was sampled, and all solutions were analyzed directly, without treatment. Drying, ashing and double atomization temperature and time programs were respectively: Cu, 100°C (60 sec), 800°C (30 sec), 2550°C (5 sec), 2600°C (5 sec); Cd, 100°C (60 sec), 300°C (30 sec), 1900°C (5 sec), 2650°C (5 sec); Pb, 100°C (60 sec), 300°C (30 sec), 2400°C (5 sec), 2650°C (5 sec). Simultaneous non-atomic absorption compensation was made using a deuterium lamp. Some Pb measurement were carried out on a Jarrell-Ash 811 atomic spectrometer in conjunction with the above systems, at a wavelength of 283.3 nm, using the 282 nm non-absorbing line for non-atomic compensation. After blind analysis by these methods, concentrations were compared with those obtained by differential pulse anodic stripping voltammetry in the same institute, and some samples with too great a discrepancy between these values were reanalyzed applying the standard additions technique. The methodology code 2A refers to preliminary data obtained by not pushing the technique to its full potential; 2B refers to an extensive second set of results obtained using the full capability of the method.

Differential Pulse Anodic Stripping Voltammetry with Hanging Mercury Drop Electrode (DPASV/HME), and with Mercury Film Electrode (DPASV/MFE).  
- M. Stoeppler and P. Valenta

Concentration data for early analysis of a small number of samples was obtained using the DPASV/HME technique. All other (the bulk) analyses were done with the technique of DPASV/MFE (Nürnberg *et al.* 1976, Valenta *et al.* 1976) using an adapted Polarographic Analyzer Model 174A (Princeton Applied Research) in connection with a Hewlett-Packard X-Y recorder Model 7004B. The sensitive rotating mercury film-coated glassy carbon electrode was a modified construction of Sipos, Magjer and Branica (1974). Both  $\text{HNO}_3$ - and  $\text{HCl}$ -preserved sample solutions were analyzed, with the latter acid matrix

preferred, and results were provided for Cu, Cd and Pb. All analyses were done in duplicate, and again, only supernatant liquid of unfiltered natural water samples was sampled.

Varian Techtron Carbon Rod Atomizer/Atomic Absorption Spectrometry  
- S.S. Berman and A. Desaulniers.

Measurements for all four elements were conducted with a Varian Techtron electrothermal atomizer, CRA 63, with a modified Model AA5 spectrometer using 5  $\mu$ l injections. All solutions were analyzed with no treatment except dilution of those too concentrated for this technique, and those samples with insolubles were analyzed by sampling only the supernatant liquid. Calibration was done with standards of the elements prepared in 0.1 M HNO<sub>3</sub>. A total of 12 measurements on each of the five standard solutions were made each day and the 60 points (with rejections of odd outliers) were fitted with regression curves. Points for Cu, Cd and Pb were fitted with linear regression lines while a quadratic fit was used for Zn. Each sample was analyzed four times sequentially and averaged absorbances of these four firings, with no rejections, were used to calculate element concentrations. Confidence intervals were computed from the fits of calibration curves. Non-atomic absorption compensation using a H<sub>2</sub> hollow cathode lamp, operated simultaneously, was applied for Zn, Cd and Pb in ca 2/3 of the samples using a custom-made background corrector. When element levels are very low, multiple 5  $\mu$ l injections were made with drying in-between, and absorbances were read from calibration curves prepared in an identical manner.

Solvent Extraction/Flame Atomic Absorption Spectrometry - J.D. Gaynor

The metals Cu, Zn, Cd and Pb were determined by direct solvent extraction from water samples and flame atomic spectrometry (Gaynor, 1977). They were concentrated 10x in a separatory funnel from 100 ml of water with an extracting solution containing 0.4 g dithizone, 6.0 g quinolinol, and 200 ml acetylacetone in 1 L n-butylacetate. Twenty ml of 5% ammonium tartrate and 2 drops of p-nitrophenol indicator was added and the sample adjusted to pH 6 with 1:2 NH<sub>4</sub>OH or tartaric acid crystals. The water sample was saturated with 2 ml n-butylacetate after which 8 ml of the extractant was added. The mixture was shaken one minute and the aqueous phase discarded after separation for 20 min. The organic phase was permitted to stand 10 min and the remaining aqueous phase discarded.

The stem of the separation funnel was dried with a filter paper and the organic phase diluted to 10 ml and analyzed by atomic absorption spectrometry. Organic standards were prepared by adding metal of known concentration to 100 ml deionized water and extracting as indicated for samples. Organic solutions were aspirated into an air-acetylene flame of an IL 251 atomic spectrometer (Instrumentation Laboratory Inc., Lexington, Mass.) and absorbances were read at a 4 sec integration time.

Table 2. Stream water sampling sites in agricultural watersheds <sup>a</sup>

Watershed	Outlet site location <sup>b</sup>	
	metres east	metres north
AG1	374,750	4,672,100
AG3	466,300	4,793,500
AG4	532,000	4,834,700
AG5	503,000	4,775,000
AG10	618,800	4,770,400
AG13	372,500	4,657,500

<sup>a</sup> Location of water sampling site is taken to be given by location of watershed stream outlet site due to proximity of the two. For 1977 samplings in AG5, samples from two sites denoted 1 and 5 were provided. Site 5 was at the outlet site, whereas site 1 was a short distance away at the source of erosion from the field.

<sup>b</sup> All in UTM zone 17; taken from Agriculture Canada, 1975.

Table 3. Analytical methods for water analysis

Description	Principal investigators	Code
<b>Analysis of water samples</b>		
Heat evaporation/ flame atomic absorption spectrometry	M. Ihnat and A.D.Gordon CBRI, Agriculture Canada Ottawa	Evap/FAAS(1)
Perkin-Elmer heated graphite atomizer/ atomic absorption spectrometry	M. Stoepler, Institute for Chemistry, 4 Nuclear Research Centre Juelich, Federal Republic of Germany	HGA/AAS(2A,2B)
Differential pulse anodic stripping voltammetry with hanging mercury drop electrode	M. Stoepler and P. Valenta	DPASV/HMDE(3A)
Differential pulse anodic stripping voltammetry with mercury film electrode	M. Stoepler and P. Valenta	DPASV/MFE(3B)
Varian Techtron carbon rod atomizer/atomic absorption spectrometry	S.S. Berman and A. Desaulniers Analytical Chemistry Section Division of Chemistry, National Research Council of Canada, Ottawa	CRA/AAS(4)
Solvent extraction/flame atomic absorption spectrometry	J.D. Gaynor, Research Station Agriculture Canada, Harrow	Sol. ext/FAAS(5)
<b>Analysis of sediment samples</b>		
Acid digestion/flame atomic absorption spectrometry	M. Ihnat and A.D. Gordon	
Optical emission spectrography	D.S. Russell and P. Tymchuk Analytical Chemistry Section Division of Chemistry, National Research Council	

AGRICULTURAL WATERSHED # 1, BIG CREEK (ESSEX COUNTY)  
PART OF LOWER THAMES DRAINAGE BASIN

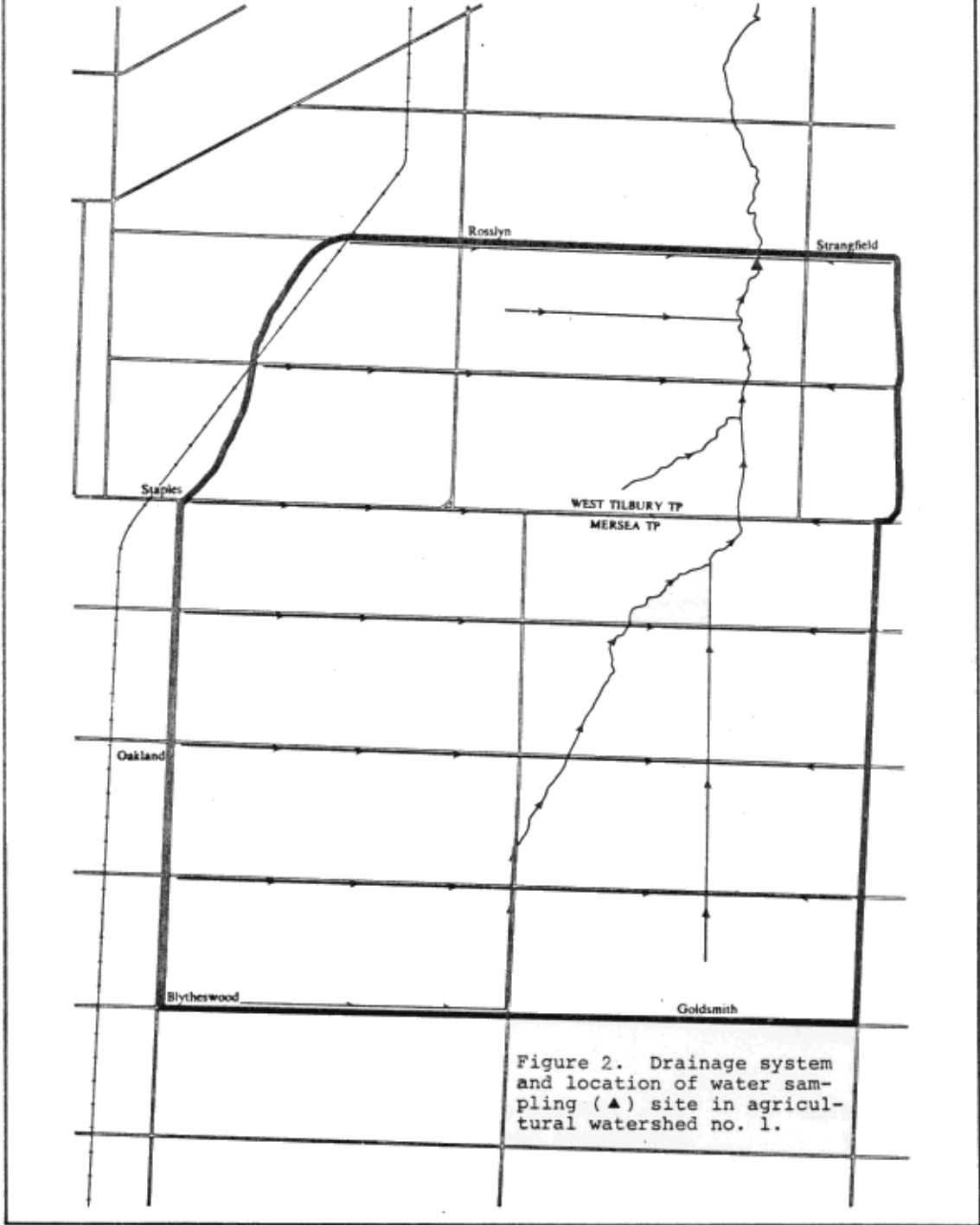


Figure 2. Drainage system and location of water sampling (▲) site in agricultural watershed no. 1.

AGRICULTURAL WATERSHED #3, UPPER LITTLE AUSABLE (HURON COUNTY)  
PART OF AUSABLE DRAINAGE BASIN



Figure 3. Drainage system and location of water sampling site (▲) in agricultural watershed no. 3.

AGRICULTURAL WATERSHED #4, CANAGAGIGUE CREEK (WEST BRANCH)(WELLINGTON COUNTY)  
PART OF GRAND RIVER DRAINAGE BASIN

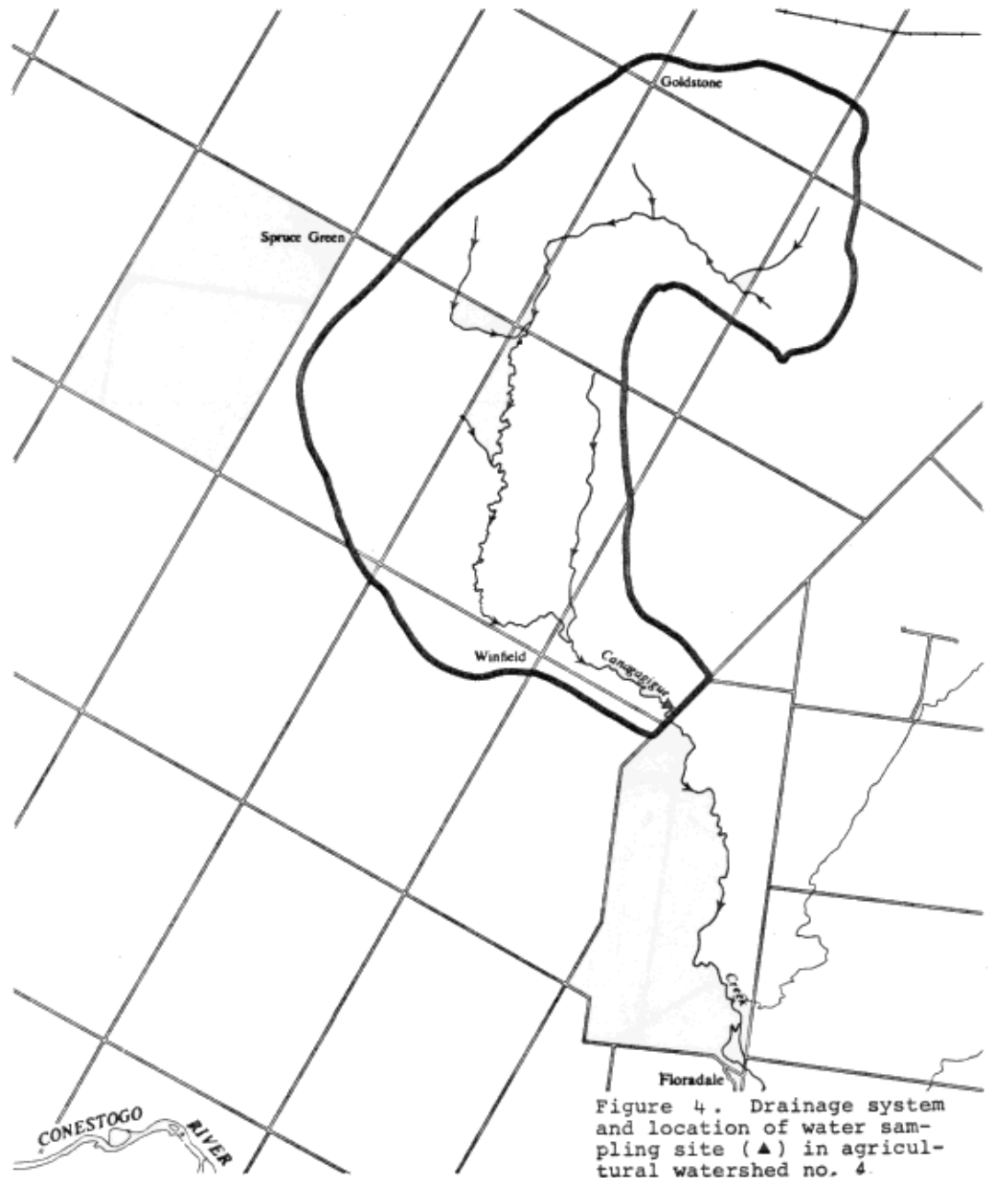


Figure 4. Drainage system and location of water sampling site (▲) in agricultural watershed no. 4.

AGRICULTURAL WATERSHED #5, HOLIDAY CREEK (OXFORD COUNTY)  
PART OF MIDDLE THAMES DRAINAGE BASIN

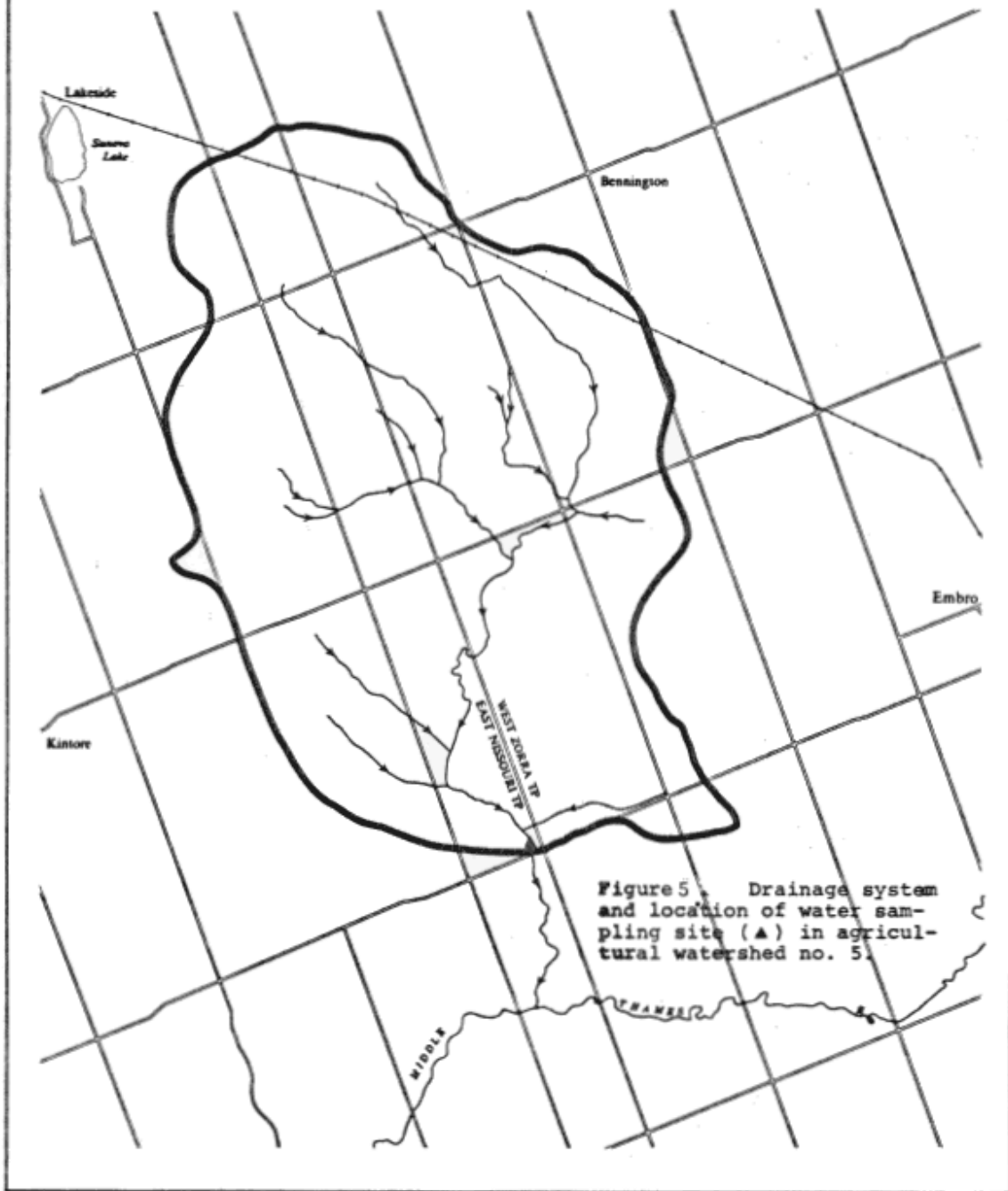


Figure 5. Drainage system and location of water sampling site (▲) in agricultural watershed no. 5.

AGRICULTURAL WATERSHED # 10. NORTH CREEK (LINCOLN COUNTY)  
PART OF TWENTY MILE CREEK DRAINAGE SYSTEM

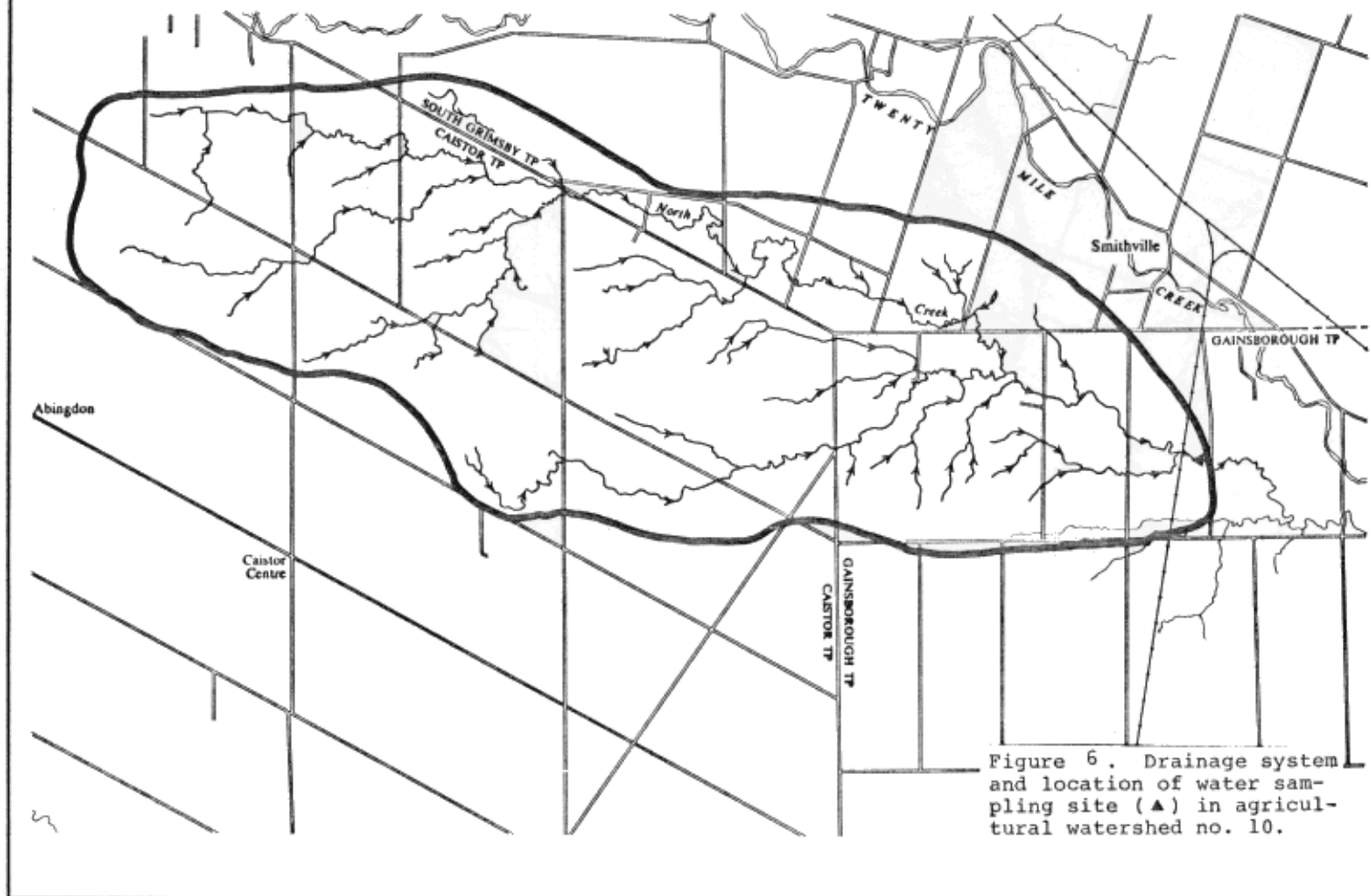
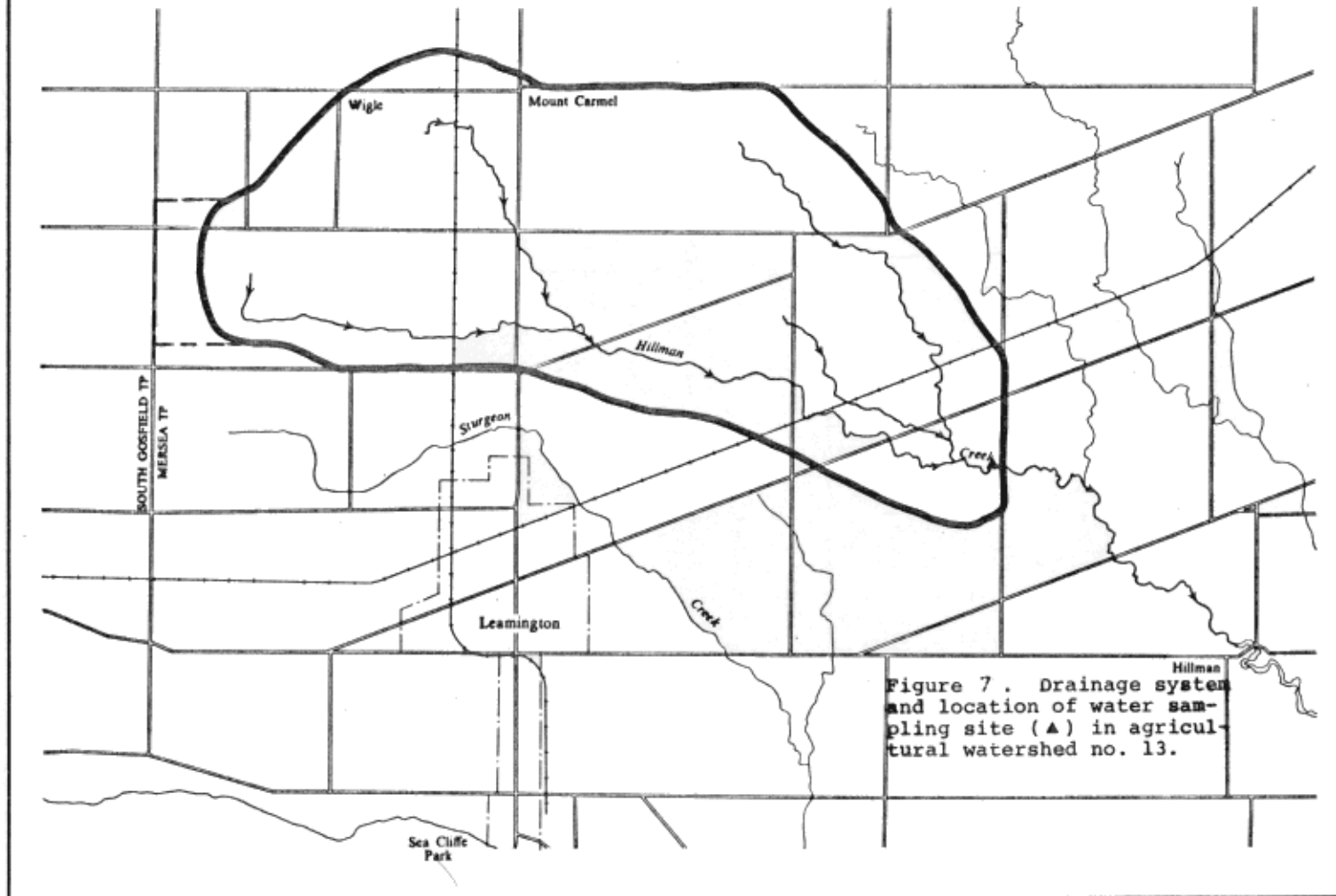


Figure 6. Drainage system and location of water sampling site (▲) in agricultural watershed no. 10.

AGRICULTURAL WATERSHED # 13, HILLMAN CREEK (WEST BRANCH)(ESSEX COUNTY)  
PART OF HILLMAN CREEK DRAINAGE BASIN





## EXPERIMENTAL RESULTS

The out-come of the extensive experimental deliberations described in the preceding section, was a body of data from which were extracted fairly reliable estimates of trace element levels in water samples of streams draining the selected Agricultural watersheds. These results are summarized in the tables and figures in this section. Values presented are means over different subsamples and analytical methodologies, and the standard errors associated with each datum give measures of precision and accuracy. Details are given in footnotes and more information is presented in the two appendices. The sampling dates are day/month/year.

Concentrations of suspended sediments in stream waters are presented in Table 4. Watersheds AG 1,3, 4, 10 and 13 were sampled on four different occasions during 1976 and the spring of 1977, whereas AG5 was sampled a total of eight times; the number of samplings for which trace element and sediment data are available ranged from 11 to 21 for the former and was 27 for the latter. Suspended sediment concentrations ranged from  $2 \pm 12$  (mean  $\pm$  standard error) to  $740 \pm 10$  mg/L, or 19,000 mg/L including data for the field erosion site in AG5, with a median of *ca* 20 mg/L. Although a few "event" samples were collected during periods of rapid flow, after rainfall and during spring run-off, the bulk of samples were collected during slower flow periods and have rather low suspended sediment levels; one half of samples had concentrations below 20 mg/L. Weights of residues after acid-leaching of unfiltered water samples were converted to concentrations on the original sample basis and are listed in Table 4 for comparison. Residue concentrations appear invariably lower than the corresponding suspended sediment levels, a relationship brought out graphically in Figure 8. When the ratio, residue concentration/suspended sediment concentration, is plotted against the suspended sediment concentration, an even more dramatic relationship is revealed, as depicted in Figure 9. Whereas at the two intermediate and two high sediment levels, the ratio is constant at 0.70, it appears to drop, with decreasing sediment concentration, to a value of *ca* 0.1 in the vicinity of 10 mg/L. This trend is somewhat uncertain because six data points leading to a higher ratio have been ignored; four of these, however, have associated standard errors very large compared to the uncertainties of the 10 points considered. If in fact this relationship is correct, it indicates increasing acid-solubility of the suspended sediments with decreasing sediment level, and suggests different physical and/or chemical properties for suspended sediments at low and high concentrations, with a gradation of

character in-between. It is logical to expect suspended sediments from low level streams to consist of smaller, lighter particles capable of being supported by the low energy stream. It would be of interest to relate these findings with mineralogical investigations on similar suspended sediments anticipated from project 8 (Wall, 1978). The scarcity of data from this study precluded comparison of suspended sediment levels, and thus a comparison of soil erosion rates, among the six watersheds.

Concentrations of the four trace elements in the suspended sediments, on a dry basis, are listed in Table 5. Ranges of concentrations ( $\mu\text{g/g}$ ) for the six watersheds were found to be 23-119 for Cu, 50-290 for Zn, 0.1-7.9 for Cd, and 21-280 for Pb, with median concentrations  $\pm$  standard error of  $52 \pm 5$ ,  $165 \pm 39$ ,  $1.1 \pm 0.8$ , and  $70 \pm 36$  for Cu, Zn, Cd and Pb respectively. Standard errors of medians relate to precision and not to the distributions of the populations from which medians were extracted. When the concentration of the trace element in the suspended sediment is plotted against the suspended sediment concentration (Figure 10), some interesting relationships are observed. The clearest relationship exists for Cu due to the good analytical precision. In this case, the level of Cu in the sediments drops from *ca* 100  $\mu\text{g/g}$  at sediment levels in the vicinity of 10 mg/L, to a constant value of *ca* 30  $\mu\text{g/g}$  for waters with high suspended sediment levels. Due to higher uncertainties in the data, such relationships are not as clearly evident for the other three elements, but the graphs are suggestive of "enrichment" of low level sediments occurring for Cd and Pb. Curiously, such a trend is not evident for Zn, an element closely related to Cd, which shows a rather constant level of 170  $\mu\text{g/g}$  over all samples. In all instances, the points for the extremely high sediment level of 19,000 mg/L fall into the patterns suggested by the remaining data. The scatter of data beyond individual error limits suggest, however, that exceptions to the general trends occur; it would indeed be interesting to ascertain whether these relationships agree with mineralogical and chemical characterizations of these suspended sediments or whether in fact our estimates of error are too conservative.

Contributions of suspended sediment to trace element levels in the stream waters were computed from concentrations of suspended sediments in the water samples and concentrations of trace elements in the sediments, and are listed in Table 6. Over all the samples, suspended sediments contributed 0.3-437  $\mu\text{g Cu/L}$ , 1.3-2850  $\mu\text{g Zn/L}$ , 0.00-11.4  $\mu\text{g Cd/L}$  and 0.3-399  $\mu\text{g Pb/L}$ , with corresponding median concentrations  $\pm$  standard error of  $4.3 \pm 0.6$ ,  $9.1 \pm 2.8$ ,  $0.09 \pm 0.06$ , and  $3.1 \pm 1.1$   $\mu\text{g/L}$ .

Concentrations of dissolved trace elements, defined as levels in natural water filtrates passing through 0.40.45 µm filters, are compiled in Table 7. Dissolved, as defined here, thus encompasses the sum of the trace elements distributed over a range of all possible species present in solution ranging from true solutions of hydrated and complexed forms through elements associated with larger organic species to colloidal dispersions and particles up to ca 450 nm in diameter. The term is not restricted to true molecular solutions but does have a practical significance. Levels listed in the Table have rather large associated relative errors resulting from the necessity to apply some rather large corrections for filtration procedure contamination and because the levels are very low. These considerations together with the possibility of trace element adsorption by the membrane filters and other experimental uncertainties at such low levels, lead to accepting these values as estimates of dissolved trace element concentrations. For samples from all the watersheds, ranges of element concentrations in dissolved form were found to be (µg/L): Cu, 0.5-18.5; Zn, 0.111.4; Cd, 0.00-0.57; and Pb, 0.0-13.1, with medians ± standard error of  $2.0 \pm 1.8$ ,  $3.1 \pm 2.7$ ,  $0.07 \pm 0.06$  and  $0.1 \pm 0.2$  µg/L for Cu, Zn, Cd and Pb respectively.

Total concentrations of trace elements in stream waters are tabulated in Table 8. These concentrations may be defined as the sums of contributions from suspended sediment and dissolved forms discussed above. They were in fact determined in two independent ways, as discussed in Appendix I, based on concentrations measured in unfiltered and filtered water samples plus the appropriate contributions of suspended sediments and residues, and the best selected values have been listed here. Total concentration (µg/L) ranges and medians ± standard error for the six watersheds were: Cu, 2.2-445,  $3.9 \pm 2.6$ ; Zn, 4.32500,  $17.2 \pm 4.9$ ; Cd, 0.03-13.4,  $0.08 \pm 0.02$ ; and Pb, 0.9-433,  $3.7 \pm 1.0$ . This, plus all the preceding information is presented in summary form in Table 9, and is depicted graphically in Figures 11-18.

Concentrations of dissolved and total Cu, Zn, Cd and Pb are diagrammatically presented in Figures 11, 12, 13 and 14 respectively, as functions of watershed and sampling times. Suspended sediment concentrations are also plotted for information and for relation to metal levels. Each point represents one sampling date with the exception that the last two (RHS) points for AG5 represent two sites sampled on the same date. Where total concentrations were unavailable, dissolved + acid - and solvent - extractable concentrations, have been included for completeness, as estimates of total concentrations.

Total, dissolved and suspended sediment-contributed levels of Cu, Zn, Cd and Pb are plotted, as functions of suspended sediment concentration, in Figures 15, 16, 17, and 18 respectively. Reasonably firm relations could be established for Cu, Zn and Pb, particularly for the first two elements, but not for Cd due to the scarcity and imprecision of data. The most striking observation is the general independence of concentrations of dissolved trace element, over the range *ca* 10-740 mg of suspended sediment/L, and even extending to the one field erosion site sample with 19,000 mg sediment/L. Ignoring for the moment, the two high Cu and Pb values, we calculate for samples from the six watersheds, mean dissolved-form concentrations  $\pm$  standard deviation (No. of sampling dates) of  $2.2 \pm 1.2$  (20) $\mu\text{g}$  Cu/L,  $3.6 \pm 3.1$  (17) $\mu\text{g}$  Zn/L,  $0.12 \pm 0.17$  (13)  $\mu\text{g}$  Cd/L, and  $0.32 \pm 0.50$  (10)  $\mu\text{g}$  Pb/L. This means that, with 95% confidence, we can say that a sample of water from any of the streams from AG 1, 3, 4, 5, 10 and 13, will contain, in dissolved form, 0-4.6  $\mu\text{g}$  Cu/L, 0-10  $\mu\text{g}$  Zn/L, 0-0.50  $\mu\text{g}$  Cd/L, and 0-1.5  $\mu\text{g}$  Pb/L. Getting back to the high values for dissolved Cu and Pb, these concentrations of 18.5  $\mu\text{g}$  Cu/L and 13.1  $\mu\text{g}$  Pb/L are *ca* 9x and 40-130 x large as the respective mean or median values. Curiously, both are for one sampling on 260376 of AG 4. Unfortunately, both also result from one analysis by one method, and consequently no significance can be attached to them on the basis of existing information. They may be true anomalies of AG 4 but may also be artifacts of sampling and analysis. Levels of dissolved Zn and Cd for the same sample look "normal".

Concentrations of suspended sediment-contributed, and total trace elements, on the other hand, are related to suspended sediment concentration in a *ca* linear fashion over the 10-740 mg/L range. Three outlying points may be noted, a suspended Pb, and a total Cu and Pb concentration, all of which are again associated with the AG4260376 sampling. One sample of suspended sediment and residue were analyzed by two independent analytical methods. Rather large differences between results for Pb were observed, and this consideration together with high values for dissolved levels for Cu and Pb suggest that no significance should be attached to these outliers.

Using the slopes of lines drawn through points over the 10-740 mg sediment/L range, it is of interest to predict, by extrapolation, concentrations of suspended and total elements in the water sample with 19,000 mg sediment/L. Predicted concentrations of suspended Cu, Zn and Pb of 820, 4260 and 780  $\mu\text{g}$ /L respectively, compare with corresponding actual levels of 440, 2850, and 400  $\mu\text{g}$ /L. Predicted total concentrations of Cu, Zn and Pb of 990, 5450 and 870  $\mu\text{g}$ /L respectively, compare with corresponding actual

levels of 430, 2000 and 430  $\mu\text{g/L}$ . Agreement between predicted and measured levels is within a factor of two. The behavior of suspended and total data for Cd is rather uncertain.

The proportion of the element carried by the suspended sediment, expressed as a percentage of the total concentration in the stream water, is plotted as a function of the suspended sediment level in Figure 19. Something regarding the mechanism of metal transport can be said by reference to these plots. For Cu and Zn, the proportion of the total element level associated with particulate stream material, was observed to increase with suspended sediment concentration over the range *ca* 10-100 mg/L, and thereafter remained constant at 80-90% up to 740 mg/L. These proportions would be expected to increase slowly with sediment load to approach 100% at High sediment levels as suggested by the 19,000 mg/L point. The two curves cross 50% at a suspended sediment concentration of *ca* 20 mg/L. Thus, in waters with low suspended sediment levels, below *ca* 20 mg/L, the majority of Cu and Zn is transported in the dissolved state, whereas the particulate material accounts for most of these trace elements at higher suspended sediment levels. Rather large errors arising from experimental uncertainties and propagation of error for the quotients, however, suggest that these conclusions be accepted with reservation. No such trends were noticed for Cd and Pb; the very low levels of Cd and Pb in natural waters, coupled with the experimental difficulties associated with their measurement, precludes firm conclusions regarding these elements.

Concentrations of the four trace elements in residues (acid-leached suspended sediments) on a dry basis are listed in Table 10. Ranges of concentrations ( $\mu\text{g/g}$ ) for samples from the six watersheds were found to be 0.0 - 16.9 for Cu, 4-300 for Zn, 0.0-4.3 for Cd, and 0-98 for Pb, with median concentrations  $\pm$  standard error of  $9.0 \pm 1.8$ ,  $30 \pm 13$ ,  $0.0 \pm 0.2$  and  $16 \pm 12$  for Cu, Zn, Cd and Pb respectively. This information is included in Table 9 for comparison with corresponding data for suspended sediments. Relationships between trace element concentrations in residues and suspended sediments are demonstrated in Figure 20. Almost invariably, levels of Cu, Zn, Cd and Pb in suspended sediments are higher than those in corresponding residues. These relationships are further explored in Figure 21 in which the ratios, concentration of element in residue/concentration of element in suspended sediment, are plotted against suspended sediment concentrations. Data for Cd as well as ratios greater than unity have been omitted. For Cu and Zn, ratios of *ca* 0.3 and 0.4 respectively, at suspended concentration levels in the range 300-740 mg/L, fall toward zero as the sediment level decreases. This behavior

shows that an increasing proportion of the trace element in the suspended sediment is leached-out by acid as the suspended sediment level decreases, and suggests a gradual change in the physical and/or chemical character of the particulate material with its concentration in the stream. The point for the extremely high sediment level of 19,000 mg/L in the Cu graph, at a ratio of *ca* 0.7 indicates an even smaller fraction of Cu susceptible to acid leaching at this sediment level; this datum can easily be accommodated into the trend over the 300-740 mg/L range by ascribing a barely perceptible slope of  $2 \times 10^{-5}/\text{mgL}^{-1}$  to the straight line. A similar trend, as for Cu and Zn, cannot be ascribed to Pb with the data available; a constant ratio of *ca* 0.25 is evident over the entire range of sediment concentration.

Table 4. Suspended Sediment and residue concentrations in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13.

Watershed sampling date	Mean concentration (no. of analyses) $\pm$ standard error		s/ $\sqrt{n}$ , mg/L <sup>a</sup>	
	Suspended sediment <sup>b</sup>		Residue <sup>c</sup>	
		$\pm$		$\pm$
Watershed AG1				
290376	71 (2)	8	30.0 (2)	1.3
260776	11 (1)	12	74.5 (4)	1.0
051176	80 (5)	5	26.0 (1)	1.9
130377	740 (1)	10	532 (2)	6.4
Watershed AG3				
050476	10 (1)	12	-	
080676	16 (3)	7	0.8 (1)	0.7
190776	15 (3)	7	3.6 (5)	0.3
141076	64 (3)	7	6.2 (4)	0.4
Watershed AG4				
260376	329 (2)	8	228 (1)	9
010676	-		1.0 (7)	0.3
120776	47 (3)	7	16.8 (1)	1.9
071076	13 (3)	7	13.5 (3)	1.1
Watershed AG5				
310376	2 (1)	12	-	
030676	12 (1)	12	2.0 (1)	0.7
150776	16 (4)	6	14.4 (2)	1.3
210776	33 (4)	6	28.5 (2)	1.0
250876	7 (2)	8	0.6 (3)	0.4
051076	11 (1)	12	0.9 (2)	0.5
250377-1	19.0 x10 <sup>3</sup> (1)		13.4 x10 <sup>3</sup> (est) <sup>d</sup>	
250377-5	350 (1)	10	247 (2)	6
Watershed AG10				
300376	125 (2)	8	118 (2)	1
020676	31 (2)	8	-	
140776	48 (4)	6	23.8 (1)	1.9
121076	79 (2)	8	42.4 (2)	1.3
Watershed AG13				
290376	6 (1)	12	4.6 (2)	0.5
270776	9 (2)	8	5.6 (4)	0.4
041176	9 (3)	7	12.5 (2)	1.3
030377	685 (1)	10	466 (2)	6

(a) Data have been averaged over 1-4 subsamples and analyses by 1-3 laboratories.

(b) Means of selected values obtained in 1-3 laboratories.

(c) Residue refers to solid material remaining after evaporation of acidified water sample to a small volume. All data are for unfiltered water samples and therefore represent acid-leached suspended sediments. Weights of residue obtained have been converted to a concentration in the original sample volume. Determined by M. Ichnat.

(d) Rough estimate based on relationship, residue level = 0.70x suspended sediment level, found for the other three 1977 samples.

Table 5. Concentrations of Cu, Zn, Cd and Pb in suspended sediments of Waters of agricultural watersheds 1, 3, 4, 5, 10 and 13.

Watershed Mean and sampling date	Concentration (no. of analyses) ± standard error, s/√n, µg/g <sup>b</sup>							
	Cu		Zn		Cd		Pb	
		±		±		±		±
Watershed AG1								
290376(LC)	94 (2)	5	280 (2)	39	6.2 (2)	1.0	36 (2)	26
260776	30 (6)	3	120 (6)	23	1.6 (5)	0.6	31 (6)	15
051176	54 (4)	3	160 (4)	28	1.1 (3)	0.8	75 (5)	16
130377	37 (2)	5	290 (2)	39	1.4 (2)	1.0	34 (2)	26
Watershed AG4								
260376(LC)	32 (5)	3	110 (5)	25	0.1 (3)	0.1	130 (5)	16
120776	65 (1)	6	150 (1)	55	-	-	150 (1)	36
071076(LC)	23 (2)	5	140 (2)	39	3.8 (1)	1.4	82 (2)	26
Watershed AG5								
150776(LC)	119 <sup>c</sup>	6	240 <sup>c</sup>	55	0.1 <sup>c</sup>	0.2	64 <sup>c</sup>	36
210776(LC)	71 <sup>c</sup>	6	200 <sup>c</sup>	55	0.1 <sup>c</sup>	0.2	23 <sup>c</sup>	36
250377-1	23 (4)	3	150 (4)	28	0.6 (4)	0.1	21 (4)	18
250377-5	27 (2)	5	170 (2)	39	0.3 (2)	0.1	28 (2)	26
Watershed AG10								
020676	25 (1)	6	50 (1)	22	-	-	100 (2)	26
140776(LC)	90 (2) <sup>d</sup>	5	230 (2) <sup>d</sup>	39	7.9 (2) <sup>d</sup>	1.0	270 (2) <sup>d</sup>	26
121076	60 (5)	3	80 (5)	25	0.2 (1)	0.2	280 (5)	16
Watershed AG13								
041176	90 (1)	6	200 (1)	55	-	-	200 (1)	36
030377	50 (2)	5	240 (2)	39	3.8 (2)	1.0	45 (2)	26

(a) LC refers to suspended sediment provided by Dr. L. Whitby Costescu; the other 1976 samples were provided by K. LaHay, whereas the 1977 samples were prepared in the author's laboratory from water samples supplied by Dr. G. J. Wall.

(b) Means of selected data from one or two laboratories (M. Ihnat and D. S. Russell) using different analytical methods are reported on a dry sample basis. Means are weighted according to the number of analyses conducted by each laboratory and represent pooled estimates over subsamples and analytical methodologies. Standard deviations for the entire populations of suspended sediment and residue data are, µg/g (concentration range, degrees of freedom):

Cu, 2.5 (0-20, 24); Cu, 6.4 (20-100, 19); Zn, 22 (0-70, 19); Zn, 55 (70-300, 19);  
Cd, 0.18 (0-1, 19); Cd, 1.4 (1-6, 6); Pb, 4.4 (0-50, 18).

(c) Value provided by Dr. L. Whitby Costescu, but the author's standard deviations (b) have been associated with these values.

(d) Values are unreliable as only limited sample weights ( $\leq 1$  mg) were available for analysis.

Table 6. Contributions of suspended sediments to concentrations of Cu, Zn, Cd and Pb in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13.

Watershed and sampling date	Concentration of the trace element $\pm$ standard error, $s/\sqrt{n}$ , $\mu\text{g/L}$ <sup>a</sup>							
	Cu		Zn		Cd		Pb	
		$\pm$		$\pm$		$\pm$		$\pm$
Watershed AG1								
290376	6.6	0.8	19.9	3.6	0.44	0.09	2.6	1.9
260776	0.3	0.4	1.3	1.5	0.02	0.02	0.3	0.4
051176	4.3	0.4	12.8	2.4	0.09	0.06	6.0	1.3
130377	27.4	3.7	215	29	1.04	0.74	25.2	19.2
Watershed AG3								
050476	-	-	-	-	-	-	-	-
080676	-	-	-	-	-	-	-	-
190776	-	-	-	-	-	-	-	-
141076	-	-	-	-	-	-	-	-
Watershed AG4								
260376	10.5	1.0	36.2	8.3	0.03	0.03	42.8	5.4
010676	-	-	-	-	-	-	-	-
120776	3.1	0.5	7.1	2.8	-	-	7.1	2.0
071076	0.3	0.2	1.8	1.1	0.05	0.03	1.1	0.7
Watershed AG5								
310376	-	-	-	-	-	-	-	-
030676	-	-	-	-	-	-	-	-
150776	1.9	0.7	3.8	1.7	0.00	0.00	1.0	0.7
210776	2.3	0.5	6.6	2.2	0.00	0.01	0.8	1.2
250876	-	-	-	-	-	-	-	-
051076	-	-	-	-	-	-	-	-
250377-1	437	-	2850	-	11.4	>1.9	399	>364
250377-5	9.5	1.8	59.5	14	0.11	0.04	9.8	9.1
Watershed AG10								
300376	-	-	-	-	-	-	-	-
020676	0.8	0.3	1.6	0.8	-	-	3.1	1.1
140776	4.3	0.6	11.0	2.3	0.38	0.07	13.0	2.0
121076	4.7	0.5	6.3	2.1	0.02	0.02	-	-
Watershed AG13								
290376	-	-	-	-	-	-	-	-
270776	-	-	-	-	-	-	-	-
041176	0.8	0.6	1.8	1.5	-	-	1.8	1.4
030377	34.3	3.5	164	27	2.60	0.69	30.8	17.9

(a) Contributions of suspended sediments to the trace element levels in the streams were computed from concentrations of suspended sediments in the water samples and concentrations of trace elements found in the suspended sediments. Standard errors were calculated by propagation of error formulas.

Table 7. Concentrations of dissolved Cu, Zn, Cd and Pb in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13<sup>a</sup>

Watershed and sampling date	Mean concentration $\pm$ standard error, $s/\sqrt{n}$ , $\mu\text{g/L}^b$							
	Cu		Zn		Cd		Pb	
	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$
Watershed AG1								
290376	-		-		0.12	0.04	-	
260776	3.1	1.9	-		-		-	
051176	1.6	2.8	0.2	2.8	-		-	
130377	3.6	2.0	3.8	1.6	0.11	0.04	-	
Watershed AG3								
050476	1.9	1.9	2.2	2.5	0.01	0.04	0.2	0.2
080676	3.2	2.1	0.1	2.5	-		-	
190776	1.4	1.8	7.3	6.5	0.01	0.05	-	
141076	1.5	1.8	-		0.08	0.05	0.1	0.2
Watershed AG4								
260376	18.5	2.8	6.5	2.8	-		13.1	0.3
010676	2.2	1.8	0.8	2.5	-		0.1	0.2
120776	0.9	2.6	3.1	2.7	-		1.6	0.3
071076	0.5	2.8	-		0.07	0.06	-	
Watershed AG5								
31037	-		-		0.02	0.04	0.1	0.3
030676	2.0	1.8	2.9	2.5	-		-	
150776	-		-		-		-	
210776	-		-		-		-	
250876	0.8	1.8	-		-		-	
051076	1.8	1.8	-		-		0.1	0.2
250377-1	2.0	2.0	0.8	1.3	0.03	0.04	-	
250377-5	1.4	2.0	5.3	1.3	0.08	0.04	-	
Watershed AG10								
300376	-	-	4.8	2.8	0.57	0.06	-	
020676	2.2	1.8	11.4	3.9	-		-	
140776	3.0	1.8	0.8	2.5	-		-	
121076	-		0.7	2.8	-		-	
Watershed AG13								
290376	-		7.0	2.9	0.00	0.05	0.1	0.2
270776	2.3	1.8	-		-		0.0	0.2
041176	2.0	1.8	-		0.05	0.05	0.1	0.2
030377	5.6	2.0	4.1	1.3	0.41	0.04	0.8	0.5

a These are estimates of trace element levels in water filtrates passing through 0.4 - 0.45  $\mu\text{m}$  filters, representing "dissolved" concentrations.

b Concentrations,  $\bar{X}$ , measured in filtered water samples have been corrected for estimated filtration procedure contamination based on levels found in distilled and deionized water control samples, to give the data reported here. Standard errors reported above were calculated by propagation of error formulas from errors in  $\bar{X}$  and in the correction factors. Refer to Table 40 and Appendix II for details.

Table 8. Total Concentrations of Cu, Zn, Cd and Pb in waters of agricultural Watersheds 1, 3, 4, 5, 10 and 13 <sup>a</sup>

Watershed and sampling date	Mean concentration $\pm$ standard error, $s/\sqrt{n}$ , $\mu\text{g/L}$ <sup>b</sup>							
	Cu		Zn		Cd		Pb	
	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$
Watershed AG1								
290376	-	-	-	-	-	-	2.5	1.9
260776	4.8	1.7	17.2	4.9	0.04	0.04	3.0	0.8
051176	5.6	2.0	8.0	1.0	0.03	0.02	2.7	0.9
130377	32.8	5.1	252	43	1.44	0.52	28.7	13.6
Watershed AG3								
050476	-	-	-	-	-	-	-	-
080676	-	-	-	-	-	-	-	-
190776	-	-	-	-	-	-	-	-
141076	2.2	0.7	4.3	1.0	0.07	0.02	1.1	0.8
Watershed AG4								
260376	37.5	10.7	58.2	19.4	0.29	0.02	45.6	12.8
010676	-	-	-	-	-	-	-	-
120776	3.9	2.6	7.2	3.9	-	-	8.7	2.0
071076	2.3	0.7	10.6	3.5	0.14	0.05	1.4	0.7
Watershed AG5								
310376	-	-	-	-	-	-	-	-
030676	-	-	-	-	-	-	-	-
150776	3.1	0.7	11.1	1.1	0.05	0.02	1.2	0.7
210776	3.7	0.8	11.2	3.5	0.06	0.02	4.6	0.8
250876	-	-	-	-	-	-	-	-
051076	-	-	-	-	-	-	-	-
250377-1	445	>26	2500	500	13.4	>1.9	433	257
250377-5	11.6	1.9	64.0	9.9	0.37	0.24	13.5	6.5
Watershed AG10								
300376	9.2	0.8	37.0	3.5	0.08	0.03	4.3	1.2
020676	3.2	1.3	-	-	0.04	0.02	2.6	0.8
140776	2.9	0.9	-	-	0.4	>0.07	8.1	6.1
121076	3.9	2.0	19.4	3.0	0.08	0.02	3.7	1.0
Watershed AG13								
290376	-	-	-	-	-	-	-	-
270776	-	-	-	-	0.05	0.02	0.9	0.8
041176	2.8	1.4	5.0	0.8	0.08	0.02	1.6	1.0
030377	41.3	5.1	175	19	3.34	0.49	36.5	12.6

(a) Values are based on concentrations measured in unfiltered or filtered water samples plus the contributions of suspended sediments or residues.

(b) Selected data are presented, averaged over all subsamples and analytical methodologies. Standard errors have been computed using propagation of error formulas. Refer to appendix for additional information.

Table 9. Summary of Cu, Zn, Cd and Pb concentrations in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13

Element	Concentration range <sup>a</sup>	n <sup>b</sup>	Median ± standard error <sup>c</sup>
Dissolved trace element, µg/L			
Cu	0.5 - 18.5	21	2.0 ± 1.8
Zn	0.1 - 11.4	17	3.1 ± 2.7
Cd	0.00 - 0.57	13	0.07 ± 0.06
Pb	0.0 - 13.1	11	0.1 ± 0.2
Contribution of suspended sediment, µg/L			
Cu	0.3 - 437	16	4.3 ± 0.6
Zn	1.3 - 2850	16	9.1 ± 2.8
Cd	0.00 - 11.4	13	0.09 ± 0.06
Pb	0.3 - 399	15	3.1 ± 1.1
Total concentration of trace element, µg/L			
Cu	2.2 - 445	17	3.9 ± 2.6
Zn	4.3 - 2500	15	17.2 ± 4.9
Cd	0.03 - 13.4	17	0.08 ± 0.02
Pb	0.9 - 433	19	3.7 ± 1.0
Concentration of trace element in suspended sediment, µg/g			
Cu	23 - 119	16	52 ± 5
Zn	50 - 290	16	165 ± 39
Cd	0.1 - 7.9	13	1.1 ± 0.8
Pb	21 - 280	16	70 ± 36
Concentration of trace element in residue, µg/g			
Cu	0.0 - 16.9	16	9.0 ± 1.8
Zn	4 - 300	15	30 ± 13
Cd	0.0 - 4.3	15	0.0 ± 0.2
Pb	0 - 98	17	16 ± 12

<sup>a</sup> Range of mean concentrations, one per sampling date, found in samples from the six watersheds.

<sup>b</sup> Total number of associated sampling dates.

<sup>c</sup> Standard error is the error associated with the median value or the larger of the errors of the two values averaged for the median; it does not relate to the distribution of the population from which the median was extracted.

Table 10. Concentrations of Cu, Zn, Cd and Pb in residues from waters of agricultural watersheds 1, 3, 1,5, 10 and 13<sup>a</sup>

Watershed and sampling date	Mean concentration (no. of analyses) ± standard error, s/√n, µg/g <sup>b</sup>							
	Cu		Zn		Cd		Pb	
		±		±		±		±
Watershed AG1								
260776	4.5 (6)	1.0	25 (6)	9	0.0 (4)	0.1	18 (6)	5
051176	3.8 (4)	1.2	4 (1)	22	0.0 (1)	0.2	53 (4)	18
130377	12.8 (2)	1.8	110 (2)	39	0.0 (2)	0.1	5 (2)	8
Watershed AG3								
141076	15 (2) <sup>c</sup>	2	15 (2) <sup>c</sup>	16	0.0 (2) <sup>c</sup>	0.1	33 (2) <sup>c</sup>	26
Watershed AG4								
260376	9.1 (3)	1.4	17 (3)	13	0.0 (1)	0.2	44 (3)	21
071076	1.0 (3)	1.4	7 (3)	13	2.3 (3)	0.8	16 (3)	7
Watershed AG5								
150776	16.5 (1)	2.5	300 (1)	55	1.8 (1)	1.4	16 (1)	12
210776	12.9 (4)	1.2	20 (5)	10	0.0 (1)	0.2	98 (4)	18
250377-1	16.9 (2)	1.8	70 (2)	39	0.3 (2)	0.1	12 (2)	8
250377-5	8.9 (2)	1.8	65 (2)	16	0.1 (2)	0.1	4 (2)	8
Watershed AG10								
300376	11.0 (2)	1.8	55 (2)	16	0.0 (2)	0.1	3 (2)	8
020676	0.0 (1)	2.5	8 (1)	22	0.0 (1)	0.2	0 (1)	12
140776	6 (1)	2.5	-	-	-	-	80 (1)	36
121076	4.9 (5)	1.1	30 (3)	13	0.2 (3)	0.1	38 (4)	18
Watershed AG13								
270776	<sup>c</sup>		<sup>c</sup>		4.3 (1) <sup>c</sup>	1.4	6 (1) <sup>c</sup>	12
041176	0.0 (2)	1.8	35 (2)	16	1.8 (2)	1.0	8 (2)	8
030377	13.7 (2)	1.8	130 (2)	39	0.0 (2)	0.1	5 (2)	8

<sup>a</sup> Residue refers to solid material remaining after evaporation of acidified water sample to a small volume. All data are for unfiltered water samples and therefore relate to acid-leached suspended sediment.

<sup>b</sup> Means of selected data from one or two laboratories (M. Ilnat and D.S. Russell) using different analytical methods are reported on a dry sample basis. Means are weighted according to the number of analyses conducted by each laboratory and represent pooled estimates over subsamples and analytical methodologies. Standard deviations for the entire populations of suspended sediment and residue data are, µg/g (concentration range, degrees of freedom):

Cu, 2.5 (0-20, 24); Cu, 6.4 (20-100, 19); Zn, 22 (0-70, 19); Zn, 55 (70-300, 19);  
Cd, 0.18 (0-1, 19); Cd, 1.4 (1-6, 6); Pb, 4.4 (0-50, 18).

<sup>c</sup> Values are unreliable as only limited (< 2 mg) sample weights were available for analysis.

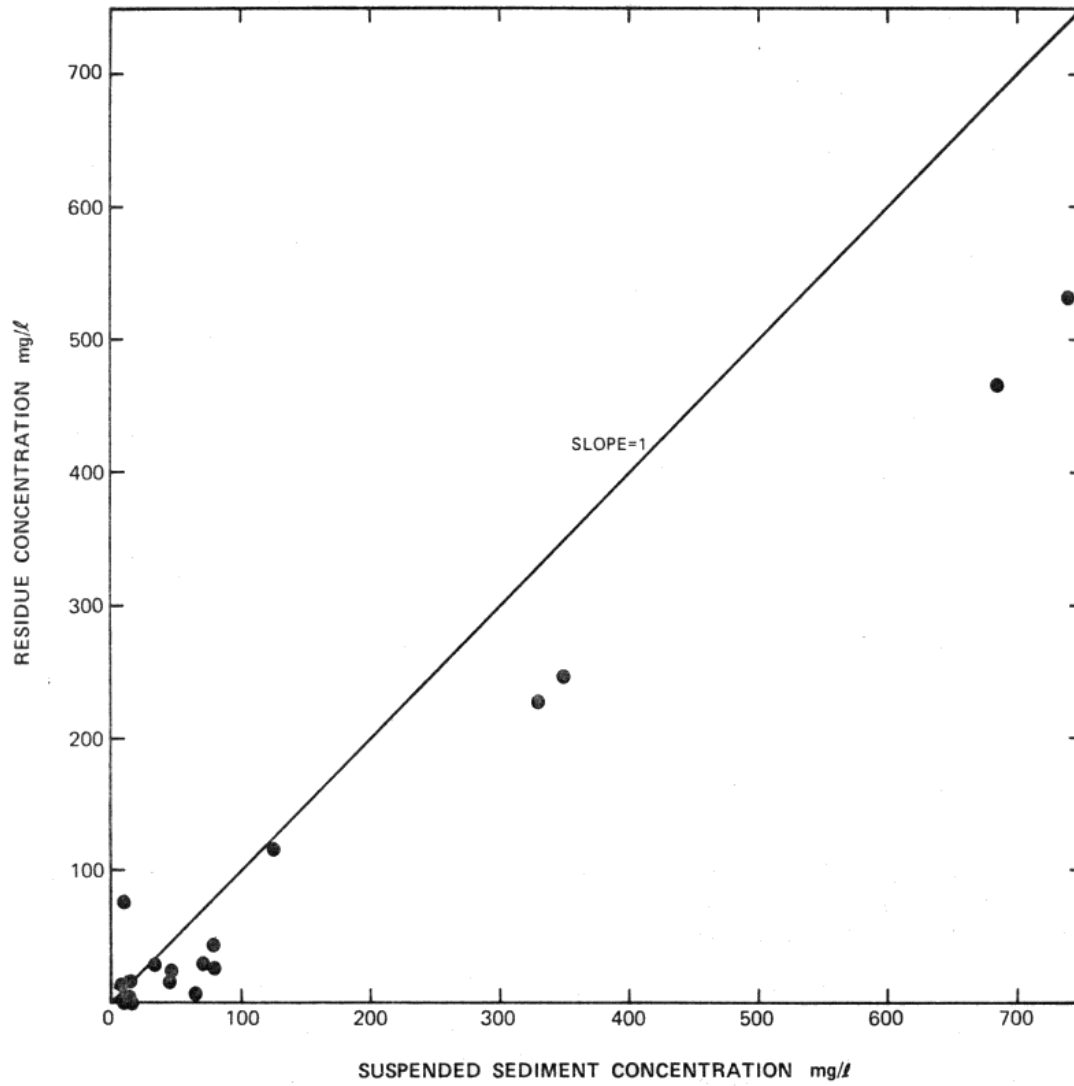


Figure 8. Relationship between residue (acid-leached suspended sediment) and suspended sediment concentration.

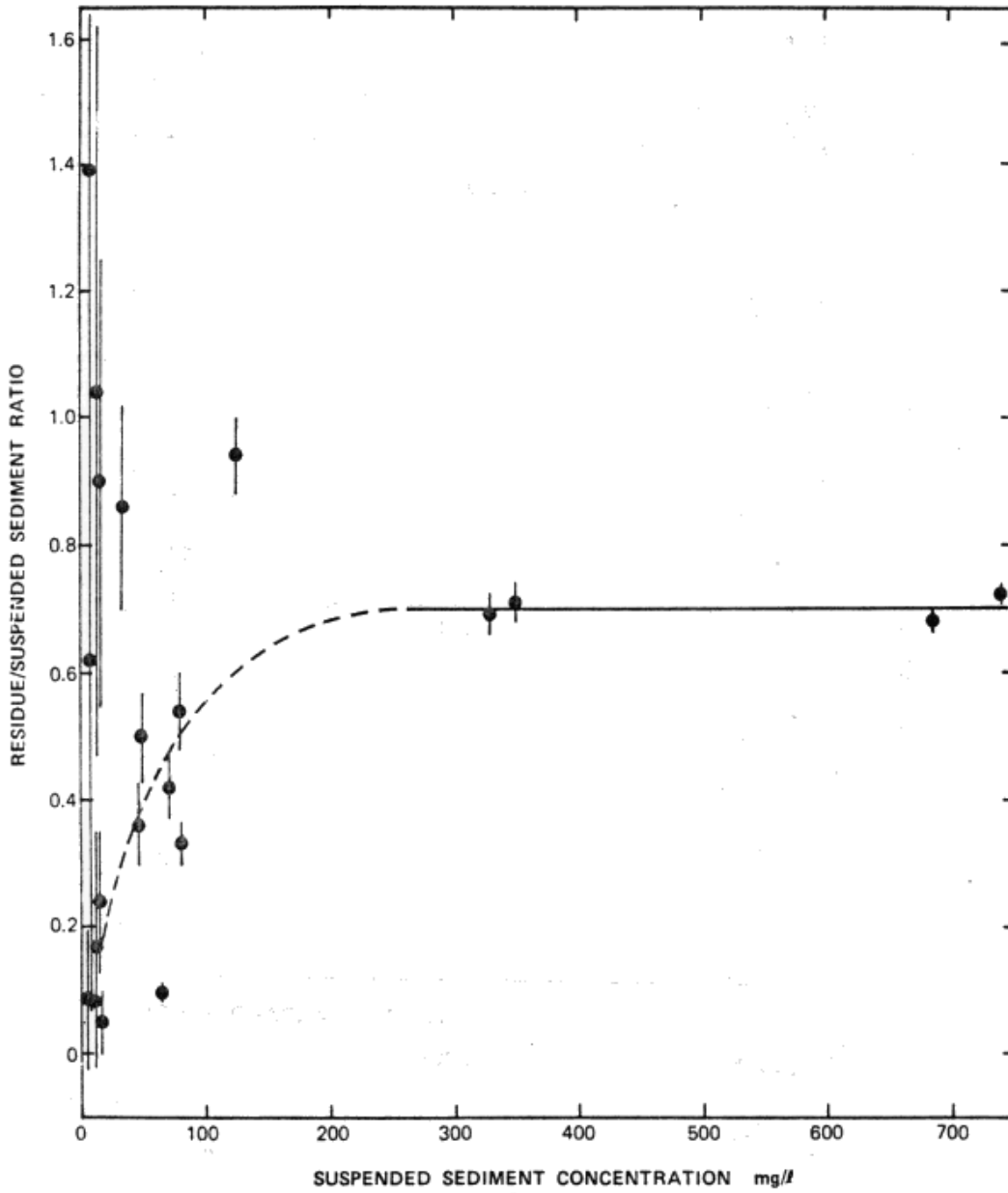


Figure 9. Residue concentration/suspended sediment concentration ratio as a function of suspended sediment concentration. Error bars here and in all subsequent figures represent standard errors,  $s/\sqrt{n}$

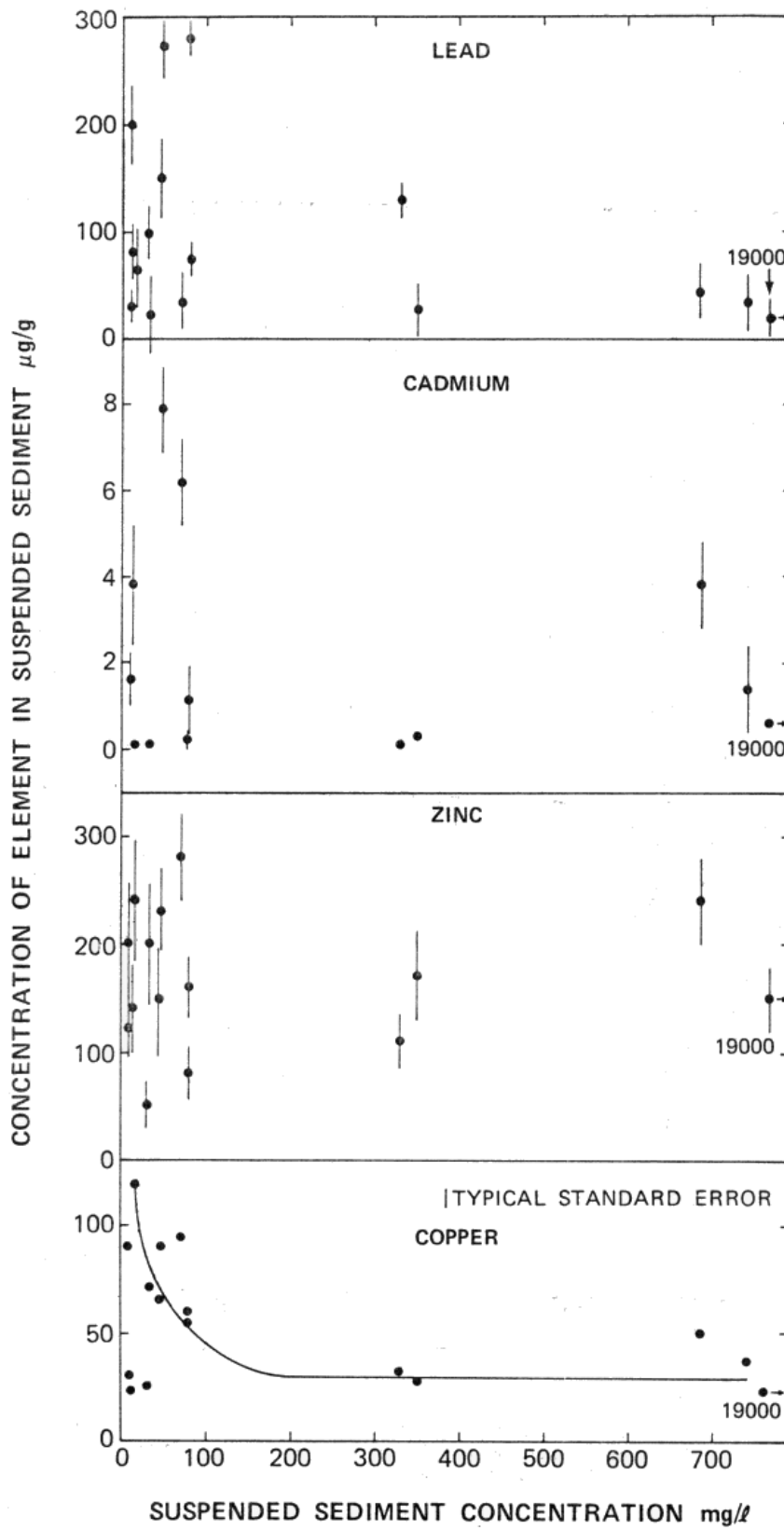


Figure 10. Concentration of trace element in suspended sediment as a function of suspended sediment concentration.

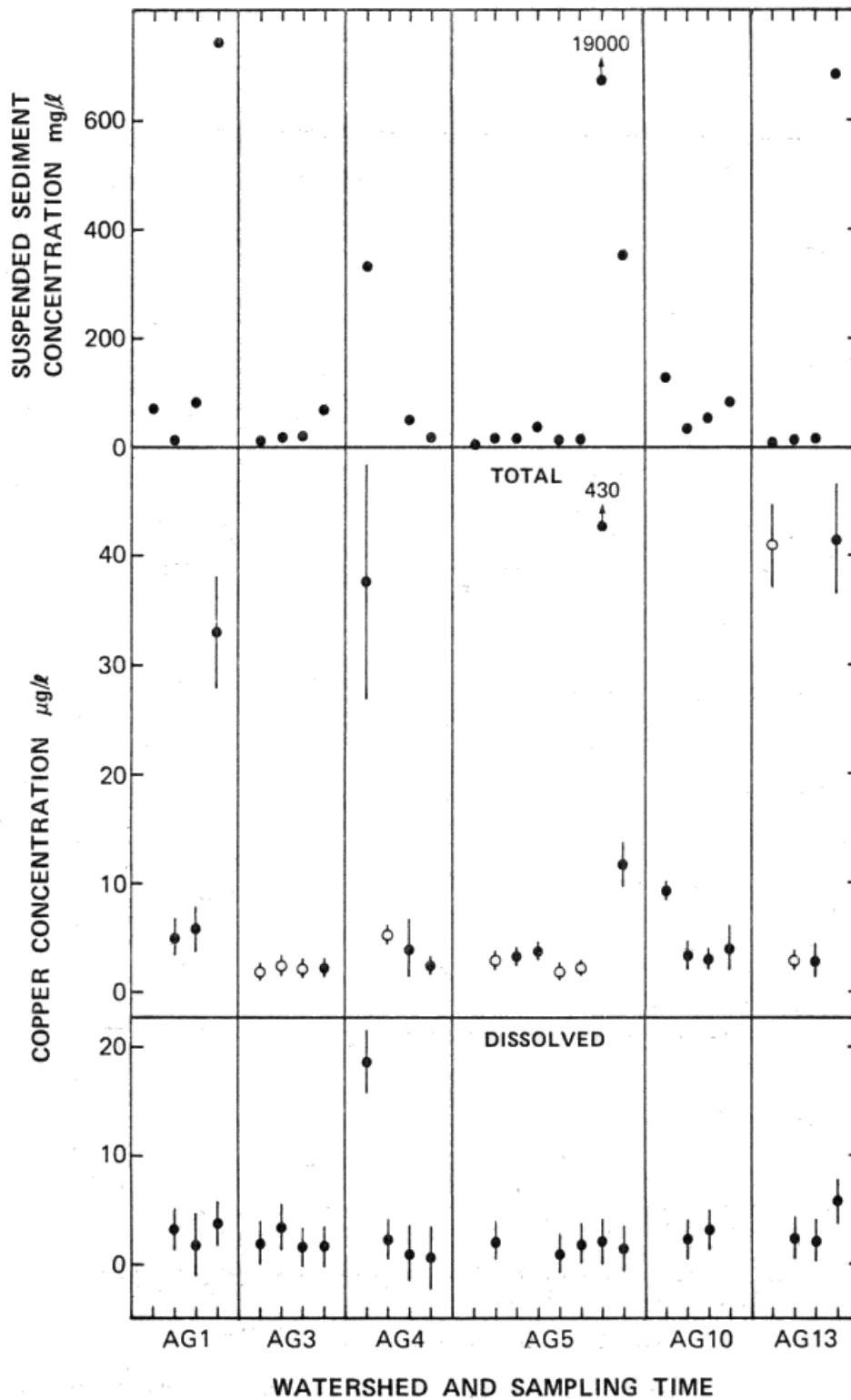


Figure 11. Concentrations of dissolved and total copper and suspended sediment in water samples from the six agricultural watersheds. Each point represents one sampling date with the exception that the last two points for AG5 represent two sites sampled on the same date 25/03/77. Where total concentrations were unavailable, dissolved + acid- and solvent-extractable concentrations, denoted o, have been included as estimates of total concentrations.

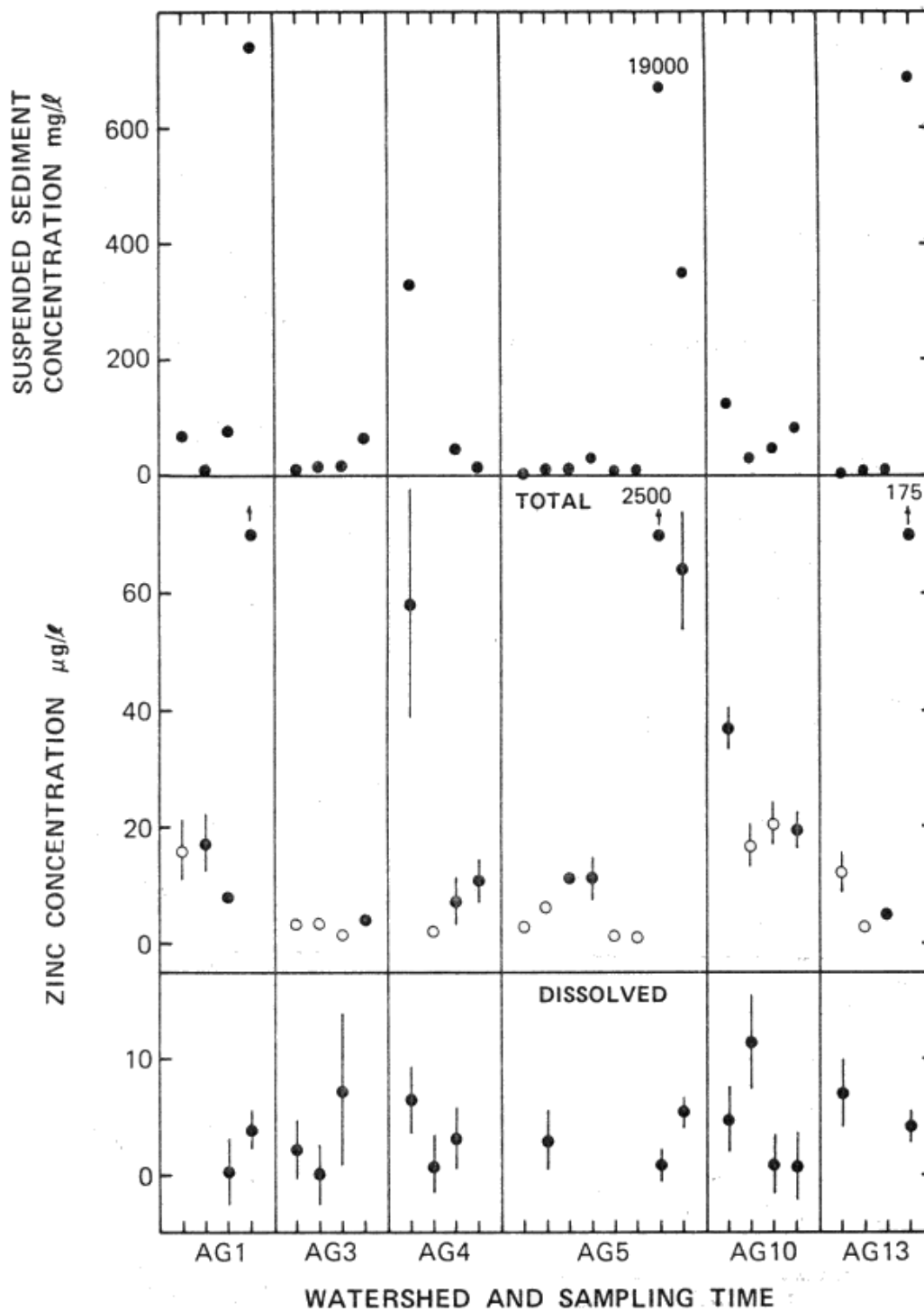


Figure 12. Concentrations of dissolved and total zinc and suspended sediment in water samples from the six agricultural watersheds. Each point represents one sampling date with the exception that the last two points for AG5 represent two sites sampled on the same date 25/03/77. Where total concentrations were unavailable, dissolved + acid- and solvent-extractable concentrations, denoted o, have been included as estimates of total concentrations.

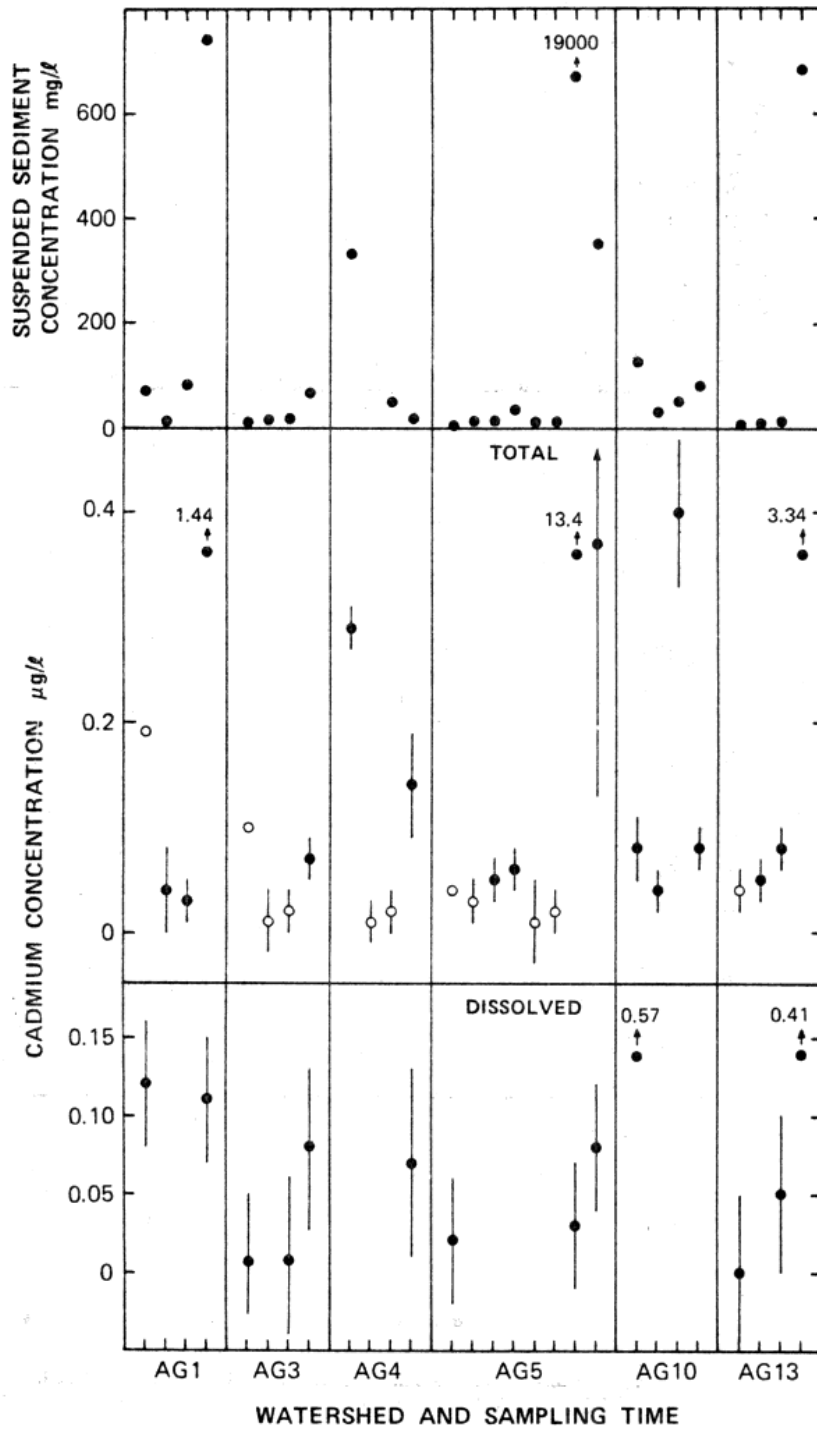


Figure 13. Concentrations of dissolved and total cadmium and suspended sediment in water samples from the six agricultural watersheds. Each point represents one sampling date with the exception that the last two points for AG5 represent two sites sampled on the same date 25/03/77. Where total concentrations were unavailable, dissolved + acid- and solvent-extractable concentrations, denoted o, have been included as estimates of total concentrations.

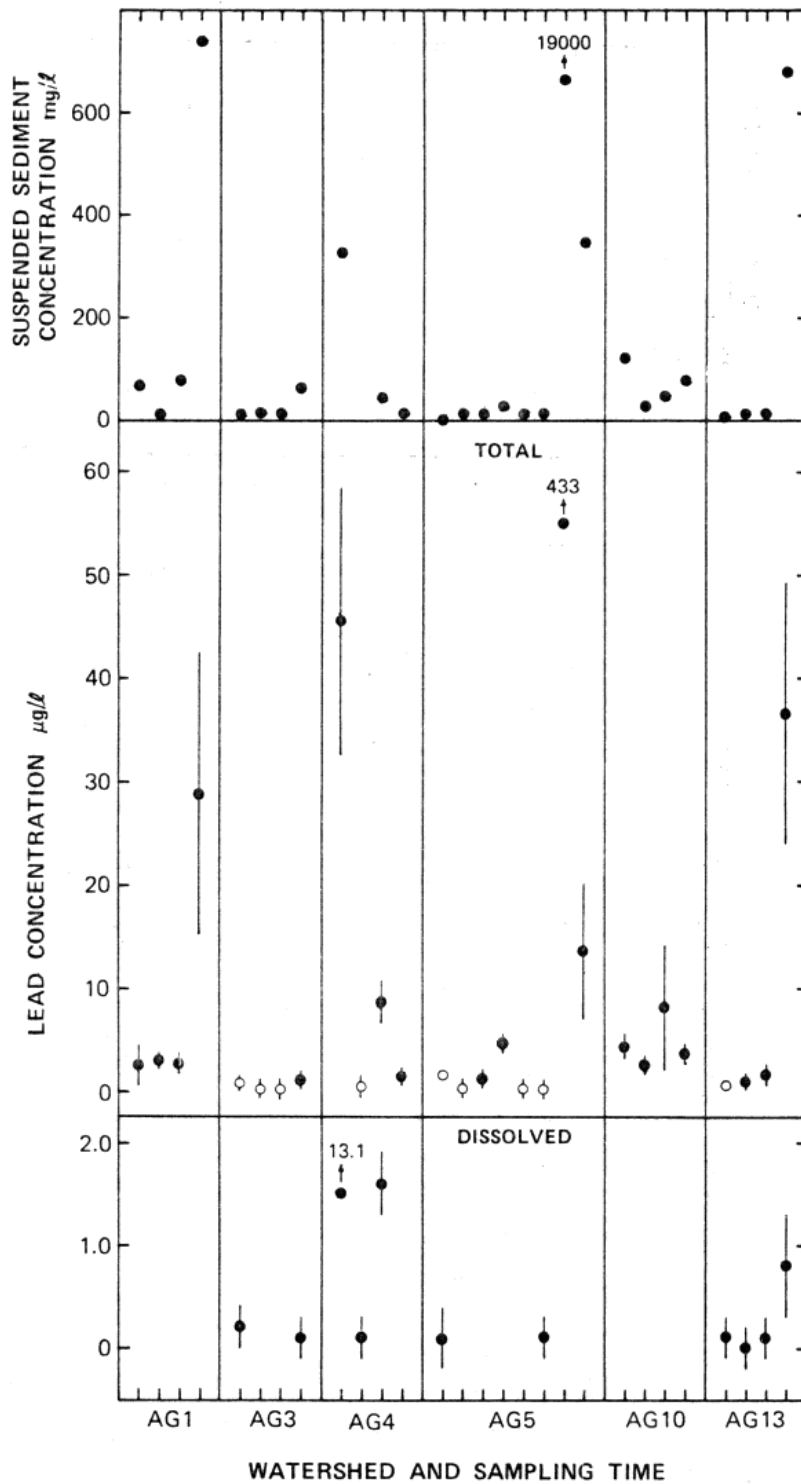


Figure 14. Concentrations of dissolved and total lead and suspended sediment in water samples from the six agricultural watersheds. Each point represents one sampling date with the exception that the last two points for AG5 represent two sites sampled on the same date 25/03/77. Where total concentrations were unavailable, dissolved + acid- and solvent-extractable concentrations, denoted o, have been included as estimates of total concentrations.

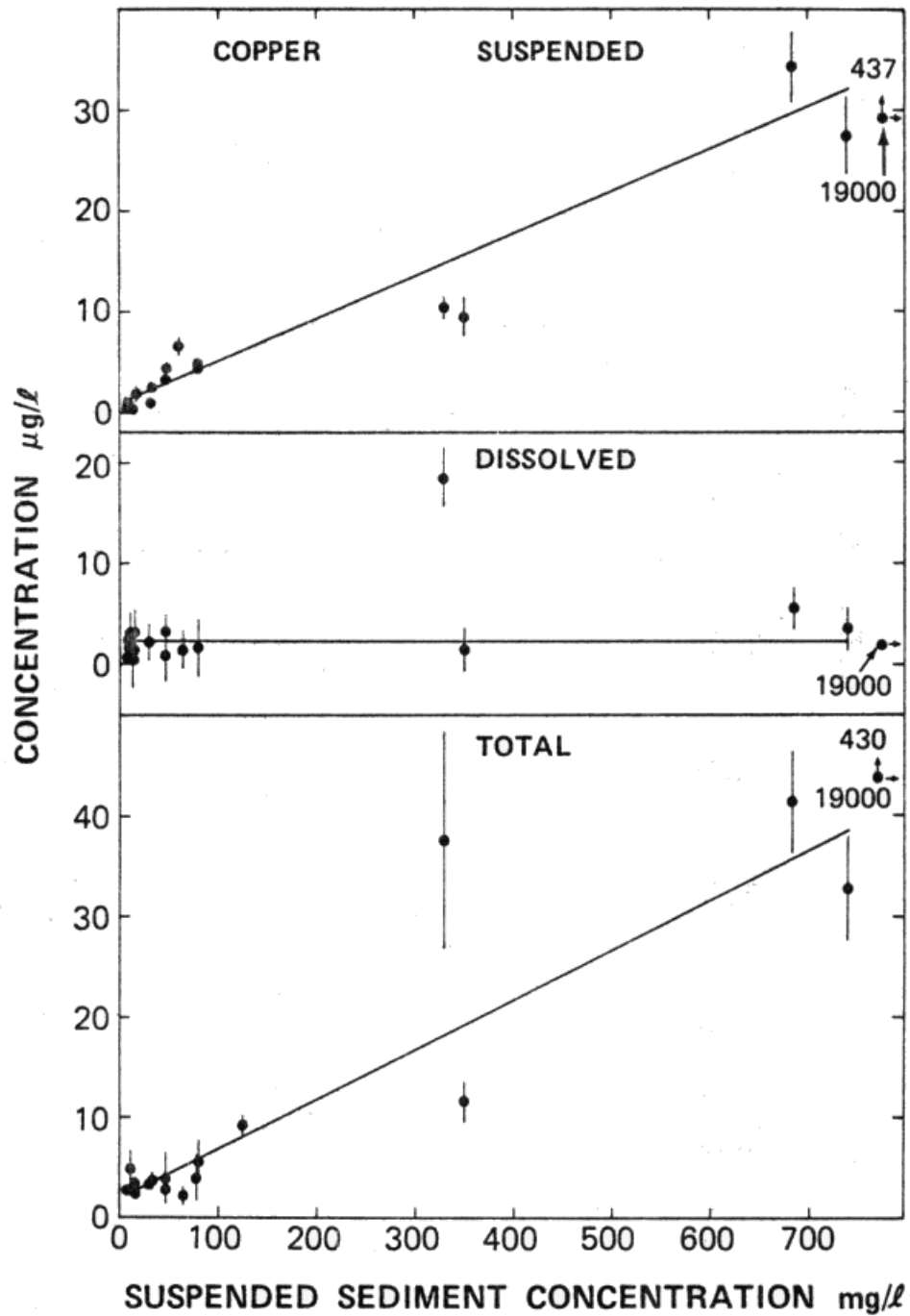


Figure 15. Total, dissolved, and suspended sediment-contributed levels of copper as functions of suspended sediment concentration in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13.

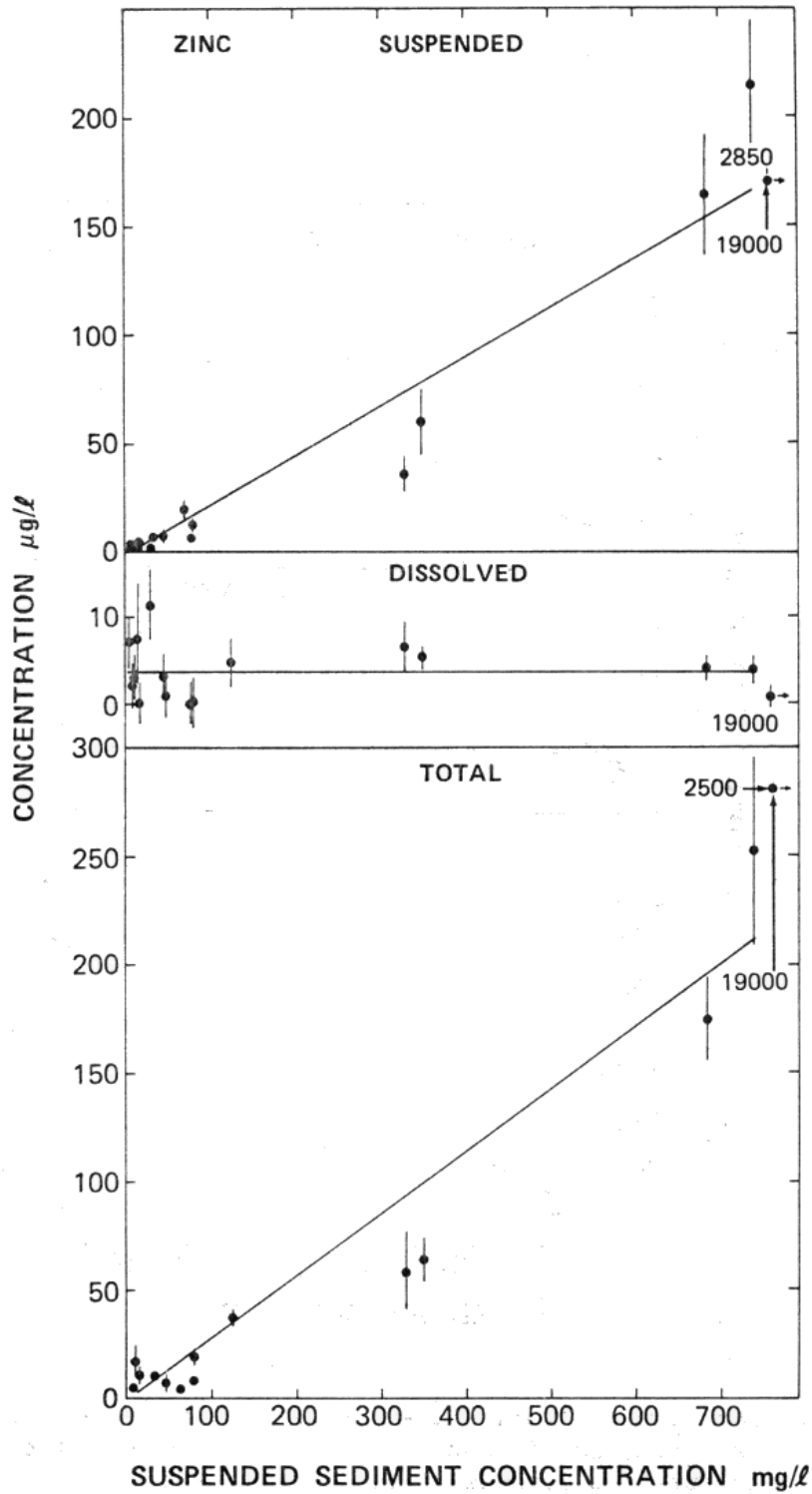


Figure 16. Total, dissolved, and suspended sediment-contributed levels of zinc as functions of suspended sediment concentration in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13.

Figure 17 missing

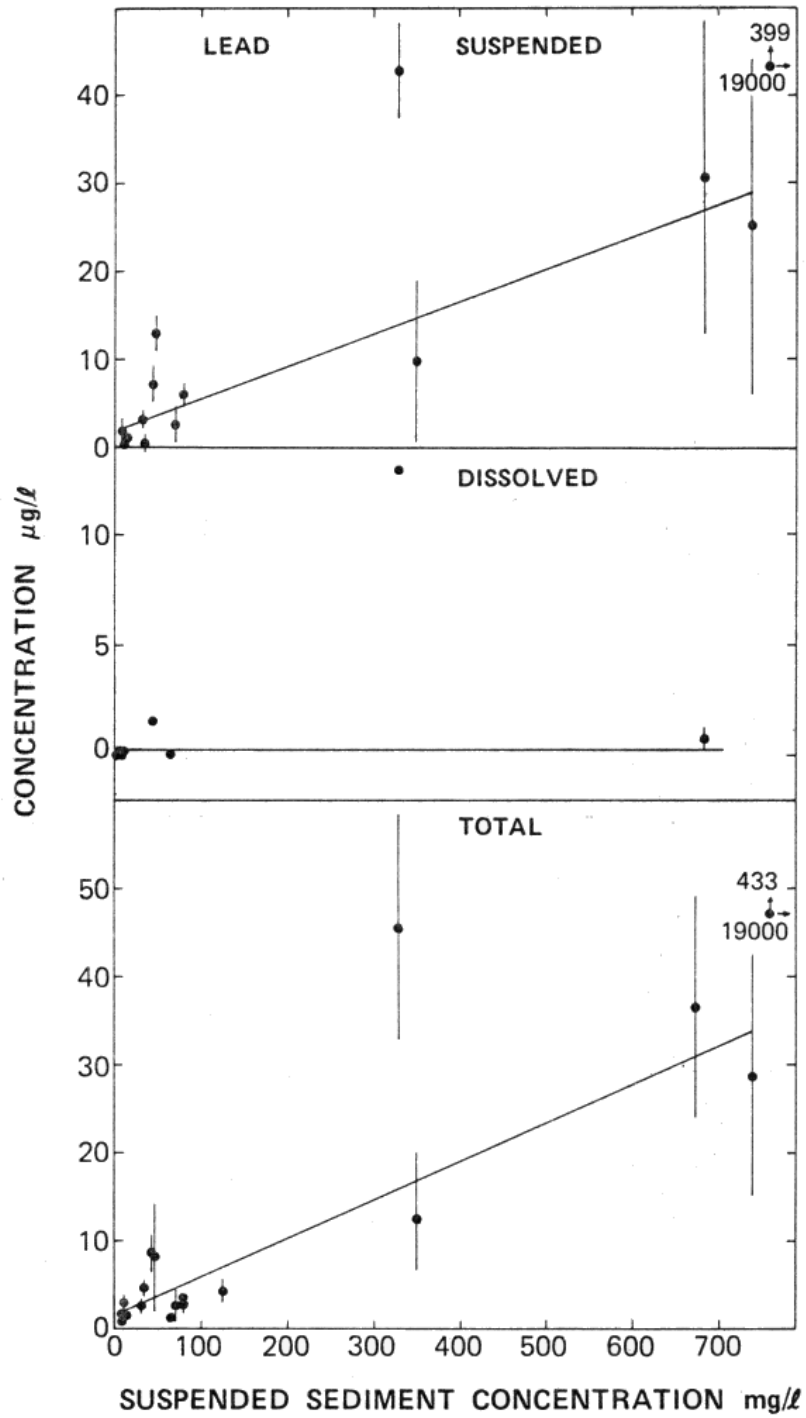


Figure 18. Total, dissolved, and suspended sediment-contributed levels of lead as functions of suspended sediment concentration in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13.

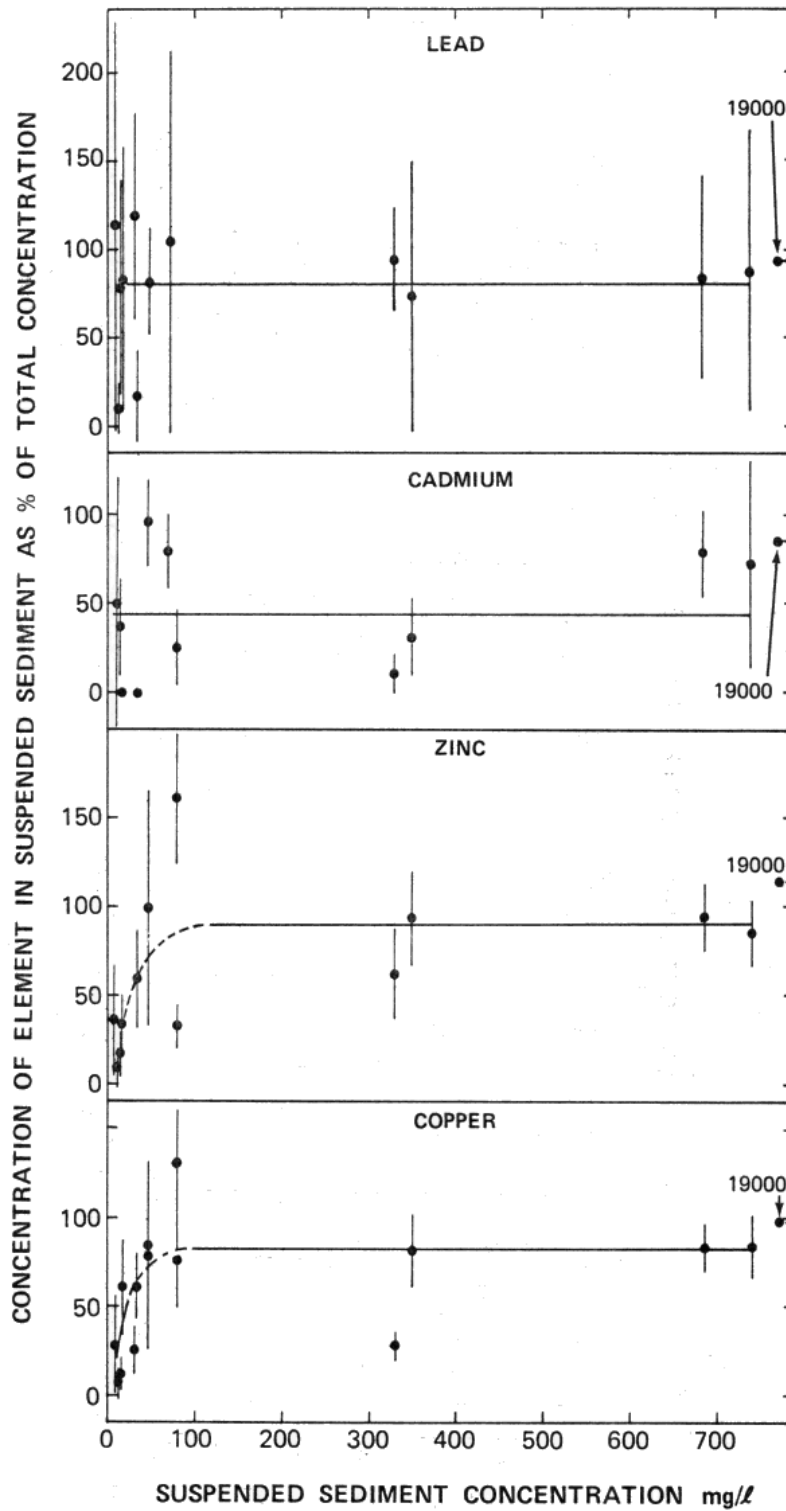


Figure 19. Percentage of total element concentration contributed by suspended sediment as a function of suspended sediment concentration in agricultural watersheds 1, 3, 4, 5, 10 and 13.

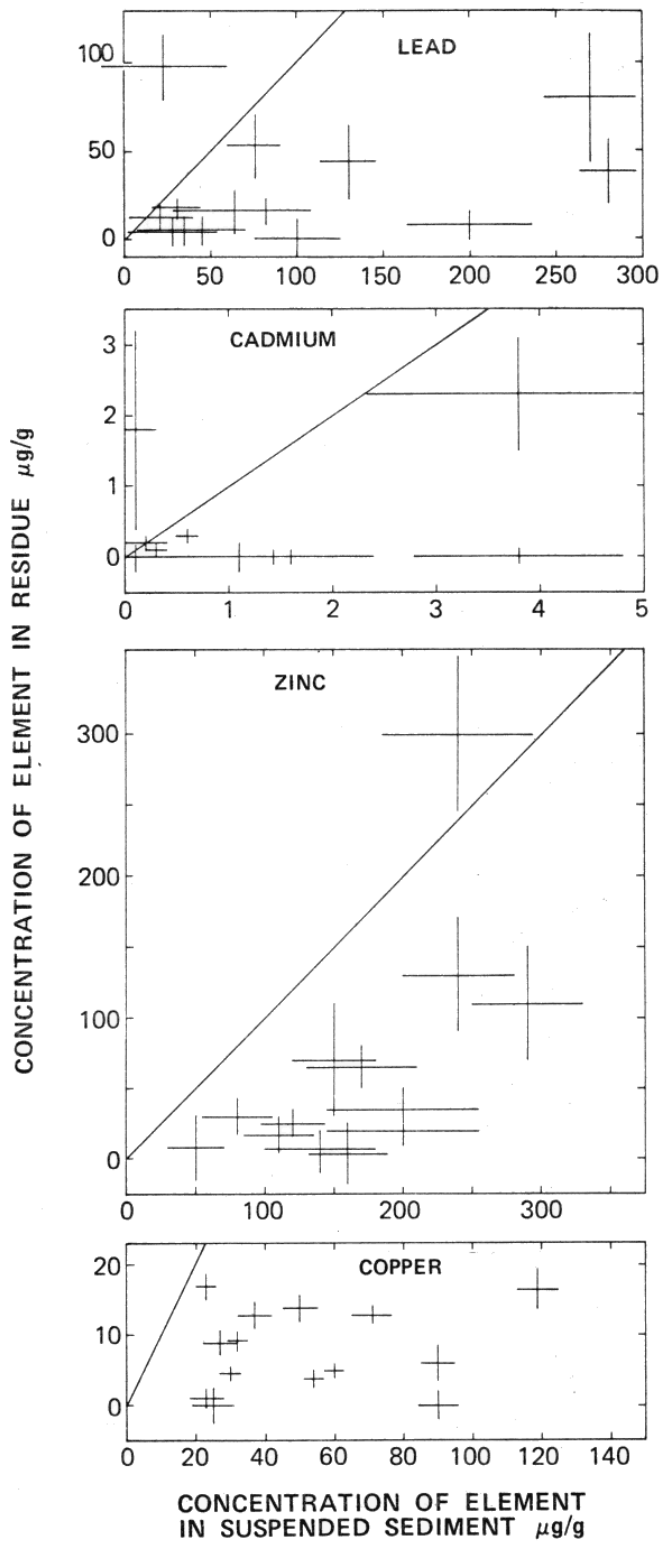


Figure 20. Concentrations of Cu, Zn, Cd and Pb in residues as functions of the respective concentrations in suspended sediments. The straight lines represent slopes of unity.

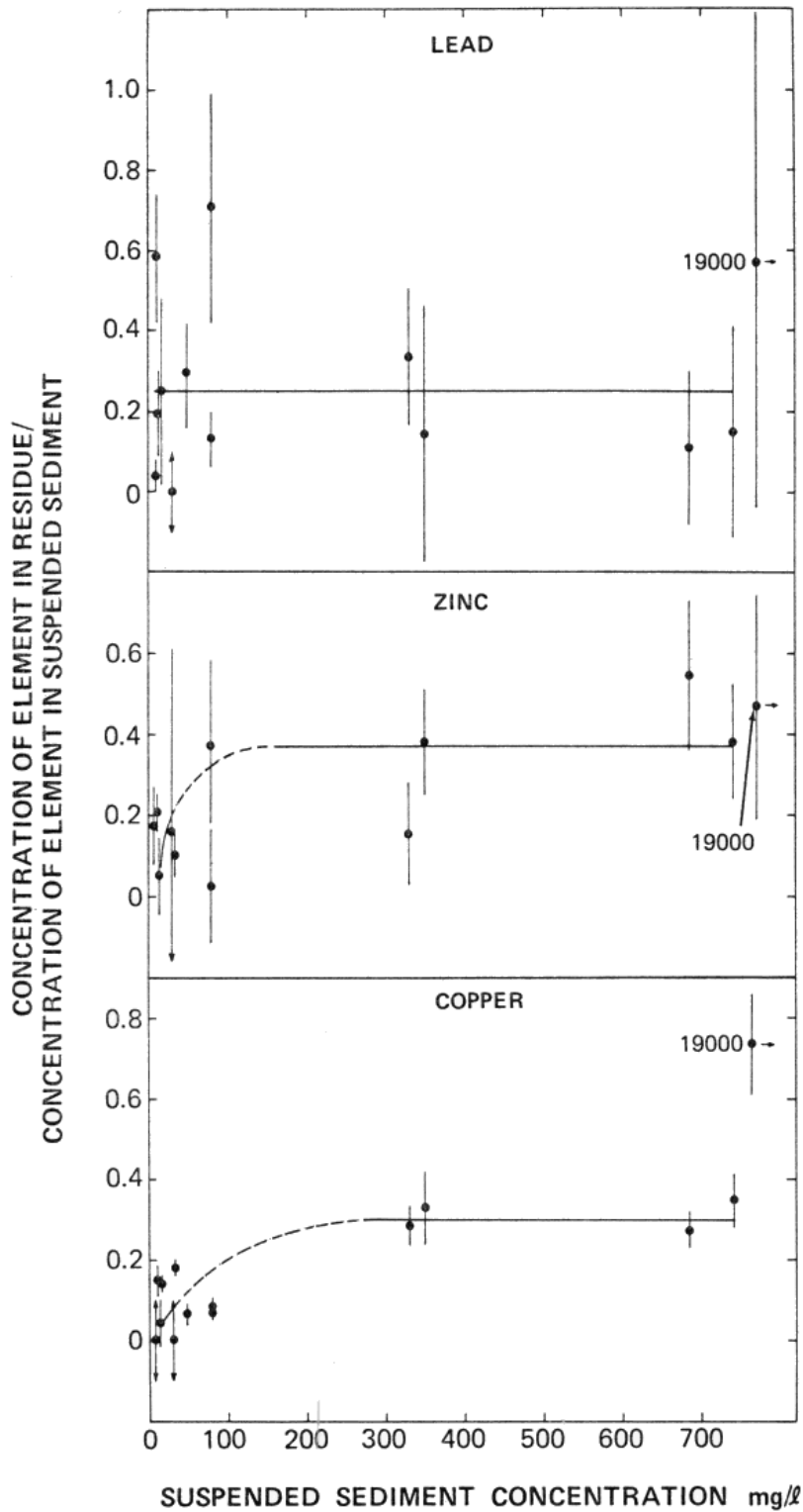


Figure 21. Ratio of concentration of element in residue to its concentration in suspended sediment, as a function of suspended sediment concentration. Arrows on both ends of standard error bars indicate that the error is unknown and greater than indicated.



## DATA ANALYSIS AND INTERPRETATION

### DISCUSSION OF RESULTS AND DATA INTERPRETATION

Prior to dealing with analysis and interpretation of the data obtained in this study, a brief discussion of data reliability and comparability might be appropriate at this point. As sound conclusions rely intimately on sound data, and inorganic analyses at trace and ultratrace levels are subject to errors from a multitude of sources, emphasis was placed on data quality control. Of all aspects of quality control, the incorporation of well characterized reference materials with accurately known analyte levels is the simplest and ultimate technique by which to gauge analytical method accuracy. Although reference solutions of metals in aqueous acid solution (EPA) were available and used for method testing, no reference natural water samples were available. We therefore resorted to an alternate technique for quality control involving independently different analytical methodologies and analysts in several cooperating laboratories of which three (Stoeppler, Berman and Russell) were very experienced in analytical chemistry and analysis of natural waters. The premise was that concordance of analytical results for subsamples of the same sample, from diverse methods suggests confidence in the reliability of the data for that sample. Whether the same confidence could be transferred to the actual stream components is another question dependent on sampling and sample handling prior to analysis; this aspect was at least partially attacked by replicate sampling.

A large proportion of the data resulted from analyses in two or more laboratories, and virtually all the data reported in the main body of this report has been averaged over all subsamples and analytical methodologies. Every datum has associated with it an uncertainty in the form of a standard error, which indicates the precision of the datum; since independent methodology was brought to bear on the work, the standard error can also be taken to give an estimate of accuracy (cf, however, later discussion of Pb). Some results exhibit rather large confidence limits and do not appear exact. This stems from the many factors entering the picture of ultratrace analysis including propagation of error in data manipulation, and systematic errors between the different methodologies. The latter would inflate the error of the average results but the incorporation of data from different methodologies would also be expected to lead to results closer to the truth. In spite of experimental limitations related to the foregoing, sample weight limitations, field

contamination and other problems, we have hopefully extracted fairly reliable information for discussion. More complete discussion of quality control procedures and interlaboratory results is presented in Appendix I; detailed data are contained in Appendix II.

It was of interest to compare the data for stream water components obtained in this work, with results for natural waters reported by other workers. In particular, it was of interest to compare this data with other PLUARG work on the same watersheds, encompassing identical sampling dates, and in fact, similar samples. Detailed comparisons of suspended sediment concentrations, and suspended sediment-contributed, dissolved and total trace element levels determined in this study, with values reported by Whitby *et al.* for project 9A (1978), and by Ontario Ministry of the Environment (OME) from their monitoring are tabled in Appendix II and only summarily discussed here. The water samples used in this study, and the ones reported on by Whitby *et al.* were often essentially subsamples of the same sample, whereas data from OME "monitoring and estimates" print-outs from NAQUADAT files were chosen to correspond in respect of watershed and sampling date.

Suspended sediment concentrations reported in Table 4 are generally in fair agreement with those reported by OME. That better agreement was not realized for such an easily measurable parameter (cf, however, McGirr 1974), might stem from imprecision of measurement but also from the dependence of suspended sediment level on stream flow and thus time of sampling. Comparison of our data with data from project 9A are not strictly valid as values from the latter were used to arrive at averages for the former.

Values for the contributions of suspended sediments to concentrations of Cu, Zn, Cd and Pb in waters of four of the watersheds (Table 6) agree within ca -80 to +200% (referred to our values) with the corresponding data reported by Whitby *et al.* This is considered to be good agreement considering the independence of analysis and the severe limitations imposed on us by having to analyze very small samples in the ca 1-30 mg range. Comparability of dissolved and total concentrations of trace elements between the two studies, however, is not as encouraging. The two sets of data are discordant with variations between corresponding results ranging from ca -100 to +15,000% referred to our values. Concentrations of Cu, Zn and Pb in dissolved form reported by Whitby *et al.* were particularly high. The very high values for total and dissolved concentrations listed by

Whitby *et al.* are considered aberrant. Levels for Cd reported in project 9A were often below the limit of detection.

It was possible to compare our total concentrations with levels obtained by OME during their extensive monitoring program. OME values are conceptually not total concentrations but would be expected to be fairly close to total levels to permit comparison. Comparisons of total level data from this study, with the few corresponding concentrations for identical watersheds and sampling dates reported by OME (obtained as NAQUADAT printouts) show some concordance for Cu and Zn but are inconclusive due to limited data; Pb levels appeared to be below OME detection limits. The low natural levels of Cd were generally not detected by OME monitoring and were typically reported as <0.00 mg/L. This suggests a detection limit of 10 µg/L, but could be as low as 1 µg/L according to the method of analysis followed by OME (NAQUADAT code 48006, Fisheries and Environment Canada (1978)).

The foregoing discussion referred to comparison of data for identical watersheds, sampling dates, sampling sites and even samples. A final comparison was made of ranges and medians of this data with this type of information reported by other investigators for the PLUARG watersheds and other "unpolluted" surface natural waters. Comparative summaries for total and dissolved concentrations of the four trace elements are presented in Table 11 and 12 respectively, with detailed information contained in Appendix II. For total concentrations, information was available for the PLUARG watersheds (Gaynor 1977, OME) and for a wide variety of other waters throughout the world. Median values for Cu and Zn found in this study agree well with medians for these agricultural watersheds reported by Gaynor and OME, although the Zn result seems to be higher. For Cd, and Pb, it appears that the analytical methodologies used by Gaynor and OME were insufficiently detective to measure the low natural levels of these elements and no comparisons can be made. With regard to literature data for other waters, the median total Cu level determined in this study is in excellent agreement with the typical median reported in the literature, median values for Zn and Pb are higher than the corresponding literature data, and Cd cannot be compared because of the generally poor detectivity of literature methods. For concentrations of dissolved trace elements only data for water from other than PLUARG sites are available for comparison. Our medians for Cu, Zn, Cd and Pb are in excellent agreement with the corresponding means reported by Chan, 1977, and the Cu value also

agrees excellently with the 2.24 µg/L obtained from the work of Silker, 1964. Other literature median data for the four elements are higher.

The ranges of dissolved and total concentrations and medians/means for these four trace elements reported in the literature are large. Their ranges could reflect real situations for the waters investigated, especially in respect of total levels which depend on suspended sediment concentrations, but could depend on pollution by man's activities as all waters may not be truly unpolluted, and could also reflect insufficiencies in analytical methodologies and contamination during sampling and analysis. The literature data listed in Tables 11 and 12 was reported between 1956-1977; it is conceivable that methodology and contamination considerations are relevant, particularly to the earlier information. Comments by Patterson and Settle (1976) in respect of the reliability of Pb determinations in natural systems are particularly relevant here. These authors have stated that "In most present analytical practices, lead concentrations in plants, animals, and foodstuffs cannot be determined reliably at the 1 µg/g level or in waters at the 1 ng/g level... The unreliability of analyses for lead is caused by a universal lack of familiarity with the extent, sources and control of industrial lead contamination during sample collecting, handling and analysis. As a consequence, the great mass of published lead data in plants and animal tissues and in waters is associated with gross positive errors and the error noise in lead concentration data below a few µg/g obscures the meaning of most work dealing with lead at these concentration levels". Hirao and Patterson (1974) found an average 0.015 µgPb/L in stream runoff from Thompson Canyon, California, which was 1/30 of the median Pb concentration of 0.5 µg/L measured by Bradford et al (1968) in 170 High Sierra Lakes. The use of a leaded fueled helicopter by the latter investigators was deemed responsible for their elevated levels. These observations suggest that information for Pb gathered from this study and reported in the literature be treated with reservation. On the basis of the foregoing comparisons, discussions and observations, we conclude that, with perhaps the exception of Pb, and within the stated confidence limits, the concentrations of Cu, Zn, and Cd reported here are reasonably reliable estimates of the levels of these elements in streams draining the six agricultural watersheds.

The behaviour of the suspended sediment fraction of the water samples with regard to acid solubility demonstrated in Figs. 8 and 9, suggests increased acid solubility at lower suspended sediment concentrations, and suggests a variation of physical and/or chemical

properties with sediment level. Suspended sediments from low level streams were substantially more soluble during the acid evaporation step and could conceivably consist of smaller and/or more soluble particulates. The solubility behaviour is paralleled by trace element extractability depicted in Figs. 20 and 21, the latter demonstrating, for Cu and Zn, increasing solubility with decreasing suspended sediment concentration. No trend is evident for Pb, and data for Cd were too inaccurate to consider in this context. In these and all other figures dealing with suspended sediment concentration relations, curves have been drawn without consideration of the point for 19,000 mg suspended sediment/L. Fig. 21 again demonstrates a gradual change in the physical and/or chemical character of the particulate material with its concentration in the stream. For bottom sediments from the Saguenay Fjord, Loring (1976) observed a clear increase in non-detrital (acetic acid-soluble) contribution to total Zn content going from sands to muds (decreasing particle size); similar but less conclusive trends were evident for Cu and Pb. If we assume low suspended sediment concentrations to be synonymous with smaller particle size, then the trace element-extractability phenomenon observed in this study is akin to that reported by Loring.

Plots of trace element concentrations in suspended sediments as a function of suspended sediment concentration in Fig. 10, show interesting enrichment relationships. The case is clear for Cu exhibiting increasing concentration levels with decreasing sediment levels; similar trends seem to occur for Cd and Pb although not for Zn, but the greater uncertainties in and scatter of data make these relations less clearly evident. The very high 19,000 mg suspended sediment/L point from the field erosion event sample falls in line with behaviour for points over the range ca 0-740 mg/L. Several investigators (Perhac and Whelan, 1972, Oliver, 1973, Loring, 1976) studying suspended and bottom sediments observed a correlation of increasing trace element concentration with decreasing particle size. Turekian and Scott, (1967), however, reported no significant differences in trace element contents of different size fractions of bottom sediment from one river, and Angino (1974) reported the composition of stream water and sediment to be discharge independent. Our observations, in conjunction with some of the literature reports, suggest decreasing particle size with decreasing suspended sediment concentration.

Garrett and Hornbrook (1976) found a strong relationship between Zn and organic content in lake bottom sediments, with the concentration of the element increasing with

increasing organic content, estimated from loss on ignition, over the range 0-12% loss on ignition. With this information we may speculate increasing organic content of suspended sediments occurring at decreasing sediment levels in stream waters. It is interesting to observe the similarity of the three suspended sediment parameters, acid-solubility, trace element extractability and trace element concentration depicted in Figs. 9, 21 and 10 respectively. In all three cases transitions between behaviour at low and high suspended sediment levels occur in the region 80-330 mg/L. The transition points cannot be pinpointed more accurately due to the absence of information in that region. It should be very interesting indeed to relate the relationships observed in this study to particle size, organic content and mineralogy of these or similar suspended sediments from these agricultural watersheds anticipated from concurrent studies by Wall (1978) and Whitby *et al.* (1978). Several samples were event samples collected after rainfall and during spring runoff; suspended sediment levels were at both extremes. With the limited data, it is impossible to assess whether the character of suspended sediment in event samples (possibly not yet in equilibrium with the water) differed from that of sediment in normal-flow water samples.

Due to scarcity of data, concentrations of dissolved and total trace elements and suspended sediments presented in Figs. 11 to 14 cannot be related to watershed and sampling time. Much more representative information for each watershed gathered from a more detailed sampling program covering normal and event flows is needed to characterize the different streams. Relations between trace element concentrations and suspended sediment levels evident in these Figs. are brought out more clearly in Figs. 15-18 where total, dissolved and suspended sediment-contributed trace metal concentrations are plotted as functions of suspended sediment concentration over all the watersheds. Whereas total and suspended sediment-contributed trace element levels are dependent, as might be expected, on suspended sediment concentration, dissolved levels of Cu, Zn, Cd and Pb are strikingly invariable with suspended sediment concentration over the range *ca* 10-740 mg sediment/L and even up to 19,000 mg/L. Similar observations of the independence of dissolved trace element levels on concentration and composition of suspended solids have been reported by Turekian and Scott (1967), Kharkar *et al.* (1968), Turekian (1971) and Angino (1974), and determined by the author from data reported by Silker (1964). In both this work and literature reports, dissolved trace element levels exhibit scatter about median values. It would be of interest to seek out the parameter correlated with this and ascertain whether unattainment of equilibrium (Turekian, 1971), among the

dissolved and particulate fractions of stream waters is a factor responsible for extreme values.

Some conclusions in respect of storage and mechanism of transport of Cu and Zn can be drawn from information presented in Figs. 15-18 and particularly in Fig. 19. It appears that the dominant mechanism of storage and transport depends on the suspended sediment level in the stream. In waters with low suspended sediment levels, below *ca* 20 mg/L, the majority of the Cu and Zn is transported in dissolved form, whereas the suspended sediment accounts for most of the transport of these trace elements at higher particulate levels. Fully one half of the water samples collected had suspended sediment concentrations below *ca* 20 mg/L. Thus both dissolved and suspended transport mechanisms are of importance in these watershed streams, and in general, suspended sediment levels should be quoted when discussing transport mechanisms. Sediment transport during rainstorms and spring runoff, however, seems like the most important mechanism for removing large amounts of elements from these watersheds over the course of a year. Only scant reference to details concerning transport mechanisms of Cu, Zn, Cd and Pb have been found in the literature although the behaviour of other trace elements has been reported. Relations of transport mechanisms to sediment loads have not generally been mentioned. Kopp and Kroner (1968) reported on a comparison of dissolved and suspended Cu, Zn and Pb based on analytical data from a water quality surveillance program. Over a number of different locations mean levels of dissolved Cu and Zn were higher than the corresponding suspended levels; data for Pb was said to be in error due to sampling problems. It is difficult to read more information into their findings as comparisons for the individual waters were not made, and no sediment levels were reported. Gibbs (1973) investigated the distribution of Cu and several other trace elements among five mechanisms of transport and observed a similar distribution for the widely separated Amazon and Yukon rivers. The majority of the Cu (93.1-96.7%) was transported with the particulate load, and incorporation into the crystal structures of the sediments was the most important mechanism. Lead was found by Angino (1974) to be approximately equally divided between dissolved and suspended phases in waters from Kansas rivers in contrast to the occurrence of the bulk of the load of Fe and Mn in the suspended phase. In an interesting study of stream supply of dissolved trace elements to the oceans, Kharkar *et al.* (1968) discussed relations between dissolved and desorbable (from suspended sediment) concentrations for several elements but not for those of interest here. Turekian

(1971) concluded that more cationic but not anionic species of trace metals are absorbed effectively on particles carried by streams and have very little chance of leaving an estuary in solution. Analyses by David and Soper, (1975) of ocean water, for dissolved and particulate forms of Cu, Zn, Cd and Pb, indicated 66, 85, 100 and 44% respectively, to be in dissolved form. In none of these studies, however, was an attempt made to relate distributions of trace elements between dissolved and particulate forms to suspended sediment concentrations.

In his study on PLUARG watershed AG13, Gaynor (1977) concluded that Cu was transported on suspended solids but that Zn was transported as soluble species. These conclusions were based on correlations between (dissolved plus extractable) metal levels and suspended sediment levels. Close correlations between total metal levels in stream waters from the six watersheds and suspended sediment levels therein were found in this work (cf Figs. 15-18) for all four metals, including Zn, in contrast to Gaynor's observation for Zn. Such correlations indicate the general association between transport and sediment load, but the situation can be more clearly assessed by observing relations of total metal found in the suspended or dissolved phase to suspended sediment concentration as depicted, for example, in Fig. 19. Whitby *et al.* (1978) reported that Cu and Pb, although present in the particulate, were found primarily in the dissolved fraction, whereas Zn appeared more particulate. These conclusions, particularly for Cu, must be accepted with reservation on account of the aberrant concentration data for dissolved and total Cu reported by these authors. Conclusions regarding Pb, arising from investigations not applying the essential techniques and careful execution followed by experienced laboratories, must be treated with caution (Patterson and Settle, 1976); this comment applies to the work reported here and, likely elsewhere.

## CONCLUSIONS

Data collected over a one year period from a study of the six agricultural watersheds 1,3,4,5,10 and 13 lead to the following conclusions:

- (1) Ranges of concentrations ( $\mu\text{g/L}$ ) of Cu, Zn, Cd and Pb in dissolved form in stream waters from the six watersheds were found to be 0.5-18.5, 0.1-11.4, 0.00-0.57 and 0.0-13.1 respectively, with median concentrations  $\pm$  standard errors of  $2.0 \pm 1.8$ ,  $3.1 \pm 2.7$ ,  $0.07 \pm 0.06$  and  $0.1 \pm 0.2$  respectively. With the exceptions of several high values, concentrations of these dissolved trace elements were invariable over watersheds, and suspended sediment levels.
- (2) Suspended sediments with a concentration range 219,000 mg/L and a median of ca 20 mg/L, contributed ( $\mu\text{g/L}$ ) 0.3-437 of Cu, 1.3-2850 of Zn, 0.00-11.4 of Cd and 0.3-399 of Pb with corresponding medians  $\pm$  standard errors of  $4.3 \pm 0.5$ ,  $9.1 \pm 2.6$ ,  $0.09 \pm 0.06$  and  $3.1 \pm 1.1$   $\mu\text{g/L}$ . Ranges of total concentrations and (medians  $\pm$  standard errors) were Cu: 2.2-445 ( $3.9 \pm 2.6$ ); Zn, 4.3-2500 ( $17.2 \pm 4.9$ ); Cd, 0.03-13.4 ( $0.08 \pm 0.02$ ); Pb, 0.9-433 ( $3.7 \pm 1.0$ )  $\mu\text{g/L}$ . Total and suspended sediment- contributed levels were related to the sediment levels in the streams.
- (3) The concordance of results for dissolved and total concentrations of these elements with literature data for other natural waters suggests no gross effects of agricultural practices on trace element levels in streams. An exact statement must await more exact information on levels in these and other natural water systems and the establishment of relationships between these levels and the geologic nature of the areas drained.
- (4) For Cu and Zn, the dominant mechanism of transport within the stream depends on the suspended sediment level. In waters with low suspended sediment levels, below ca 20 mg/L, the majority of the Cu and Zn is transported in dissolved form, whereas the suspended sediment accounts for most of the transport of these trace elements at higher particulate levels. Thus, sediment transport during spring run-off and rain-storms seems like the most important mechanism for removing large amounts of elements from these watersheds over the course of a year.

- (5) The physical and/or chemical characteristics of the suspended sediment depended on its concentration in the water. Both acid-solubility and trace element extractability increased with decreasing sediment levels. Sediment from low level streams was enriched with Cu in relation to levels of Cu in suspended sediments from higher level streams.
- (6) Trace element concentrations in water samples determined by acid leaching or solvent extraction, without complete dissolution of suspended sediment (often referred to as "total" concentrations) were lower than total concentrations determined by complete destruction of particulate matter; they approached total concentrations when suspended sediment levels were low, but were more deviant at higher suspended sediment levels.
- (7) Although considerable effort and diligence were directed to the generation of analytical information regarding trace element concentrations in stream waters, and reasonably reliable data was realized for Cu and Zn, and occasionally for Cd and Pb?, somewhat large imprecision is associated with some data, and their accuracy cannot be firmly defined. Specifically, the very low levels of Cd and Pb in natural waters, coupled with experimental difficulties associated with their measurement, gave rise to uncertain data and precluded firm conclusions regarding these two elements. This suggests that accurate trace and ultratrace analysis is a rather complex and demanding task requiring a good measure of analytical and technical competence. Reliable, detailed, and representative information in respect of important trace elements in natural water systems is sorely needed to fully address PLUARG objectives, to conclusively interrelate trace element levels among the various stream components, to get a good understanding of the sources and mechanisms of element transport and to provide a reliable data base for current and future comparisons. Reliable analytical and environmental information is a prerequisite to the formulation of firm conclusions and sound decisions. Consideration of the following proposals, directly related to all of the PLUARG objectives in the Detailed Studies Program (International Reference Group, 1974), would answer more completely PLUARG's questions and would conveniently benefit from the intensive efforts expended thus far in identifying and characterizing agricultural watersheds.

(i) Relation of this work to other studies. Given the many other investigations concerning the characteristics of the six watersheds, detailed relationships between trace element levels reported here and soil, suspended sediment and bottom sediment mineralogy, and chemistry should be investigated. Relations should be sought between trace element information reported here and the variety of other parameters resulting from other detailed studies in the PLUARG program, such as land use information, stream flow, precipitation chemistry, soil inventory, nutrient and other component levels in streams, erosional losses from land, sediment delivery, and mechanisms of transport delineated in other studies.

(ii) Levels of Trace Elements in Streams. Much more accurate and representative concentration data are required to get a grasp of the partition of trace elements, such as Cu, Zn, Cd and Pb, between suspended and soluble forms. In particular, should one be interested in trends of trace element levels with time, that is, comparisons of future data with the present information to monitor effects of changed land uses and anthropogenic pollution, then very accurate data indeed is a prerequisite for any serious comparisons. Much data in the literature in respect of low trace element levels in natural waters (and other systems) is either suspect, or the result of insufficiently detective methodology, and it is only with the work of recent years that we have begun to approach some degree of reliability in this area. It is very difficult if not impossible to follow trends with time using information with a spotty reliability record. It is difficult enough to generate good data let alone look for differences between them. Levels of Cd, for example, reported 10 years ago as  $<10 \mu\text{g/L}$  cannot be related to levels found today in the vicinity of  $0.01\text{-}0.1 \mu\text{g/L}$ . Detection limits for trace elements suggested by PLUARG to be at the  $1 \mu\text{g/L}$  level are too high for Cd and Pb. The very low levels of these elements in natural waters suggests the need for analytical detection limits 100-1000 fold lower, in the range  $0.001\text{-}0.01 \mu\text{g/L}$ .

Data obtained in this work suggest that dissolved levels of trace elements are fairly invariable with watershed and suspended sediment load. Several results, however, deviate substantially from medians. Whether these are non-representative, aberrant values or represent real behaviour of the systems cannot be conclusively assessed. This interesting question could be answered through more careful studies. Much effort has gone into defining, choosing and characterizing these representative agricultural watersheds, setting up instrumentation and amassing details; this can be put to good use in respect of detailed

trace element studies. Much valuable and interesting information regarding levels of selected trace elements in the streams, sources, storage and transport mechanisms and loadings can be obtained with only moderate effort from a continued small scale investigation of these six watersheds. This situation presents an excellent opportunity, through careful experimentation, to provide a good data base in respect of total, suspended sediment-contributed and dissolved trace element concentrations and loadings, to provide for firm conclusions now and for comparisons in the future. This information can be related to stream flow and suspended sediment characteristics and integrated with respect to these parameters. Very sparse data is available on the behavior of the toxic elements Cd and Pb and no firm conclusions resulted from this work. Particular attention should thus be devoted to these elements. Even extremely low levels of elements in waters could be of significance given the phenomenon of bioaccumulation which can result in one million-fold enhancement of concentration in living organisms.

(iii) Speciation of Trace Elements: From the standpoint of toxicology and detailed information regarding transport mechanism, knowledge of element speciation, that is the chemical form and location of the element in the solution/suspended sediment matrix is imperative. It is recommended that the gross partition (dissolved/suspended sediment) studies mentioned in (ii) be extended further to include investigation of relations between element levels and suspended sediment mineralogy and extractability with selective reagents. Such important basic information on partition of trace elements in these "unpolluted" streams can serve as a basis for comparison with levels and behavior of trace elements in other "unpolluted" natural waters and in water courses contaminated by trace elements from anthropogenic and natural sources. Further study of gross and detailed partition would shed light on the enrichment phenomenon uncovered for Cu and ascertain whether a similar situation exists for Zn, Cd and Pb. (Speciation in solution where the metal can be present as hydrated ions, complexes with inorganic or organic ligands, and adsorbed on or occluded in inorganic and organic colloids, is another consideration too complex, however, to envisage within the present context, but important for complete understanding of the sources, fate, and behavior of metals in the environment).

## DEGREE TO WHICH PROJECT OBJECTIVES WERE MET

The main objective of this study was to obtain reliable analytical information regarding concentrations of Cu, Zn, Cd and Pb in waters and suspended sediments from six agricultural watersheds, in support of project 9 goals related to assessing relationships between concentrations of these elements in stream components and soils, and elucidating storage and transport mechanisms. Other objectives were related to development of analytical methodology, and elucidation of metal transport mechanisms. All objectives were met.

Appropriate analytical methodology with detection limits equal to or generally better than the 1µg/L requested by PLUARG was developed and adapted to the measurement of trace and ultratrace levels of the elements of interest in water and sediments. Application of in-laboratory data quality control procedures and cooperation of other experienced analytical laboratories gave reliable results for dissolved, suspended sediment-contributed, and total concentrations of the elements. Comparison of results from this study with literature information on levels of trace elements in other natural waters suggested no gross effects of agricultural practices on trace element levels in streams. Conclusions regarding partition between dissolved and suspended phases and mechanisms of transport of Cu and Zn were formulated. Some conclusions regarding the physical and/or chemical characteristics of the suspended sediment as a function of its concentration in the stream were also presented.

Table 11 Comparison of total concentrations of Cu, Zn, Cd and Pb in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13 with literature data for these and other "unpolluted" fresh surface natural waters <sup>a</sup>.

Element	Concentration, ug/L				
	This work <sup>b</sup>		Literature <sup>c</sup>		Water <sup>d</sup>
	Range	Median	Range	Medians or means	
Cu	2.2-445	3.9 ± 2.6	<1-230	5, 8	A
			0.4-150	1.16, 1.2, 2.0 ± 1.8, 3, 4.7, 6.9, 15	O
Zn	4.3-2500	17.2 ± 4.9	<1-820	5.5, 12	A
			0.3-620	1.5, 7.8, 8, <10	O
Cd	0.03-13.4	0.08 ± 0.02	<0.6, <1	<0.6, <1	A
			0.02-6	0.045, < 0.5, < 1, 1.0	O
Pb	0.9-433	3.7 ± 1.0	<1-76	<2, <11	A
			0.3-200	0.015, 0.26, 0.5, 0.7 ± 0.8, 0.8, 4, 5.4	O

<sup>a</sup> Refer to Appendix II for detailed information.

<sup>b</sup> Refer to Table 9 for details; 15-19 samples of 6 watersheds.

<sup>c</sup> All levels reported in the literature may not, strictly speaking, be total concentrations; ranges and medians were either reported or estimated by this author from data reported; means were reported. Agricultural watershed data based on *ca* >123 to 1028 samples from 6 watersheds; data for other waters based on *ca* >52 to >674 samples from >28 to >203 waters throughout the world.

<sup>d</sup> A-PLUARG agricultural watershed; 0-other natural water. All waters may not be truly unpolluted.

Table 12 Comparison of concentrations of dissolved Cu, Zn, Cd and Pb in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13 with literature data for other "unpolluted" fresh surface natural waters <sup>a</sup>.

Element	Concentration ug/L			
	This work <sup>b</sup>		Literature <sup>c</sup>	
	Range	Median	Range	Medians or means
Cu	0.5 - 18.5	2.0±1.8	0.20 - 280	1.6 <sup>d</sup> , 2.24, 5.3, 15
Zn	0.1 - 11.4	3.1±2.7	0 - 1183	0, 3.5 <sup>d</sup> , 14.4, 64
Cd	0.00 - 0.57	0.07±0.06	0.004 - 120	0.2 <sup>d</sup> , 9.5
Pb	0.0 - 13.1	0.1±0.2	0.058 - 140	0.2 <sup>d</sup> , 4.0, 23

<sup>a</sup> Refer to Appendix II for detailed information. All waters may not be truly unpolluted.

<sup>b</sup> Refer to Table 9 for details; 11-21 samples of 6 watersheds.

<sup>c</sup> Analyses of typically 0.45 m-filtered water samples. Medians or means reported in literature; medians estimated by this author from data reported. Data based on *ca* >1690 samples from >131 waters.

<sup>d</sup> Data of Chan 1977.

## RELATIONSHIP OF PROJECT RESULTS TO PLUARG OBJECTIVES

The objective of this study was to determine concentrations of Cu, Zn, Cd and Pb in waters and suspended sediments from six detailed study watersheds with the aim of assessing relationships of these heavy metals among stream components and elucidating storage and transport mechanisms.

Reliable estimates of trace element levels in stream components were provided.

Comparison of results from this study with literature information on levels of trace elements in other natural waters suggested no gross effects of agricultural practices on trace element levels in streams.

Conclusions regarding partition between dissolved and suspended phases and mechanisms of transport of Cu and Zn were formulated. Some conclusions regarding the physical and/ or chemical characteristics of the suspended sediment as a function of its concentration in the stream were also presented.

Information was provided to permit estimation of the extent of trace element loadings to surface waters, in conjunction with flow data expected from other studies of these watersheds.



## APPENDIX I: ANALYTICAL METHODOLOGY AND DATA QUALITY CONTROL

This appendix presents supporting information on and performance characteristics of the analytical methodologies used to generate results discussed in this report. It also contains description of and results from experiments conducted to monitor contamination of samples by the filtration procedures and losses by absorption, discusses quality control procedures and inter-laboratory comparisons as guides to data reliability, presents additional detailed information on the analytical procedures used in the author's laboratory, and presents a critique of the study together with recommendations for future work and points to consider with the view of improving the quality of information.

### EVAPORATION/FLAME ATOMIC ABSORPTION SPECTROMETRY - CBRI LABORATORY

Performance characteristics - precision, detection limits, recoveries of added analytes and accuracy determined with EPA reference solutions - of the Evap/FAAS method and the FAAS determination procedure are presented in Tables 13-16. These characteristics were measured at various times during the course of this project, and thus reflect analytical performance for the PLUARG study; they refer solely to the analytical procedures and do not include sampling and subsampling variances. Standard deviations depicted, were calculated for different concentration ranges, from 12 to 912 duplicate analyses or determinations on unfiltered and filtered natural, synthetic natural and deionized water samples and related solutions. Calculations were by means of the equation  $s = \sqrt{(\sum d^2/2n)}$ , where s is the standard deviation, and d is the difference between each of the n duplicate analyses, or the tabular form of this equation as used by the Laboratory Services Branch, Ontario Ministry of the Environment (OME), Toronto. Standard deviations used to estimate precision of analyses of virtually all samples in this study are indicated in Table 14. Detection limits were taken as 3x standard deviations of blanks and low level samples (41-456 degrees of freedom) as advocated by Kaiser (1968) and IUPAC (1976), and are given in Tables 13 and 21 for the FAAS determination procedure and the Evap/FAAS method respectively. For Cu, Zn and Pb, precisions of the Evap/FAAS method were observed to be similar for both and 50-fold concentration; precision of Cd analyses, however, was dependent on concentration, with standard deviations of 0.12 and 0.038 µg/L for 20- and 50-fold reductions respectively.

Results of analyses of EPA Trace Metals Quality Control Samples shown in Table 15, are in excellent agreement with EPA values with an overall deviation (this work-EPA) of

-1 µg/L. Solution 1-575 was subjected to heat-concentration prior to atomic spectrometric determination whereas the two other solutions, 2-575 and 3-575, containing higher levels of the elements were analyzed by direct aspiration-FAAS. Analyses were performed blindly on solutions, each prepared from two different ampoules containing the metal concentrates.

Mean recoveries of 1.00-40.0 µg/L of Cu, Zn, Cd and Pb added from composite standard solutions, to deionized, synthetic natural and natural waters prior to taking the samples through the Evap/FAAS procedure (Table 16) ranged from 83% to 114% with an overall mean of 100.2% (108 analyses). Fairly respectable performance was obtained even at 0.20 µg/L added element, a level at or below detection limits.

Because the Evap/FAAS procedure involved the measurement of low levels of trace elements in concentrated solutions, it was felt that non-atomic absorption resulting from relatively high salt matrix concentrations would have to be considered. It may be observed from Figure 22 that although distilled water solutions generally exhibited no non-atomic absorption problem, concentrated solutions of natural waters did, and operation of the spectrometer in the corrected mode was imperative.

Another interesting phenomenon was related to acid reagent blanks and 20-fold concentrated synthetic natural water quality control solutions, AA. A range of positive and negative concentrations (expressed as µg/L in the sample as measured) were observed, reflecting apparent and real concentrations of trace elements in these matrices, nominally expected to contain 0 µg/L. For about 10 sets of analytical data, each set representing typically 10 calibration runs and an identical number of determinations on acid reagent blanks, RBA, and AA solutions, respective overall mean concentrations,  $\bar{c}_{RBA}$  and  $\bar{c}_{AA}$  of 1.0 and 56, -10.6 and -3.2, and -1.5 and -4.1 µg/L were found for Cu, Zn, and Cd respectively. Pb exhibited strikingly different behaviour with  $\bar{c}_{RBA}$  and  $\bar{c}_{AA}$  being highly variable and ranging from -176 to +9 and -221 to +93 µg/L respectively over the 10 measurement sets. Within each set, however, both parameters for Pb, as for the other three elements, were fairly invariable. Instrument parameters were adjusted prior to measurements in each set, but once adjusted, remained unaltered for all measurements within the set.

The fact that solutions RBA and AA are different (both are 1.6 M with respect to HNO<sub>3</sub> but the latter contains a heavy salt matrix) can account for the different trace element levels measured, by virtue of contamination (reflected in positive concentrations) and instrumental measurement system biases (positive or negative concentrations). Consideration of the latter

suggested that blank measurements on AA rather than on RBA would be the more appropriate to use in calculations of trace element concentrations in samples, as solution AA more closely approximated sample matrices. These blank considerations are in addition, of course, to processing reagent blanks obtained by taking reagents, devoid of sample through the entire analytical procedure. Solution AA would have provided an excellent reagent blank if it contained no extraneous trace elements; having been prepared from reagent grade but not ultra-pure salts, this could not be assured. In fact, without a solution prepared from pure salts to serve as a matrix reference, contamination levels of Zn, Cd and Pb in solution AA could not be measured with certainty (cf the negative values for Zn, and Cd, and the positive and negative values for Pb); an estimate, however, of ca 56 µg/L could be made for Cu, the only element to give consistent, positive concentration data. Solution RBA thus served as the reagent blank for Cu and Zn, but it was decided to use AA in conjunction with Cd and Pb analyses, the assumption being that Cd and Pb levels, in AA were 0. Later independent analyses (through the courtesy of D.S. Russell and P. Tymchuk, NRC) by optical emission spectrography for Cu and Pb and by spark source mass spectrometry for Pb revealed ca 5 µg Cu/g and 3 µg Pb/g of the dry solid salts constituting this solution. These concentrations translate to ca 40 and 30 µg/L for Cu and Pb respectively in solution AA. The former is in very good agreement with our estimate of 56 µg Cu/L; these concentrations are 2-3 times the FAAS detection limit for Cu and support the decision not to use this solution as a blank for Cu. On the other hand, the estimated 30 µg Pb/L (possible range 10-50 µg/L) being less than the FAAS detection limit for Pb, justified the choice of AA as a blank for Pb. No independent analyses were available for Zn and Cd. The maximum limit of total heavy metal concentration in AA, estimated from manufacturers' limits in the salts and HCl used to prepare the solution, was 80 µg/L. Quality control solution AA thus proved useful in assisting analysis.

The procedure adopted for determining total trace metal levels, of separately analyzing the liquid and solid components of natural waters, proved superior to the one-step approach of treating the entire sample. Attempts at total dissolution of unfiltered natural water components using treatment with HNO<sub>3</sub>-HClO<sub>4</sub>-HF met with difficulty due to the large amount of dissolved (and occasionally suspended) solids. It was convenient, however, to analyze separately, the four components, supernatant, residue, filtered water and suspended sediment, and get total metal concentrations by summing results from the former two and/or the latter two. The simple Evap/FAAS procedure proved successful; even 50-fold heat-concentration of filtered water samples resulted in clear solutions with a typical residue weight of 0.5 mg/500 mL.

DETERMINATION of SUSPENDED SEDIMENT and RESIDUE, and ANALYSIS of SOLIDS for TRACE METALS by ACID DIGESTION/FLAME ATOMIC ABSORPTION SPECTROMETRY

At the author's request, all membrane filters, beginning with the June 1976 sampling, which were used for field filtering of the natural water samples and distilled water control samples, were forwarded together with the water samples, to CBRI. The intention was to analyze the suspended particulate of the streams for Cu, Zn, Cd and Pb to get directly the levels of these elements in the suspended fraction for corroborative and mass balance calculations with data obtained separately for unfiltered and filtered samples (as discussed previously). A second purpose, that of determining suspended sediment concentrations, became evident after it was realized that measurements of this parameter in the Guelph laboratory were based on weights of wet membrane filters and contents, and would not have been sufficiently accurate for our purpose. Although a number of analyses of this particulate material were completed, the total attainment of these two objectives was precluded by the following experimental difficulties: (i) The high weight (ca 80 mg) and variability (standard deviation ca 4 mg) of each 47mm diameter Sartorius membrane filter, together with the need to use four filters for filtration, and the small weights of suspended sediment often found in the water samples, made impossible, sediment concentration determinations of any decent accuracy, (ii) The sediment, especially when present as only a thin film, adhered tenaciously to the Sartorius filter and was difficult if not impossible to remove; in addition, the fragile filter tended to break upon manipulation, (iii) Analyses of the combination, filter plus contents could not be reliably conducted, as the weight of sample on the filter was unknown, and serious trace metal contamination from the filter upon complete digestion was anticipated in relation to the amounts of metal expected in sediment samples. In respect of (iii), considering as much as 10 mg of suspended sediment with median concentrations of Cu and Zn of 52 and 165 pg/g respectively, and levels of Cu and Zn of 0.5-0.8, and 0.2 µg/47 mm diameter filter respectively estimated from those reported for Millipore filters by Robertson (1968, 1972), the filter would be the source of 50-60% and 10% of the Cu and Zn respectively in the analytical sample.

All of these problems were obviated by the use of poly-carbonate, Nuclepore membrane filters (N 040, 0.4 µm, 47 mm diameter) for filtration experiments in the author's laboratory. These filters have a smaller weight and variability (mean weight and standard deviation of 11 different filters from one box = 15.93 ± 0.15 mg), a greater tensile strength and lower trace element content. Sediment and residues could be weighed reliably in

amounts in the milligram range and could be easily, conveniently, and semi-quantitatively removed from the membrane filters, permitting digestion of the sample alone.

With these filters, the detection limit for determination of solids by filtration, based on 3x the standard deviation of the weights of blank filters, was 0.5 mg. Performance characteristics are detailed in Table 17; they pertain to actual analyses of real samples and reflect uncertainties from both the analytical procedure (filtration, drying, weighing) and subsampling. These figures of merit apply to measurements in the author's laboratory and were associated with the few determinations of suspended sediment and all residue concentration data obtained in this laboratory and reported in Table 4. The bulk of the suspended sediment information, however, was calculated from direct and indirect measurements of this parameter in two other laboratories. The standard deviation associated with these data was estimated to be 12 mg/L, for concentrations in the range 0-340 mg/L, rather large in relation to the low sediment levels encountered, and to the 0.7-9.1 mg/L for 0-500 mg/L sediment and residue concentrations obtained in the author's laboratory (see also Appendix II and Table 45). Precise suspended sediment information was thus not available. Difficulties in precisely determining suspended sediment (also denoted nonfilterable residue) in natural waters have been discussed by McGirr (1974) who reported standard deviations from inter-laboratory studies of *ca* 2 and 12 mg/L for sediment concentrations of *ca* 2 and 32 mg/L respectively.

The much lower trace element contents of Nuclepore filters (Robertson, 1972; Nuclepore Corp. 1973) would make them superior supports for analysis of solids for trace elements where complete dissolution of sample plus filter is necessary. Again considering 10 mg of suspended sediment with median concentrations of Cu, Zn, Cd and Pb of 52, 165, 1 and 70 µg/g respectively, and levels of these elements of *ca* 0.04, 0.07, <0.001 and <0.001 µg/47 mm diameter filter respectively, the filter would contribute 8, 4, <10, and <2% of the Cu, Zn, Cd and Pb respectively, in the analytical sample. As solid samples were easily removable, however, it was unnecessary to involve the filter in the analytical scheme.

Performance characteristics of the acid dissolution/FAAS procedure for determining total trace element levels in milligram quantities of suspended sediment and residue samples are listed in Tables 18 and 19. Detection limits of 7, 22, 0.5 and 13 µg/g for Cu, Zn, Cd and Pb respectively, reflect uncertainties from subsampling and analysis of small samples. The performance of the procedure (accuracy) in measuring the four trace elements in USGS rocks, G-2, BCR-1 and AGV-1, is shown in Table 19. For two of the three samples, our

values for Cu and Pb agreed closely with those reported in the literature by Flanagan (1973), Rantala and Loring (1973), and Abbey (1975), whereas a negative bias was suggested for Cu in G-2 and Pb in BCR-I. Zn values were 20-35% higher than those reported, and Cd could not be detected in any USGS sample. Considering the necessity for working with unusually small sample weights, precision and accuracy were considered quite adequate for this work.

#### DATA QUALITY ASSURANCE PROCEDURES

A good deal of effort went into assuring that analytical data resulting from this investigation were reliable as far as possible under the control of the author. The following components formed the data quality assurance program followed by the author:

- (1) Field filtration and processing of distilled water control samples to establish filtration contamination corrections.
- (2) Duplicate-quadruplicate collection of unfiltered and filtered natural water samples.
- (3) Analysis of blind replicate samples of unknown nature and trace element content.
- (4) Duplicate analyses of many samples, duplicate FAAS determinations on virtually every sample.
- (5) Systematic incorporation of quality control solutions Q1, Q2, AA and BB simulating standard solutions and real water samples into the FAAS measurement scheme.
- (6) Determination of recoveries of trace elements, at concentrations expected in real systems from deionized water, synthetic natural water and natural water samples.
- (7) Performance studies of analytical methodologies using reference samples, EPA Trace Metals Quality Control Samples, and USGS rocks.
- (8) Testing of acids used for field-preservation of water samples.
- (9) Systematic and frequent determinations of appropriate reagent blanks under conditions of analysis of water and solid samples.

- (10) Participation in PLUARG-sponsored round robin studies for trace metals in water.
- (11) Conduction of laboratory experiments with deionized water and natural waters to estimate adsorption/contamination.
- (12) Participation of three other laboratories applying four different analytical methodologies to analysis of water subsamples; participation of one other laboratory using a different method for the analysis of solid samples.

Items 5-7 have already been discussed. It may be mentioned however, that all the levels of Cu, Zn, Cd and Pb in the three EPA reference solutions (after dilution as prescribed by EPA) were substantially higher than levels found in natural waters (Table 15). Even the most dilute EPA solution (1-575) had Cu, Zn, Cd and Pb concentrations 8, 4, 75 and 220 times, respectively, the median levels of dissolved elements found in this work. Concentrations of these elements in the two more concentration solutions were in fact sufficiently high to permit determination by direct aspiration/FAAS. In addition, these three solutions are not natural water samples but pure solutions of trace elements in acidified distilled water. Measurements thus made on these reference solutions, although providing some estimate of method accuracy, do not fully indicate the performance of the methodology in respect of natural waters. No bona fide certified natural water reference samples were available to us. Recovery studies conducted in this laboratory covered a range of added concentrations, encompassing for Cu, Zn and Pb, normal levels present in natural waters.

A total of seven blind replicate samples (item 3) of unfiltered and filtered natural and presumably distilled water were collected and prepared by sampling personnel and forwarded to the author's laboratory (as requested by PLUARG). Analyses by Evap/FAAS gave concentrations listed in Table 20. Data reported reflect dissolved + acid extractable trace element levels only, which would, however, be very close to total levels for these samples which, by inspection, did not appear to have appreciable suspended sediment levels. The data are also uncorrected for filtration contamination which, a *priori* was impossible as it was unknown which samples had been filtered. The purpose of this was to provide an additional measure of sampling/analysis precision; unfortunately, only one set of blind replicates were processed during the course of this study, and upon completion of analyses, the identities of these samples were unavailable from the sampling laboratory.

This laboratory participated in two trace metals round robins sponsored by PLUARG.

Four samples, two acid-extracted sediment, one trace metal reference solution, and one blank, all preserved with HNO<sub>3</sub>, were included in each round robin. Levels of Cu, Zn, Cd and Pb in the six non-blank samples were stated by the initiating laboratory to be in the ranges 80-1000, 360-1300, 30-250 and 200-1000 µg/L respectively. Compared to median levels of dissolved Cu, Zn, Cd and Pb reported in this project, these concentrations are 40-500, 120-430, 430-3570, and 2000-10000 times higher respectively. The levels were in fact sufficiently high to permit direct FAAS analysis without preconcentration; also, the HNO<sub>3</sub> concentration of 10% (100x the concentration expected in preserved natural water samples) was too high to permit application of our heat concentration procedure. Hence, although our FAAS method performed well in these tests, the fact that the samples did not approximate natural waters again precludes estimation of performance in respect of natural waters.

The importance of procedures covered by items 2, 4 and 9 is obvious. Duplicate collections and analyses permitted computation of precision and increased the precision of means. Reagent blanks were averaged over many analyses before subtraction from sample data to increase precision. Items 1, 8, 11 and 12 are discussed in subsequent sections. In the absence of certified natural water reference samples, the most important quality assurance step (12) was the generation of analytical information by independently different methodologies.

#### INTERCOMPARISON OF DATA OBTAINED BY DIFFERENT METHODOLOGIES

The primary objective of independent analyses of water subsamples, by the three cooperating laboratories using different analytical procedures was to arrive at improved estimates of trace metal concentrations. Performance characteristics of the methods used and intercomparison of results are presented in this section. In the following discussion, this author is responsible for management and interpretation of collaborative data provided. The methodologies cannot be seriously compared as the study was not designed with this in mind. All discussion is in respect of the role of the different methods in increasing overall data reliability; any discussion of method intercomparison is incidental and informational.

Detection limits of the five analytical methods presented in Table 21, were either provided by the investigators or were estimated by this author from data supplied as indicated in footnotes to the Table. Different definitions of detection limit were used, and no attempt was made to bring all to a common basis; the data presented should, however, fairly well demonstrate the comparative detectivities. Flame AAS methods, preceded by

concentration had the highest (poorest) detection limits followed at some distance by the electrothermal atomization AAS and electrochemical techniques both of which generally exhibited substantially lower detection limits. Whereas flame spectrometry-based procedures could measure natural levels of Cu and Zn, and occasionally Cd and Pb, electrothermal and electrochemical methods are clearly superior. Dr. Stoepler reported impressive detection limits by DPASV/ MFE of 0.0001 and 0.0002 µg/L for Cd and Pb respectively in standard solutions.

Method precisions are detailed in Table 22. These were provided by the cooperating laboratories or calculated by this author from duplicate analytical data or detection limits reported. Standard errors,  $ts/\sqrt{n}$ , for 95% confidence limits are reported for Dr. Berman's method, whereas standard deviations are associated with the remaining methods; standard deviations (or errors) used to calculate precision of data presented in this report are indicated. An overview of the performance of the five methods with EPA trace metal solutions is depicted in Figure 23. The five different symbols refer to the five analytical methods but are not identified as data from three laboratories are based on only one subsample of each of the three EPA solutions prepared by this author. Moreover, it would be unfair to make strict comparisons among the methods as these reference solutions were analyzed on a "routine" basis by three of the laboratories, but more exhaustively by the originating laboratory. With several exceptions, overall agreement with EPA-reported values is reasonable.

Intercomparisons of data from the different methods, for unfiltered and filtered natural and distilled water sub-samples are presented in Figures 24-28. Dissolved or dissolved + extractable levels (refer to later discussion) are plotted against levels determined by Evap/FAAS or CRA/AAS and are related to lines of unit slope to gauge relative performance of the different methods under the conditions of this study. All discussion of comparability must be treated in relation to considerations of (i) possible subsampling inconsistencies and subsample stability and (ii) the fact that different analytical methods may be measuring different parameters. The former question is touched upon later. The second relates to the theoretically different trace element species amenable to detection due to the nature of the sample, sample pretreatment and measurement technique. The Evap/FAAS procedure involves hot (concentrated,  $\geq 1.6$  M  $\text{HNO}_3$ ) acid leaching during the evaporation step, the electrothermal techniques (HGA and CRA) measured total trace elements in the supernatant, leached-out by the 0.016 M preserving acid, the electrochemical methods responded to free metals in the same supernatant, whereas solvent extraction relies on the extraction, via chelation, of metals from suspended and dissolved water components. No "gross"

differences were observed among data generated by the five methods and it was not the intent of this study to delineate fine details in this regard. All data thus generated have been collectively designated as dissolved + acid- or solvent-extractable, and averaged; addition of trace element levels measured in suspended sediments and residues gave total concentrations in the water samples.

In respect of analyses for Cu (Figure 24), generally good agreement was observed among the five methods. In relation to the Evap/FAAS method, the HGA/AAS method showed a positive bias and DPASV/HMDE or DPASV/MFE exhibited a negative bias for all samples and over the entire concentration range. The CRA/AAS technique seemed to have a negative bias with distilled water but a positive bias with natural water samples, whereas data from the solv. ext./FAAS method for distilled and natural water samples fell close to the unit slope line at the higher concentrations but exhibited a positive bias at lower concentrations.

Three laboratories determined Zn; values from one laboratory seemed high and were omitted from consideration leaving data from two laboratories for comparison (Figure 25). The graph of CRA/AAS- versus Evap/FAAS-generated data is characterized by highly scattered points; aside from ascertaining that data from the two methods are in the same ballpark, little can be said regarding interlaboratory bias. Contamination by Zn seems ubiquitous.

For Cd, the two electrothermal atomization/AAS and electrochemical techniques were sufficiently detective to measure this element. Considering the sub part per billion levels of Cd, and the widely divergent nature of analytical methodologies employed, agreement is excellent (Figure 26).

With reference to Pb in the higher concentration regions depicted in Figure 27, the few data available for unfiltered natural and distilled water suggest excellent agreement among the DPASV/HMDE or MFE, Evap/FAAS and CRA/AAS methodologies, whereas results from HGA/AAS analyses exhibited a positive bias compared to the CRA/AAS procedure. At low Pb concentrations, results on unfiltered natural waters obtained by DPASV/HMDE or MFE, HGA/AAS and Evap/FAAS are clearly larger than those resulting from application of the CRA/AAS method (Fig. 28). Agreement for distilled water samples, however, seems superior, but only meagre data exists. With respect to CRA/AAS, the divergence of the other three methods is similar. As sample treatment (15 hr evaporation) was an integral operation in the

Evap/FAAS method, the positive bias might easily be explained. That very similar biases occur for methods without sample processing is surprising.

An attempt was made to correlate performance of the methods with natural and distilled water samples discussed here, with performance with EPA solutions reported earlier. No consistent correlations of method bias were observable.

### DISTILLED and DEIONIZED WATER FILTRATION CONTROLS, and LABORATORY FILTRATION STUDIES

Concentrations of Cu, Zn, Cd and Pb in field- and laboratory-processed, unfiltered and filtered distilled and deionized water control samples, together with corrections for filtration procedure contamination are summarized in Table 23, and presented more comprehensively in Table 24. These data are presented with associated standard deviations rather than standard errors, to indicate the spread of values within the different populations of samples; footnotes to Table 24 give specific experimental details. Standard deviations reported in these Tables have thus been computed from the data populations in question and have not been based on standard deviations reported in Table 14. Compared to levels of Cu and Zn in deionized water produced in the author's laboratory, field-processed unfiltered distilled water from the Guelph facilities contained higher levels. Variability among different samples was also very large (for example,  $4.2 \pm 4.0$   $\mu\text{g/L}$ , mean  $\pm$  standard deviation, for Cu in the Guelph water vs.  $0.14 \pm 0.23$   $\mu\text{g/L}$  for our deionized water). Levels of these elements in the Guelph distilled water were, however, substantially lower than trace element contents in the Ottawa laboratory distilled water ( $4.2$  vs.  $50$   $\mu\text{g Cu/L}$  for example). The latter distilled water initially caused some problems in respect of trace analysis until we switched to using deionized water exclusively to meet our critical requirements. It should be noted that the values reported for deionized water represent levels actually present in deionized water at the source, plus contributions from reagents, processing procedure etc.; they represent upper limits and are in fact blanks used for corrections for the analytical procedure. Levels reported for other samples have been corrected by these or analogous reagent blanks.

Field-filtration of distilled water samples raised trace element levels, sometimes substantially (eg. Zn  $4.2 \pm 3.2$  in filtered vs.  $0.9 \pm 0.7$   $\mu\text{g/L}$  in unfiltered water), and increased the variability. Differences between paired concentrations in unfiltered and filtered water samples gave filtration procedure correction factors. Outlying values suggestive of spurious high contamination were rejected to yield selected correction factors. These proved very

useful in correcting trace element concentration data for field-filtered natural water samples, the assumption being that filtered natural waters suffered contamination identical to the controls. Unfortunately, corrections for field-filtering (mean  $\pm$  standard deviation of  $1.3\pm 1.6$ ,  $3.2\pm 2.3$ ,  $0.03\pm 0.05$ , and  $0.3\pm 0.2$   $\mu\text{g/L}$  for Cu, Zn, Cd and Pb respectively) were larger compared to dissolved trace element levels estimated in natural water samples, resulting in large uncertainties. It was decided that standard deviation rather than standard error of the mean correction term was the more appropriate error term to use in calculation of errors in the corrected concentrations. The possibility that trace elements in natural water samples may be adsorbed onto filters (Davies, 1976; Marvin *et al.*, 1970) must, however, also be considered, and is discussed below.

As a follow-up to the large contaminations observed during field processing, and to further assess the role of the filter material in contamination, a supply of Sartorius cellulose acetate filters of the type used in field preparation was obtained from sampling personnel. These, together with the 0.4  $\mu\text{m}$ , 47 mm diameter Nuclepore filters used in the CBRI laboratory, and another common filter type manufactured by Millipore Corp. (0.45  $\mu\text{m}$ , 47 mm diameter, cellulose acetate/nitrate, type HA) were tested by the author as possible sources of trace metal contamination. Both acid-cleaned and not-cleaned filters assembled in clean Sartorius filter holders were tested in duplicate as follows. Each of the 12 filters was separately assembled into the filter holder and rinsed with 250 ml of deionized water. This was followed by consecutively filtering two 500 ml portions of deionized water which were transferred to polyethylene bottles and acidified with 0.5 ml conc.  $\text{HNO}_3$ /500 ml. A total of 24 500 ml filtrates resulted. Three 1 L LPE bottles of deionized water, acidified with 1 ml conc.  $\text{HNO}_3$ /L, were set aside as controls.

All solutions were analyzed for Cu, Zn, Cd and Pb by Evap/FAAS; results are presented in Table 25. As trace element levels in the filtrates seemed to vary neither with filter type nor filter cleaning, concentrations were averaged over all conditions, and means, (22-24 samples from 11-12 filters) with rejection of three high values (out of 96 analyses) of 18.36 and 0.80  $\mu\text{g/L}$  (original filtrate basis) for Zn, and 16.2  $\mu\text{g/L}$  for Pb, are listed in the Table. Results for filtered deionized water as well as for the unfiltered deionized water control samples were all below the limits of detection, indicating undetectable contamination from the filters. Mean values for trace element levels in deionized water filtrates through all filters, were taken as upper limits of corrections for the laboratory-filtration procedure, and were applied to natural water samples filtered through Nuclepore filters. These corrections (Table 23), especially for Cu and Zn of  $0.0\pm 0.2$  and  $0.17\pm 0.12$   $\mu\text{g/L}$  (mean  $\pm$  standard deviation)

respectively, are substantially lower than the corresponding ones of  $1.3 \pm 1.6$  and  $3.2 \pm 2.3$   $\mu\text{g/L}$  for field-filtered samples. Field values for unfiltered and filtered distilled water appeared plagued by contamination problems arising from sources other than the membrane filters used. Much diminished levels obtained in the laboratory indicate the potential for very small filtration procedure contamination.

Several additional experiments with acid-cleaned Nuclepore filters were conducted using unacidified centrifuged natural water from one of the watersheds to evaluate the behaviour of real samples and deal, at least superficially, with the question of adsorption of trace elements by the filter. This water sample, obtained through the courtesy of Dr. L. Whitby Costescu, was taken to simulate  $0.45 \mu\text{m}$ -filtered water. In these experiments, 500 ml of natural water was filtered through a pre-rinsed filter, followed by re-filtering 250 ml of the filtrate through a second pre-rinsed filter. Duplicate tests gave four 250 ml filtrates which were acidified with 0.25 ml conc.  $\text{HNO}_3$ /250 ml prior to analysis by Evap/FAAS. Five hundred ml of acidified, unprocessed, centrifuged natural water was set aside as a control. Trace element concentration data are summarized in Table 25. Comparison of levels in the unfiltered control sample with levels after filtration, shows a decrease in the latter for Cu and Zn. Cd and Pb concentrations were near or below limits of detection of the Evap/FAAS method and thus cannot be discussed; analysis by more detective methods is necessary. At first glance, this may be construed as an indication of adsorption. Cu and Zn levels in filtrates resulting from first and second filtrations, however, are identical, suggesting that the decrease between unfiltered and filtered water may result from retention by the filter of solids present in the former, rather than the phenomenon of adsorption of dissolved metal species. Contamination is also unnoticeable. These observations apply in respect of Cu and Zn in natural waters filtered through Nuclepore filters, and therefore, to the few filtrations conducted in the laboratory. As such tests were not conducted with Sartorius filters, the type used for all field filtrations, the question of adsorption from, and contamination of real water samples is unsettled in respect of field-filtered samples and must be tackled in future studies.

#### IMPURITY LEVELS in ACIDS

With trace element concentrations in natural waters at the  $\mu\text{g/L}$  and sub  $\mu\text{g/L}$  levels, the purity of acids used for sample preservation and analysis, with the concomitant contamination potential must be considered. This is particularly true for filtered samples which contain very low concentrations indeed. Impurity levels of a variety of inorganic components in  $\text{HNO}_3$  from various commercial sources, as specified by the manufacturer are listed in

Table 26. Expectedly, the variation is large. Considering the highest levels of Cu, Zn, Cd and Pb of 100, 40, 5 and 200 µg/L of concentrated acid, the incorporation of 1 mL of acid/L of sample for preservation, and 4 mL of acid/L of sample for sample preparation, and median levels in natural waters of dissolved Cu, Zn, Cd and Pb of 2, 3, 0.07 and 0.1 µg/L respectively, the percentage of trace element in the analytical sample contributed by the acid is 5, 1, 7 and 67% respectively, in respect of preservation, and 20, 6, 26 and 91% respectively, in respect of the total analysis scheme. This would be the contamination level expected from reagent grade acid. Use of a high purity acid for both preservation and analysis, such as Ultrex HNO<sub>3</sub> which generally contains the lowest impurity levels of Cu, Zn, Cd and Pb of 3, <1, <1 and 2 µg/L respectively (in lot no. UA 131), would reduce trace element contribution by the acid to 0.7, <0.2, <7 and 9% respectively in respect of total analysis. These reflect considerable improvement and suggest that the use of high purity acid is mandatory to keep contamination from this source, and thus reagent blanks down to a minimum. Degree of sample concentration by evaporation also has an effect on contamination by way of the need for reduced quantity of acid for greater concentration. Only an additional 0.5 ml of concentrated acid/500 mL of sample was required for analyses involving 50-fold concentration, opposed to 2 ml/500 mL required for 20-fold concentration, resulting in a four-fold difference in contamination in favor of the former. Although reagent grade acid was used for field-preservation of samples, high purity acids were employed in the analytical laboratory for virtually all work.

Actual analyses of one lot each of HNO<sub>3</sub> and HCl used in the field, were conducted for the four trace elements. Samples of acids were dispensed by sampling personnel according the usual method employed for sample preservation, into defined volumes of deionized water in LPE bottles provided by the author, and were shipped to the CBRI laboratory for analysis by Evap/FAAS. Deionized water from this laboratory, rather than distilled water from Guelph facilities was used to prevent masking of acid trace element levels by contamination in the latter. Possible contributions of these acids, via their use as preservatives, to Cu, Zn, Cd and Pb contents of natural waters, were estimated to be 0.09, 0.005, 0.016 and - µg/L respectively for HNO<sub>3</sub>, and 0.14, 0.08, 0 and 0.13 µg/L respectively for HCl. Because analyses were only by Evap/FAAS (insufficiently detective for Cd and Pb) and only meagre information was gathered, no corrections for preserving acid contamination were applied.

## SAMPLE SOLUTION STABILITY

It was requested of collaborators that upon completion of analysis of water samples, any solutions remaining be returned, in the original containers, to the author's laboratory for re-analysis. Comparison of this information with analyses conducted by the author on his subsamples was expected to be a check on sample stability. Subsamples were received from two collaborators, and a number, especially those for which Zn concentrations measured by the collaborators differed from values obtained by the author on his subsamples, were re-analyzed. Zn was chosen due to its high levels and analytical detectivity, facilitating its determination in the small volumes returned. The two sets of analyses for the three types of samples are summarized in Table 27. In the sample codes used, AG1 - AG13 refer to agricultural watershed number, U and F denote unfiltered or filtered respectively, A - D refer to the first-fourth replicate field sampling, and the last six digits refer to date (day/month/year) of sampling. Distilled water control samples are denoted by codes including DW (AG1 AG13), indicating the watersheds where they were processed. In addition, letters A - F were affixed to each laboratory-prepared subsample to indicate the collaborating laboratory (A - C, Ilnat; D - Stoepler; E - Berman; F - Gaynor).

Analyses of the author's subsamples were by Evap/FAAS, whereas due to limitations of volume, about one half of the returned samples were analyzed by direct aspiration/FAAS. Reference to the data, plotted in Figure 29, indicates a fairly good correspondence of results for the two sample sets; the time interval between the two sets of analyses was *ca* 3-8 months. Included are data for two EPA solution subsamples which show excellent agreement. Levels of Zn appear somewhat higher, however, in several of the collaborators' natural and distilled water samples suggesting contamination. It must be emphasized that, as the two sets of analyses refer to different subsamples, the observed behaviour reflects both solution stability and subsampling variability. Moreover, no check analyses were performed for the three other elements to permit more concrete statements regarding trace element stability.

## TOTAL and EXTRACTABLE TRACE ELEMENTS in NATURAL WATERS

Most published methodologies for determination of "total" trace element levels in natural water samples advocate treatment of the sample with acid, typically HNO<sub>3</sub> followed by HCl, prior to determination (American Public Health Association, 1971; Environmental Protection Agency, 1971; Environment Canada, 1974; Fisheries and Environment Canada,

1978). Dissolution of solid material may not be complete (in fact, filtration is at times recommended) so that although fairly good estimates of total trace element concentrations may be obtained, conceptually these data are not total concentrations. Oliver (1973) and Bradshaw et al (1974) refer to the usefulness for many purposes of such dissolved + extractable concentrations, in respect of trace elements in sediments, but mention the variable efficiencies of partial extraction techniques depending on the nature of the sample. As discussed previously, the application to natural water samples of the five analytical methodologies, yielded measures of dissolved + acid - or solvent-extractable trace element concentrations. Assuming comparability of the data, values from all methods, were pooled and averaged over subsamples and methodologies to provide mean values listed in Table 28.

Graphs of the ratio: concentration of dissolved + extractable trace element/total concentration of trace element, versus suspended sediment concentration, presented in Figure 30, demonstrate some interesting relationships. Curves were drawn excluding consideration of the 19,000 mg/L point. Considering the 0-740 mg/L suspended sediment range, the ratio ranges from ca 0.7 to 1.0 depending on element and sediment concentration, indicating incomplete extraction of trace element under some sample/element conditions. In spite of the rather large errors resulting from propagation of error, some trends may be visualized. For Cu and Zn, ratios of 0.86 and 0.79 respectively, at suspended sediment concentrations greater than 100 mg/L, approached 1.0 as sediment levels approached zero. Ratios for Cd and Pb appeared invariable with sediment level and averaged 0.97 and 0.72 respectively, but the very large errors associated with these data preclude firm conclusions. The sample containing a suspended sediment level of 19,000 mg/L, showed ratios ranging from 0.46 to 0.85, in general lower than samples in the 0-740 mg/L suspended sediment range. For Cu and Zn, diminished ratios of 0.52 and 0.46 were observed for the sample with sediment level of 19,000 mg/L, whereas Cd and Pb exhibited ratios of 0.85 and 0.70 respectively, fairly unchanged from the values at the 0-740 mg/L region. This again illustrates the effect of high sediment levels in reducing extractable levels. Thus overall, we find methodology not involving complete destruction of particulate material, giving trace element concentrations in the region 0.5 - 1.0 of total levels, depending on the element in question and suspended sediment concentration in the natural water sample.

Total concentrations of Cu, Zn, Cd and Pb in natural water samples were arrived at in two distinctly different ways, viz (i) summation of trace element concentrations obtained by analysis of unfiltered samples and contributions of residues, and (ii) summation of

dissolved concentrations in filtered water samples and contributions of suspended sediments. Concentrations in unfiltered and filtered water samples refer to mean dissolved + acid- or solvent-extractable, and dissolved levels respectively, obtained by the five analytical methods, listed in Tables 28 and 7 respectively; contributions of residues and suspended sediments, based on chemical analyses by acid digestion/flame spectrometry and solid levels in the water samples, are listed in Tables 48 and 6 respectively. Total concentrations thus obtained, together with selected data are tabulated in Appendix II (Tables 41-44). Usual propagation of error formulas were used to compute standard errors; the abundance of > signs in Tables 41-44 signifies at least one missing datum in each summation, precluding calculation of error. Total concentrations calculated by (i) should agree with corresponding data obtained by (ii). A comparison of the 6-11 complete pairs of data is made in Figure 37 where (ii) is plotted versus (i). Considering the nature of trace analysis, agreement between the two is reasonably good. There does appear, however, to be a negative bias of (ii) in relation to (i) for all four elements. Whether this results from adsorption of the trace elements onto the membrane filters or other factors is unknown; meagre information is available to differentiate the behaviour of the compositionally and structurally different Sartorius and Nuclepore filters. Pursuit of these phenomena would be fruitful in relation to this kind of trace analysis.

#### CRITIQUE OF EXPERIMENTAL WORK and POINTS to CONSIDER in FUTURE INVESTIGATIONS

The importance of accurate information and proposals for future research along the lines pursued in this investigation have been presented in the conclusions. Listed here are points covering critique of this work together with experimental details to be considered for incorporation into future studies.

- (1) The sampling of natural waters with low suspended sediment levels proved very instructive as it was in these regions that transitions in transport mechanism and sediment physical and chemical properties were observable. More such samples from low and normal flow streams are required, especially those with suspended sediment level in the 0-300 mg/L range, to further delineate phenomena in this transition region. There is also, however, a need for more event and runoff samples to complement the study and to assess the trace element situation under conditions responsible for most of the annual transport of trace element out of the watershed, and to study equilibria of trace elements between dissolved and particulate phases. Samples containing the

range of suspended sediments will provide representative samples and will permit characterization of the stream in respect of sediment and trace element parameters.

- (2) Replicate sampling and replicate preparation of unfiltered and filtered waters is pertinent to assessment of variability of the sampling/field processing procedures, and the collection and preparation of duplicate-quadruplicate samples should be continued. Several more sets of blind replicates should also be provided throughout the study period to further assess sampling/analysis variability.
- (3) Incorporation of field-processed unfiltered and filtered distilled water control samples proved invaluable in correcting filtered natural waters for contamination by the filtration procedure, to arrive at estimates of dissolved trace element levels. Unfortunately, correction factors were rather large and variable and an important source of error. That filtration-contamination can be substantially reduced (at least under laboratory conditions) was demonstrated by filtration experiments in the author's laboratory using filters and equipment identical to those used in the field. Whether the contamination problem is specific to the field, or the result of other factors must be ascertained to determine whether field-filtration or laboratory-filtration be specified for future studies. Filtration must, however, be carried out as soon as possible after sample collection. Reduced correction factors increase precision substantially. Distilled water utilized for control of field processing contained high and variable quantities of trace elements of interest. Water either multiply distilled or deionized, of much better quality must be used in the sampling protocol. Deionized water prepared in the author's laboratory had very low trace element levels and that type of water is superior for this and all other phases of the work. Pressure-rather than vacuum-filtration should be considered to reduce evaporation losses.
- (4) Preservation of natural and distilled water samples with both  $\text{HNO}_3$  and  $\text{HCl}$  separately should be continued; the latter is the preferred acid matrix for electrochemical measurements. Use of volumes greater than 1 ml/L should be considered, especially for samples with high suspended sediment loads (e.g. Environmental Protection Agency, 1971), to maintain low pH and ensure solution stability. The very low natural contents of trace elements in waters suggests the use of high purity acids throughout. Trace element levels in the acids must be monitored to keep track of contamination via dispensing and handling both in the field and laboratory, to provide estimates of appropriate corrections for contamination.

- (5) Nuclepore filters were found to be superior to Sartorius filters and their use for field and laboratory filtration should be continued and advocated. With careful filtration of known volumes of water, suspended sediment concentrations can be determined by weighing the dry filters and contents, with precision and accuracy superior to those realized, as demonstrated in this laboratory. Good estimates of suspended sediment levels are essential. Many of the missing data for total concentrations (cf Tables 41-44) result from difficulties in analyzing solids due to small quantities available and difficulty in their removal from filters used in the field. Analyses of sediments and residues are integral to estimation of total trace element concentrations; use of Nuclepore filters permits analyses of filter - free solids, avoiding the question of contamination by the filter matrix.
- (6) Contamination of deionized water filtrates passing through three different types of membrane filters, under laboratory conditions, proved below the limits of detection of the Evap/FAAS method and minor for Cu and Zn. Exactly how serious contamination is for Cd and Pb in relation to the very low levels in natural waters, must be ascertained by the application of more detective analytical techniques. Although no serious adsorption of trace elements in natural waters by Nuclepore filters, seemed to occur for Cu, Zn perhaps exhibits a problem; data in Figure 31 hint at a possible problem. Again, little can concretely be said concerning Cd and Pb. More tests of filtration of distilled and natural waters must be performed, solutions and filters must be carefully analyzed for total, adsorbed and leached trace elements, and mass balance studies must be undertaken to get a grasp of the magnitude of the problem.
- (7) Stability of natural water solutions from time of collection/preparation to analysis, and storage vessel suitability in respect of adsorption and contamination must be known to permit translation of analytical information to the stream.
- (8) Successful application of the Evap/FAAS method for waters and the acid digestion/FAAS method to solids therefrom, suggests that application of these methods be continued to determination of Cu, Zn and high levels of Cd and Pb in fresh natural waters. Stability of flame spectrometry suggests incorporation of more samples per calibration curve to increase throughput. Continuation of frequent determination of appropriate reagent blanks, use of mean blanks in computations, and continued runs with standard solution and synthetic natural water quality control samples is indicated. It would be advantageous to use high purity salts for preparation

of synthetic natural water solutions, to get exact measures of measurement system bias. Use of computerized regression calculation would be an asset. Correction of non-atomic absorption was demonstrated to be imperative, and simultaneous correction should be applied to solutions containing low trace element concentrations and high salt matrices. Causes of the large reagent blank biases for Pb and suspected small biases for Cd should be sought and rectified; alignments of hollow cathode lamps should be considered. Detection capability of the FAAS methods should be increased by improvement in concentration and atomization, and reasons for deviation of data for some USGS samples should be sought. Resort to digestion of solids in teflon bombs followed by determination by electrothermal atomization/AAS should make very small (less than 1 mg) quantities of solids amenable to analysis (cf Eggimann and Betzer, 1976). Application of more detective methodologies would cut down on sample volume requirements and make easier the task of sampling.

- (9) As the collaboration in the project of other laboratories bringing to bear on the task, independently different analytical methodologies, constituted a very important factor towards the generation of reliable data, this practice should be continued. Performance of these methods in the analyses of EPA and/or similar reference samples should be monitored throughout the study. Subsamples should be circulated among the laboratories to provide a check on laboratory performance with real samples, subsampling and sample stability. Reference natural water samples should be sought and incorporated into analysis protocols. Screening of inter-laboratory data by a more systematic procedure in light of performance with circulated subsamples and reference solutions, should reduce errors in overall means.

The following literature references are pertinent to some of the points discussed: Smith, 1973 a, b; King et al, 1974; Issaq & Zielinski, 1974; Struempfer, 1973; Rattonetti, 1976; Harrison et al, 1976; Segar and Berberian, 1975; Riley, 1965; Robertson, 1968, 1972, 1976; Nürnberg et al, 1976; Davies, 1976.

Table 13 Analytical Precision and Detection Limits of Flame Atomic Absorption Spectrometry<sup>a</sup>

Concn. range µg/L	Standard deviation, µg/L (degrees of freedom)			
	Cu	Zn	Cd	Pb
0-20		1.46 (171)		
20-100		1.98 (96)		
100-500	8.37 (102)	3.71 (84)	5.36 (82)	
500-1000	15.0 (153)	5.29 (99)	6.08 (67)	
0-100	7.39 (208)		2.78 (308)	
0-1000				17.3 (456)
	Detection limit, µg/L(degrees of freedom) <sup>b</sup>			
	21.8 (91)	4.38 (171)	8.04 (232)	51.8 (456)

<sup>a</sup> MI laboratory. Standard deviations were calculated from duplicate determinations on unfiltered and filtered natural, synthetic natural and deionized water samples and related solutions on 42 different days over a 9 month period, with each result in the pair based on a different calibration curve. Other experimental conditions are as described in the text. These precisions and detection limits refer solely to the FAAS determination step and do not include variances from sample treatment and other sources, and reflect the performance of the determination step during the course of the PLUARG project.

<sup>b</sup> Detection limits are based on 3x standard deviations of low level (0-20 µg/L for Cu, Zn, Cd; 0-1000 µg/L for Pb) samples.

Table 14 Analytical Precision of the Evaporation-Flame Atomic Absorption Spectrometric Method<sup>a</sup>

Element	Typical concentration factor	Concentration range in original sample µg/L	Standard deviation µg/L	Degrees of freedom
Cu	20 and 50	0-1	0.263 <sup>b</sup>	58
		1-5	0.313	24
		5-25	0.324	15
		25-150	1.09 <sup>b</sup>	9
Zn	20 and 50	1-25	0.317 <sup>b</sup>	39
		0-1	0.111 <sup>b</sup>	54
		1-5	0.179 <sup>b</sup>	26
		5-25	0.300	23
		25-250	0.359	6
Cd	20	5-250	0.313 <sup>b</sup>	29
		0-5	0.120 <sup>b</sup>	44
		5-45	0.157	10
Pb	50	0-10	0.038 <sup>b</sup>	41
		20 and 50	0-40	0.523 <sup>b</sup>

<sup>a</sup> MI laboratory. Standard deviations were calculated from duplicate analyses of unfiltered and filtered natural, synthetic natural and deionized water samples and related solutions according to the Evap/FAAS method described in the text.

<sup>b</sup> These standard deviations were used to estimate precision of analyses of natural water samples listed in this report.

Table 15 Concentrations of Cu, Zn, Cd and Pb found in EPA Trace Metals Quality Control Samples by flame atomic absorption spectrometry

EPA solution	Mean concentration $\pm$ standard error, $s/\sqrt{n}$ , $\mu\text{g/L}$							
	Cu		Zn		Cd		Pb	
	This work	EPA	This work	EPA	This work	EPA	This work	EPA
1-575	16.2 $\pm$ 0.1 <sup>a</sup>	16	11.2 $\pm$ 0.1 <sup>a</sup>	11	5.1 $\pm$ 0.2 <sup>a</sup>	5.2	22.1 $\pm$ 0.2 <sup>a</sup>	22
2-575	67.8 $\pm$ 2.6 <sup>b</sup>	72	32.1 $\pm$ 0.7 <sup>b</sup>	30	24.1 $\pm$ 0.9 <sup>b</sup>	23	297 $\pm$ 6 <sup>b</sup>	298
3-575	96.3 $\pm$ 2.6 <sup>b</sup>	102	177.2 $\pm$ 1.3 <sup>b</sup>	174	71.2 $\pm$ 0.9 <sup>b</sup>	73	346 $\pm$ 6 <sup>b</sup>	352

<sup>a</sup> Evaporation-flame atomic absorption spectrometry; n = 5 analyses

<sup>b</sup> Direct aspiration of solution; n = 8-9 determinations.

Table 16 Recoveries of Cu, Zn, Cd and Pb from deionized water, synthetic natural water, and natural water matrices using evaporation - flame atomic absorption spectrometry<sup>a</sup>.

Concentration added, $\mu\text{g/L}$	Mean concentration found (no. of analyses) $\pm$ standard error, $s/\sqrt{n}$ , $\mu\text{g/L}$			
	Cu	Zn	Cd	Pb
0.20	0.17 (6) $\pm$ 0.10 <sup>b</sup>	0.27 (6) $\pm$ 0.04 <sup>b</sup>	0.19 (6) $\pm$ 0.02 <sup>b</sup>	0.10 (6) $\pm$ 0.07 <sup>b</sup>
1.00	1.01 (8) $\pm$ 0.15	1.06 (8) $\pm$ 0.07	1.09 (8) $\pm$ 0.10	1.14 (8) $\pm$ 0.16
2.00	1.66 (3) $\pm$ 0.08	2.14 (3) $\pm$ 0.09	1.96 (3) $\pm$ 0.02	1.93 (3) $\pm$ 0.09
10.00	9.52 (9) $\pm$ 0.17	9.73 (9) $\pm$ 0.11	9.71 (9) $\pm$ 0.11	10.16 (9) $\pm$ 0.18
40.00	39.21 (7) $\pm$ 0.40	40.08 (7) $\pm$ 0.16	39.96 (7) $\pm$ 0.24	40.28 (7) $\pm$ 0.08

<sup>a</sup> Data for all three matrices have been pooled for concentrations 0.20, 1.00, 10.00 and 40.00  $\mu\text{g/L}$ ; at the 2.00  $\mu\text{g/L}$  level, recovery studies were conducted only with deionized water. Elements were introduced as  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  prior to 20- or 50- fold heat concentration. Standard errors were calculated from actual data giving the means reported.

<sup>b</sup> Data are at or below detection limits (DL or  $\text{DL}/\sqrt{n}$ ) reported in Table 21.

Table 17 Performance Characteristics of Method for Determining Suspended Sediment and Residue Concentrations in Natural Waters and Analytical Solutions<sup>a</sup>

Concentration range mg/L	Standard deviation mg/L	Degrees of freedom	Detection Limit (3x low level standard deviation) mg/L
0-10	0.67	17	2.0
10-120	1.9	13	
120-500	9.1	7	

<sup>a</sup> MI laboratory. Standard deviations were calculated from duplicate determinations on identical and similar sub-samples and therefore reflect uncertainties from both the analytical procedure (filtration, drying, weighing) and sub-sampling.

Table 18 Performance Characteristics of Acid Digestion - Flame Atomic Absorption Spectrometry for Determining Total Trace Element Levels in Limited Quantities of Suspended Sediments and Residues<sup>a</sup>

Concentration range µg/g	Standard deviation, µg/g (degrees of freedom) <sup>b</sup>			
	Cu	Zn	Cd	Pb
0-1			0.18 (19)	
0-20	2.43 (12)			
0-50				4.36 (18)
0-105		7.4 (9)		
1-6			1.44 (6)	
20-100	3.87 (11)			
105-300		20.7 (25)		
	Detection limit, µg/g (degrees of freedom) <sup>c</sup>			
	7 (12)	22 (9)	0.5 (9)	13 (18)

<sup>a</sup> Method comprises total dissolution of sample with HNO<sub>3</sub> HClO<sub>4</sub> - HF followed by FAAS measurement.

<sup>b</sup> Standard deviations were calculated from duplicate analyses of 1-30 mg samples of suspended sediments, residues and USGS rocks and reflect uncertainties from both the analytical method and subsampling.

<sup>c</sup> Detection limits are based on 3x standard deviations of low level samples.

Table 19 Performance of acid digestion-flame atomic absorption spectrometry in determining Cu, Zn, Cd and Pb in limited weights of USGS rocks<sup>a</sup>

Sample	Concentration ± standard error, s/√n, µg/g <sup>b</sup>							
	Cu		Zn		Cd		Pb	
	This work	Lit.	This work	Lit.	This work	Lit.	This work	Lit.
G-2	5.8 ±1.4	11.7 <sup>c</sup>	102 ±4	85 <sup>c</sup>	<0.5	0.039 <sup>c</sup>	27.9 ±2.5	31.2 <sup>c</sup>
		10 ±0.6 <sup>d</sup>		77±1.0 <sup>d</sup>		0.039 <sup>e</sup>		23 ±1.7 <sup>d</sup>
		11 <sup>e</sup>		85 <sup>e</sup>				29 <sup>e</sup>
BCR-1	16.1 ±1.4	18.4 <sup>c</sup>	160 ±12	120 <sup>c</sup>	<0.5	0.12 <sup>c</sup>	5.2±2.5	17.6 <sup>c</sup>
		19 <sup>e</sup>		120 <sup>e</sup>				15 <sup>e</sup>
AGV-1	56.9 ±1.4	59.7 <sup>c</sup>	113 ±12	84 <sup>c</sup>	<0.5	0.09 <sup>c</sup>	31.1±2.5	35.1 <sup>c</sup>
		63 <sup>e</sup>		84 <sup>e</sup>				36 <sup>e</sup>

<sup>a</sup> In this work, 30 mg samples were decomposed in teflon beakers with HNO<sub>3</sub>HClO<sub>4</sub>.HF, and analytes were determined by FAAS on suitably diluted solutions.

<sup>b</sup> Means of triplicate analyses ± standard error obtained during the course of the project are reported for this work.

<sup>c</sup> Recommended values listed by Flanagan, 1973.

<sup>d</sup> Concentration ± standard deviation reported by Rantala and Loring, 1973.

<sup>e</sup> "Usable" values listed by Abbey, 1975.

Table 20 Concentrations of Cu, Zn, Cd and Pb in blind replicate samples<sup>a</sup>

Sample	Concentration ± standard error, s/√n, µg/L			
	Cu	Zn	Cd	Pb
A	1.7 ±0.3	3.0 ±0.2	0.6 ±0.1	<1.6
B	1.8 ±0.3	1.8 ±0.2	<0.4	<1.6
C	<0.8	0.7 ±0.1	<0.1	<1.6
D	2.7 ±0.2	6.1 ±0.2	<0.1	<1.6
E	0.9 ±0.2	0.6 ±0.1	<0.1	<1.6
F	<0.8	<0.3	<0.1	<1.6
G	1.0 ±0.3	<0.3	<0.4	<1.6

<sup>a</sup> Samples of unfiltered and filtered natural and presumably distilled water of unknown origins were analyzed once or in duplicate by Evap/FAAS. The mean values, uncorrected for filtration procedure contamination, reported reflect dissolved + acid extractable levels which, however, would be very close or identical to total levels for samples devoid of suspended sediment.

Table 21. Detection limits of analytical methods

Method and laboratory	Code	Detection limit $\mu\text{g/L}$				
		No	Cu	Zn	Cd	Pb
Evap/FAAS <sup>a</sup> (MI)	1	0.8	0.3	0.1, 0.4 <sup>b</sup>	1.6	
HGA/AAS <sup>c</sup> (MS)	2A	-	-	-	-	
HGA/AAS <sup>d</sup> (MS)	2B	0.5	-	0.01	0.2	
DPASV/HMDE <sup>e</sup> (MS)	3A	0.1	-	0.05	0.05	
DPASV/MFE <sup>f</sup> (MS)	3B	0.05	-	0.001	0.005	
CRA/AAS <sup>g</sup> (SSB)	4	0.1	0.05	0.005	0.05	
Sol.ext/FAAS <sup>h</sup> (JDG)	5	0.5 - 1.6	0.3 - 1.1	0.5 - 1.1	2.1 - 5.1	

<sup>a</sup> 3X the standard deviations of low level (0-1  $\mu\text{g/L}$  for Cu, Zn; 0-10 for Cd; 0-40  $\mu\text{g/L}$  for Pb) samples based on standard deviations calculated from duplicate analyses of unfiltered and filtered natural waters, reagent blanks and other related solutions; 41-109 degrees of freedom for each estimate.

<sup>b</sup> Detection limit for Cd depended on concentration factor; 0.4  $\mu\text{g/L}$  for 20-fold concentration, 0.1  $\mu\text{g/L}$  for 50-fold concentration.

<sup>c</sup> Preliminary set of furnace-AAS data was generated by this method which was not pushed to full capability; no detection limits were provided.

<sup>d</sup> Detection limits were provided by MS and are defined as 3X standard deviation of analyses of real samples. Second set of furnace-AAS results were obtained by this method.

<sup>e</sup> First set of electrochemical results was generated by this method; detection limits are 3X standard deviation of analyses of real samples.

<sup>f</sup> Second set of electrochemical data was obtained by this method. The detection limits are 3X standard deviation of analyses of real samples; MS reports that with standard solutions, detection limits are  $\mu\text{g/L}$  (element):0.002 (Cu), 0.0001 (Cd) and 0.0002 (Pb).

<sup>g</sup> Detection limits reported as 3X standard deviation of analytical blank (the calculated intercept of the calibration curve). Converted to the usual 2 or 3X standard deviation of replicate measurements, these values would be lower by about a factor of 3. The practice of Dr. Berman is not to report data below twice the detection limit i.e. 6X standard deviation of blank as defined.

<sup>h</sup> Detection limits reported as 2X standard deviation of 10 or more blank readings; values reported here reflect ranges of values reported by JDG.

Table 22. Analytical precision of analytical methods used by collaborating laboratories

Element	Method and laboratory	Code	Concentration range in original solution	Standard deviation or standard error <sup>a</sup> $\mu\text{g/L}$	Degrees of freedom
Cu	HGA/AAS(MS)	2A	0-10	0.9 <sup>b,d</sup>	18
	“ ” “		10-45	1.1 <sup>b,d</sup>	13
	“ ” “	2B	low	0.17 <sup>c</sup>	
	DPASV/HMDE (MS)	3A	low	0.033 <sup>c</sup>	
	DPASV/MFE(MS)	3B	low	0.017 <sup>c</sup>	
	CRA/AAS(SSB)	4	0-25	0.84 <sup>a,b</sup>	
			40,45 50-150	1.6 <sup>a,b</sup> 7.4 <sup>a,b</sup>	
Solv. ext/FAAS(JDG)	5	low	0.3-0.8 <sup>c</sup>		
Zn	CRA/AAS(SSB)	4	0-5	0.18 <sup>a,b</sup>	
			5-10	0.66 <sup>a,b</sup>	
			10-25	1.07 <sup>a,b</sup>	
			25-50	2.63 <sup>a,b</sup>	
			50-350	15.6 <sup>a,b</sup>	
Solv. ext/FAAS(JDG)	5	low	0.2-0.6 <sup>c</sup>		
Cd	HGA/AAS(MS)	2A	0-0.4	0.10 <sup>b,d</sup>	12
	“ ” “	2B	low	0.0033 <sup>c</sup>	
	DPASV/HMDE (MS)	3A	low	0.017 <sup>c</sup>	
	DPASV/MFE(MS)	3B	low	0.00033 <sup>c</sup>	
	CRA/AAS(SSB)	4	0-0.3	0.01 <sup>a</sup>	
	Solv.ext/FAAS(JDG)	5	low	0.3-0.6 <sup>c</sup>	
Pb	HGA/AAS(MS)	2A	0-10	0.69 <sup>b,d</sup>	18
	“ ” “		10-45	8.4 <sup>b,d</sup>	18
	“ ” “	2B	low	0.067 <sup>c</sup>	
	DPASV/HMDE (MS)	3A	low	0.017 <sup>c</sup>	
	DPASV/MFE (MS)	3B	low	0.0017 <sup>c</sup>	
	CRA/AAS(SSB)	4	0-0.8	0.1 <sup>a,b</sup>	
			10-25	0.9 <sup>a,b</sup>	
Solv. ext/FAAS(JDG)	5	low	1.1 - 2.6 <sup>c</sup>		

<sup>a</sup> Standard error,  $ts/\sqrt{n}$ , for 95% confidence limits as reported by Dr. Berman; other values are standard deviations.

<sup>b</sup> Calculated by the author of this report from data (concentrations or  $ts/\sqrt{n}$ ) provided by collaborating laboratories.

<sup>c</sup> Calculated from detection limits reported by laboratories, as DL/2 or DL/3. These standard deviations apply only to solutions with analyte levels at or near the detection limit.

<sup>d</sup> Used for estimating precision of analyses of natural water samples listed in this report.

Table 23 Concentrations of Cu, Zn, Cd and Pb in distilled and deionized water control samples and corrections for filtration procedure contamination<sup>a</sup>

Sample or item	Mean concentration $\pm$ standard deviation, $\mu\text{g/L}$ <sup>b</sup>			
	Cu	Zn	Cd	Pb
Field-processed unfiltered distilled water	4.2 $\pm$ 4.0	0.9 $\pm$ 0.7	0.02 $\pm$ 0.02	1.1 $\pm$ 1.6
Laboratory distilled water(tap)	79 $\pm$ 1	4.6 $\pm$ 2.3	<0.4	1.8 $\pm$ 0.3
Laboratory distilled water(CPE container)	50.2 $\pm$ 0.1	4.2 $\pm$ 0.0	<0.4	2.8 $\pm$ 2.0
Laboratory deionized water	0.14 $\pm$ 0.23	0.14 $\pm$ 0.13	<0.024	0.21 $\pm$ 0.40
Correction for field-filtration	1.3 $\pm$ 1.6	3.2 $\pm$ 2.3	0.03 $\pm$ 0.05	0.3 $\pm$ 0.2
Correction for laboratory-filtration	0.0 $\pm$ 0.2	0.17 $\pm$ 0.12	0.02 $\pm$ 0.04	0.16 $\pm$ 0.49

<sup>a</sup> Refer to Table 24 for details

<sup>b</sup> Standard deviations calculated from replicates giving the means reported; data for laboratory distilled water are means of two analyses.

Table 24. Concentrations of Cu, Zn, Cd and Pb in distilled and deionized water control samples and corrections for filtration procedure contamination-detailed data <sup>a</sup>.

Sample or item	Mean concentration (no. of samples <sup>b</sup> ) ± standard deviation, µg/L							
	Cu		Zn		Cd		Pb	
		±		±		±		±
1 Field-processed unfiltered distilled water <sup>c</sup>	4.2 (28)	4.0	0.9 (28)	0.7	0.02 (5)	0.02	1.1 (5)	1.6
2 Field-processed filtered distilled water <sup>d</sup>	5.9 (26)	6.8	4.2 (24)	3.2	0.06 (11)	0.06	0.5 (5)	0.3
3 Contribution of field- filtration procedure to trace element level in field-filtered samples <sup>e</sup>	2.6 (22)	4.3	3.6 (22)	2.3	0.03 (6)	0.05	0.3 (6)	0.2
4 Contribution of field-filtration procedure to trace element level in field-filtered samples (selected data) <sup>f</sup>	1.3 (18)	1.6	3.2 (21)	2.3	0.03 (6)	0.05	0.3 (6)	0.2
5 Laboratory reagent blanks using deionized water (cf 1) <sup>g</sup>	0.14 (37)	0.23	0.14 (36)	0.13	<0.024 (38) <sup>j</sup>		0.21 (36)	0.40
6 Laboratory filtered deionized water (cf 2) <sup>h</sup>	<0.15 (24) <sup>j</sup>		0.17 (22)	0.12	0.02 (24)	0.04	0.16 (23)	0.49
7 Contribution of laboratory- filtration procedure to trace element levels in laboratory filtered samples (cf 4) <sup>i</sup>	<0.15 (24) <sup>j</sup>		0.17 (22)	0.12	0.02 (24)	0.04	0.16 (23)	0.49

<sup>a</sup> Data suggestive of spurious high contamination have been eliminated from all calculations. Values less than detection limits, where available, were used in calculations for Cu and Zn.

<sup>b</sup> In cases where several laboratories analyzed the same sample, the analytical results were averaged to give one concentration per sample.

<sup>c</sup> Field-processing refers to the transfer of distilled water, obtained from the University of Guelph facilities, to IL sample containers.

<sup>d</sup> In addition to steps described in c, the distilled water samples were filtered through 0.45 µm Sartorius filters before transfer into sample containers.

<sup>e</sup> Calculated from data paired according to watershed.

<sup>f</sup> Outlying values for samples from certain watersheds and collection times were excluded to give selected corrections applicable to natural water samples other than those corresponding to the aforementioned watersheds/collection times.

<sup>g</sup> Analytical procedure (Evap/FAAS) reagent blanks determined in MI laboratory during the course of the PLUARG project, converted to original sample basis. These values represent levels of the trace elements in the deionized water plus contributions from reagents, processing procedure, contamination etc.

<sup>h</sup> Experimental results from MI laboratory have been averaged over 22-24 samples from 11-12 different cleaned, and not cleaned Nuclepore, Sartorius and Millipore filters.

<sup>i</sup> Based on difference between (5) and (6), taking 5 = 0.00µg/L, as all data except, of course the reagent blanks (5), have been corrected for appropriate reagent blanks.

<sup>j</sup> Means were negative; value quoted is the detection limit defined here as 3 s/√n.

Table 25. Effect of filtration through membrane filters on levels of Cu, Zn, Cd and Pb in deionized and centrifuged natural water.

Sample	Concentration (no. of analyses)± standard deviation, µg/L <sup>a</sup>			
	Cu	Zn	Cd	Pb
Filtered deionized water <sup>b</sup>	-0.03 (24) ±0.24	0.17 (22) ±0.12	0.02 (24) ±0.04	0.16 (23) ±0.49
Unfiltered deionized water control	0.18 (4) ±0.59	-0.03 (4) ±0.03	0.02 (4) ±0.03	-0.05 (4) ±0.21
Natural water, first filtration <sup>c</sup>	4.7 (2) ±0.3	7.6 (2) ±0.3	0.2 (2) ±0.1	0.2 (2) ±0.5
Natural water <sup>c</sup> second filtration	4.4 (2) ±0.3	7.6 (2) ±0.3	0.1 (2) ±0.1	-0.1 (2) ±0.5
Unfiltered natural water	5.3 (2) ±0.3	10.2 (2) ±0.3	0.0 (2) ±0.1	0.4 (2) ±0.5

<sup>a</sup> Negative results and values below detection limits have been included. All analyses were by Evap/FAAS. Standard deviations associated with the deionized water samples were calculated from replicates giving the means reported; standard deviations for natural water data are from Table 14.

<sup>b</sup> Means over data obtained with 12 different acid-cleaned and not cleaned 0.4-0.45 µm Nuclepore, Sartorius and Millipore membrane filters with rejection of three high values (out of 96 analyses) of 18.36 and 0.80 µg/L for Zn, and 16.2 µg/L for Pb; 50 fold concentration of all deionized water samples prior to FAAS measurement.

<sup>c</sup> These samples were filtered through acid-cleaned 0.4 µm Nuclepore filters. As only duplicate analyses were conducted, no standard deviations were calculated; standard deviations, listed previously, for entire PLUARG project of 0.32, 0.31, 0.12 and 0.52 µg/L for Cu, Zn, Cd and Pb respectively may be associated with these data; 25-fold concentration of all natural water samples prior to FAAS measurement.

Table 26 Impurity Levels Specified by Manufacturer in Nitric Acid from Various Sources. Concentration µg/L (ppb)

Component	Allied Chemical	BDH		Baker	Baker Reagent	Baker	G. Frederick Smith Chem. Co.		
	Canada Reagent ACS <sup>a</sup>	Analar Aristar (10168) <sup>a</sup>	BDH (45004) <sup>a</sup>	Reagent (9601) <sup>a</sup>	for Hg. Detn. (9603) <sup>b</sup>	Ultrex (4801) <sup>c</sup>	Reagent ACS (626) <sup>a</sup>	Redistilled (63) <sup>a</sup>	Double Distilled from Vycor (621) <sup>a</sup>
Nonvolatile	2,000	10,000	5,000	4,000	2,000	2,000	5,000	1,000	100
Al			5			5			
As	5	10	5	10	1	1	10	1	1
Au						<1			
B						9			
Ba						5			
Ca			500			7			
Cd			5			<1			
Cl	80	500	200	100	80	50	500	100	100
Co			5			<1			
Cr	100					2			
Cu	50		5	100	7	3			
F			500						
Fe	100	200	200	200	80	5	200	10	10
Hg					2	<10			
K			100			<10			
Mg			500			2			
Mn		400	5			0.6			
Na			500			30			
Ni	50		5	100	50	<1			
Pb		200	1		10	2			
PO <sub>4</sub>	200	1,000	100			<40			
Si		230	50			30			
SO <sub>4</sub>	800	2,000	500	1,000	200	300	1,000	100	100
Sr			500			<1			
Ti						5			
Zn			40			<1			
Heavy metals (as Pb)	100			200	80		200	10	10
Cost (approx.) \$ per 500 ml.		3	8	4	5	50	3	6	50

<sup>a</sup> Maximum limit of impurity; the number in parentheses is the catalogue number.

<sup>b</sup> Actual analysis of lot no. 36382.      <sup>c</sup> Actual analysis of lot no. UA 131.

Table 27 Stability and subsampling variability of distilled and natural water samples in respect of Zn concentrations

Sample code	Zn concentration $\pm$ standard error, $s/\sqrt{n}$ , $\mu\text{g/L}$ determined by Evap/FAAS or direct FAAS <sup>a</sup>			
	Analysis of author's subsample		Analysis of subsample after return from collaborator <sup>b</sup>	
Unfiltered natural waters		$\pm$		$\pm$
AG1UA290376	16.8	0.3	16.1	0.3
AG1UB290376	16.4	0.3	13.9	0.3
AG1UA260776	14.2	0.3	10.0 <sup>c</sup>	1.0
AG1UA051176	5.6	0.3	5.3 <sup>c</sup>	1.0
AG3UA050476	3.1	0.2	3.3	0.2
AG3UB050476	3.0	0.2	3.2	0.2
AG4UA071076	7.4	0.3	8.9 <sup>c</sup>	1.0
AG4UC071076	7.3	0.3	14.7 <sup>c</sup>	1.0
AG5UA150776	6.1	0.3	6.1 <sup>c</sup>	1.0
AG5UB150776	7.0	0.3	10.7 <sup>c</sup>	1.0
AG5UD150776	5.7	0.3	9.8 <sup>c</sup>	1.0
AG13UA290376	12.8	0.3	11.6 <sup>c</sup>	1.0
AG13UB041176	5.6	0.3	7.7 <sup>c</sup>	1.0
Filtered natural waters				
AG1FA290376	11.0	0.3	30.2 <sup>c</sup>	1.4
AG3FA190776	296	-	310 <sup>c</sup>	3.0
AG3FB141076	3.3	0.2	5.0 <sup>c</sup>	1.0
AG5FB310376	3.2	0.2	3.3	1.0
AG10FA140776	5.4	0.3	6.4 <sup>e</sup>	1.0
AG13FA270776	0.8	0.1	5.1 <sup>c</sup>	1.0
Distilled water				
DW(AG1)UB290376	1.0	0.2	0.9	0.1
DW (AG1) F1290376	24.0	0.3	27.3 <sup>c</sup>	1.4
DW(AG4)UB260376	1.9	0.2	2.5	0.2
DW(AG4)FA260376	8.5	0.3	8.1	0.3
DW(AG4)FB260376	8.0	0.3	8.4	0.3
DW(AG5)UA310376	1.9	0.2	1.6	0.2

<sup>a</sup> Concentrations were not corrected for filtration procedure contamination.

<sup>b</sup> Subsamples E and F were analyzed upon receipt from laboratories of two collaborators; time interval between the two sets of analyses was *ca* 3-8 months.

<sup>c</sup> Direct analysis of unconcentrated sample solution (mean of duplicate analyses). The remainder of data resulted from the Evap/FAAS procedure and each value reflects one analysis.

Table 28. Concentrations of dissolved + acid- and solvent-extractable Cu, Zn, Cd and Pb in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13<sup>a</sup>

Watershed and sampling date	Mean concentration ± standard error, s/√n, µg/L <sup>b</sup>							
	Cu		Zn		Cd		Pb	
		±		±		±		±
Watershed AG1								
290376	13.9	3.3	15.8	4.9	0.19	0.00	1.7	0.7
260776	5.8	0.8	15.3	4.9	0.08	0.02	1.7	0.7
051176	5.2	0.8	7.9	0.8	0.03	0.02	1.3	0.8
130377	27.8	7.1	228	9.0	1.75	0.04	29.4	8.5
Watershed AG3								
050476	1.7	0.7	3.0	0.7	0.10	0.0	0.7	0.8
080676	2.3	0.8	3.4	0.9	0.01	0.03	0.2	0.9
190776	2.1	0.8	1.3	1.0	0.02	0.02	0.2	0.9
141076	2.1	0.7	4.2	1.0	0.07	0.02	0.9	0.8
Watershed AG4								
260376	43.9	3.1	69.7	3.5	0.29	0.02	25.3	3.8
010676	5.2	0.8	2.0	0.7	0.01	0.02	0.4	1.0
120776	3.8	0.8	5.1	0.8	0.02	0.02	1.4	0.7
071076	2.2	0.7	10.5	3.5	0.12	0.02	1.2	0.7
Watershed AG5								
310376	9.2	0.8	3.1	0.7	0.04	0.00	1.7	0.8
030676	2.8	0.8	6.1	0.8	0.03	0.02	0.3	0.9
150776	2.9	0.7	6.8	0.7	0.02	0.02	1.0	0.6
210776	3.4	0.8	10.6	3.4	0.06	0.02	1.8	0.7
250876	1.9	0.8	1.2	0.7	0.01	0.04	0.2	0.9
051076	2.0	0.7	0.9	0.7	0.02	0.02	0.2	0.9
250377-1	223	9	1160	11.0	11.4	0.06	305	10
250377-5	10.0	1.7	47.0	5.0	0.55	0.04	16.2	8.5
Watershed AG10								
300376	7.9	0.8	30.5	2.9	0.08	0.02	4.0	0.7
020676	3.4	0.8	16.6	3.6	0.04	0.02	2.1	0.7
140776	2.7	0.9	20.4	3.6	0.07	0.02	1.3	0.8
121076	3.4	0.7	18.1	2.9	0.07	0.02	2.1	0.7
Watershed AG13								
290376	40.8	3.8	11.8	3.5	0.04	0.02	0.6	0.8
270776	2.8	0.8	2.7	0.7	0.03	0.02	0.9	0.7
041176	2.8	0.8	4.6	0.7	0.06	0.02	1.3	0.7
030377	36.4	7.1	121	9.0	3.66	0.04	39.1	8.5

<sup>a</sup> These concentrations were determined on unfiltered water samples under various conditions giving measures of dissolved + acid- or solvent-extractable levels. They are neither dissolved nor total concentrations but intermediate estimates. Refer to the text for discussion and to other tables for dissolved, total and suspended sediment trace element concentrations.

<sup>b</sup> Mean concentrations,  $\bar{X}$ , reported here have been averaged over subsamples and analytical methodologies. Refer to Table 35 and Appendix II for details.

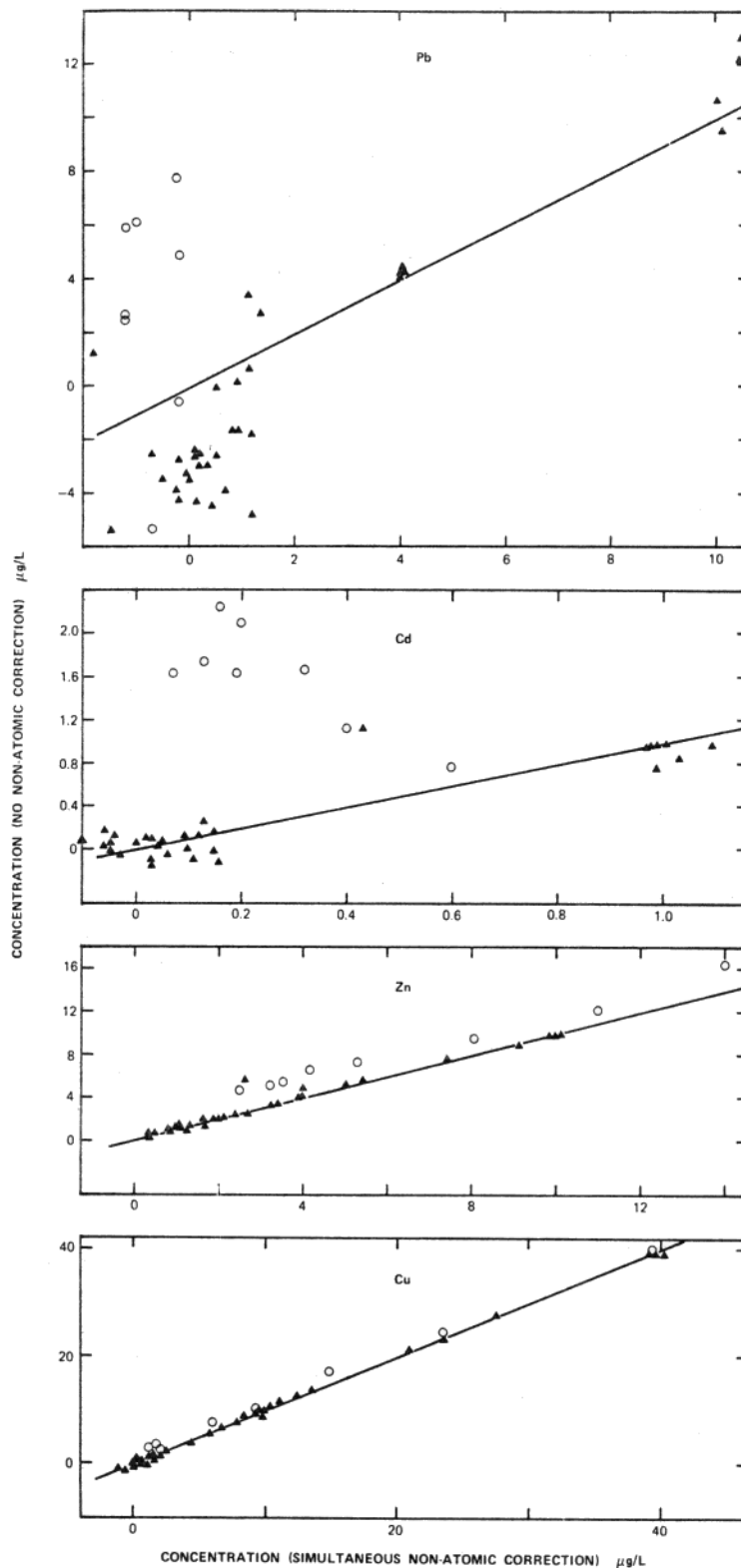


Figure 22. Effect of non-atomic absorption on determination of Cu, Zn, Cd and Pb, by flame atomic absorption spectrometry, in concentrated natural and distilled water samples, with or without added analytes in the latter matrix. Data have been converted to concentrations in the original samples. O: filtered natural water; ▲: distilled water. Three points for Cd in distilled water depicted at *ca* 1.0  $\mu\text{g/L}$ , and the four points for Pb in distilled water at 4  $\mu\text{g/L}$  represent data divided by 10 for plotting. The lines represent slopes of unity.

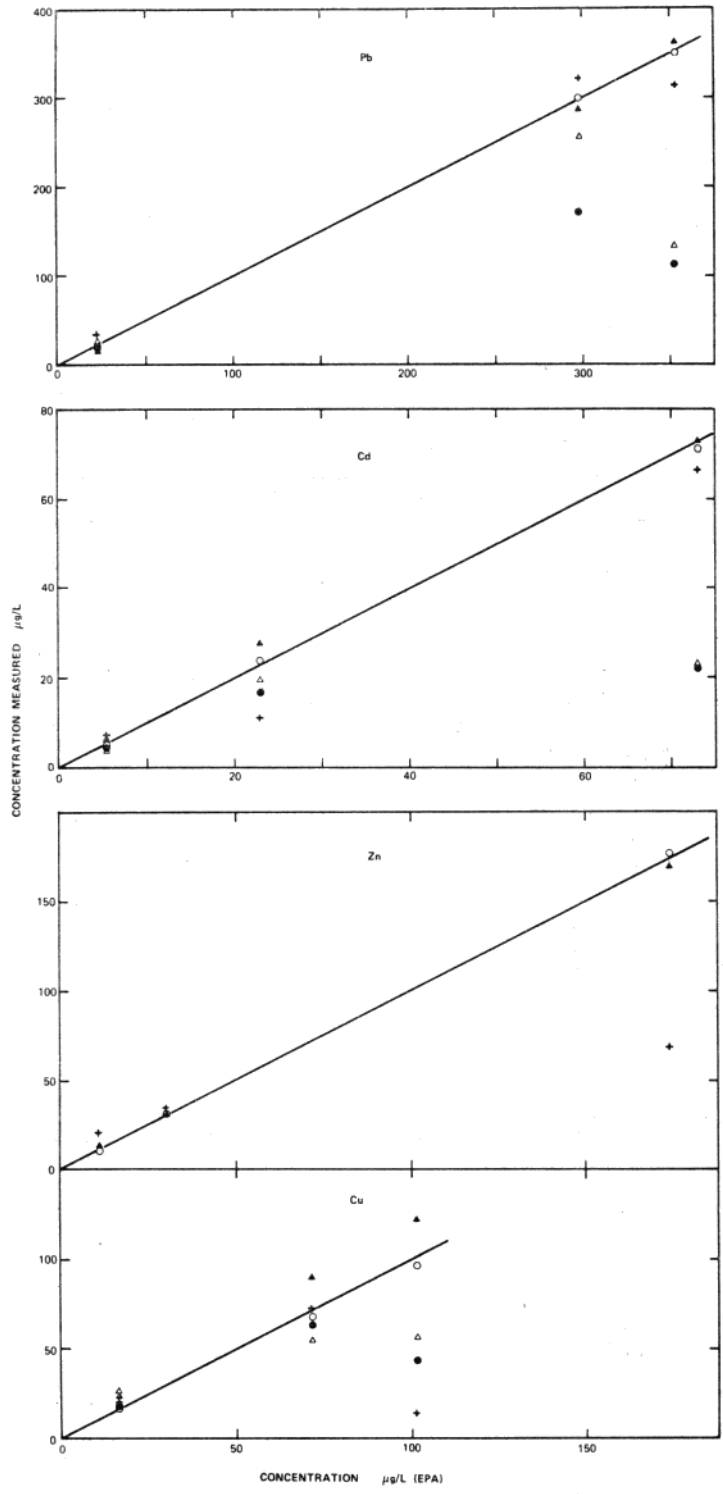


Figure 23. Concentrations of Cu, Zn, Cd and Pb in EPA quality control samples measured by five analytical methods in the four cooperating laboratories, as functions of EPA-reported levels. The lines represent slopes of unity.

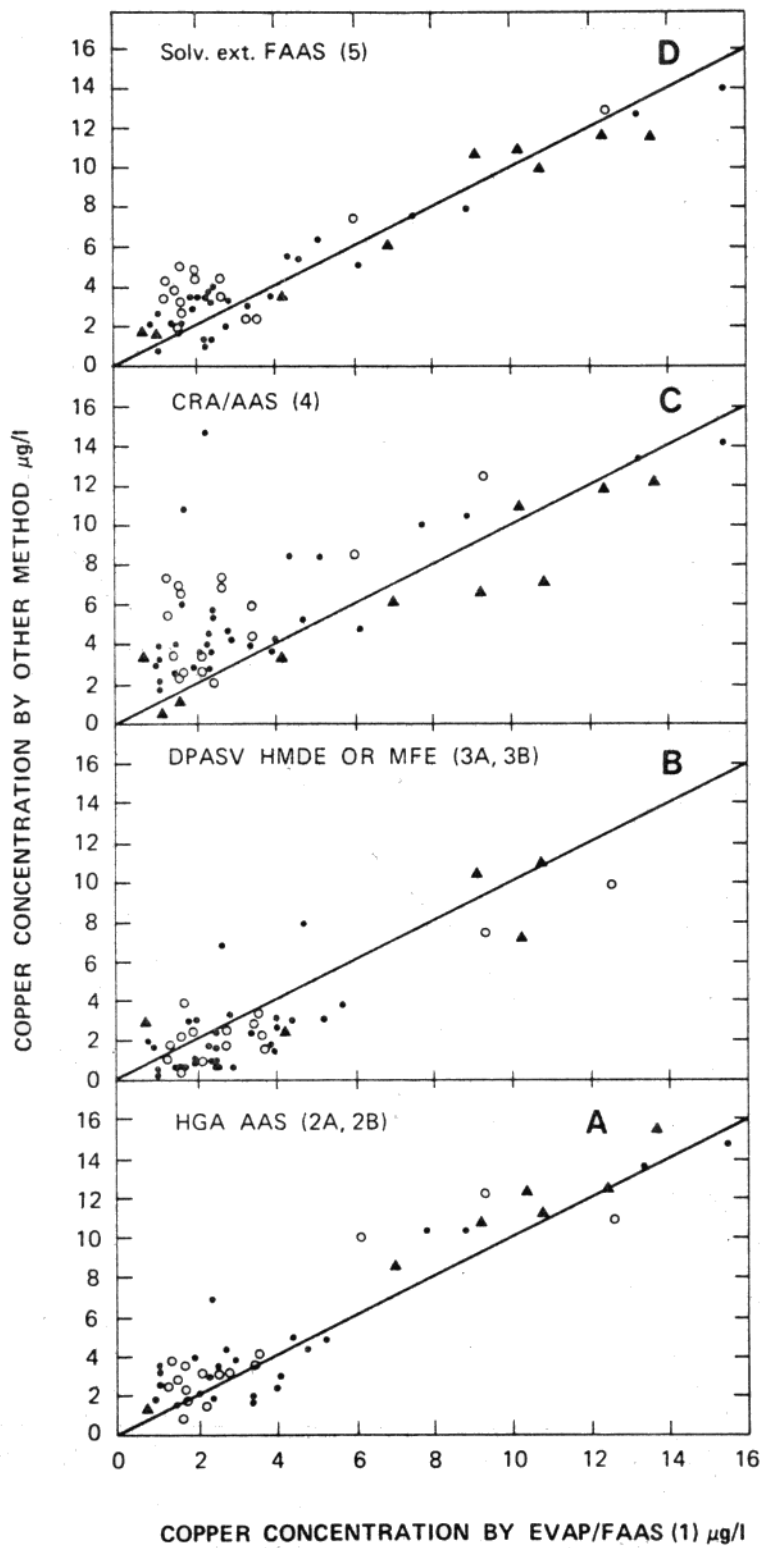


Figure 24. Relationships between copper concentrations in unfiltered and filtered natural and distilled water samples measured by different analytical methods, and values determined by evaporation/ flame atomic absorption spectrometry. ●:unfiltered natural water; ○: filtered natural water; ▲:distilled water. The lines represent unit slope.

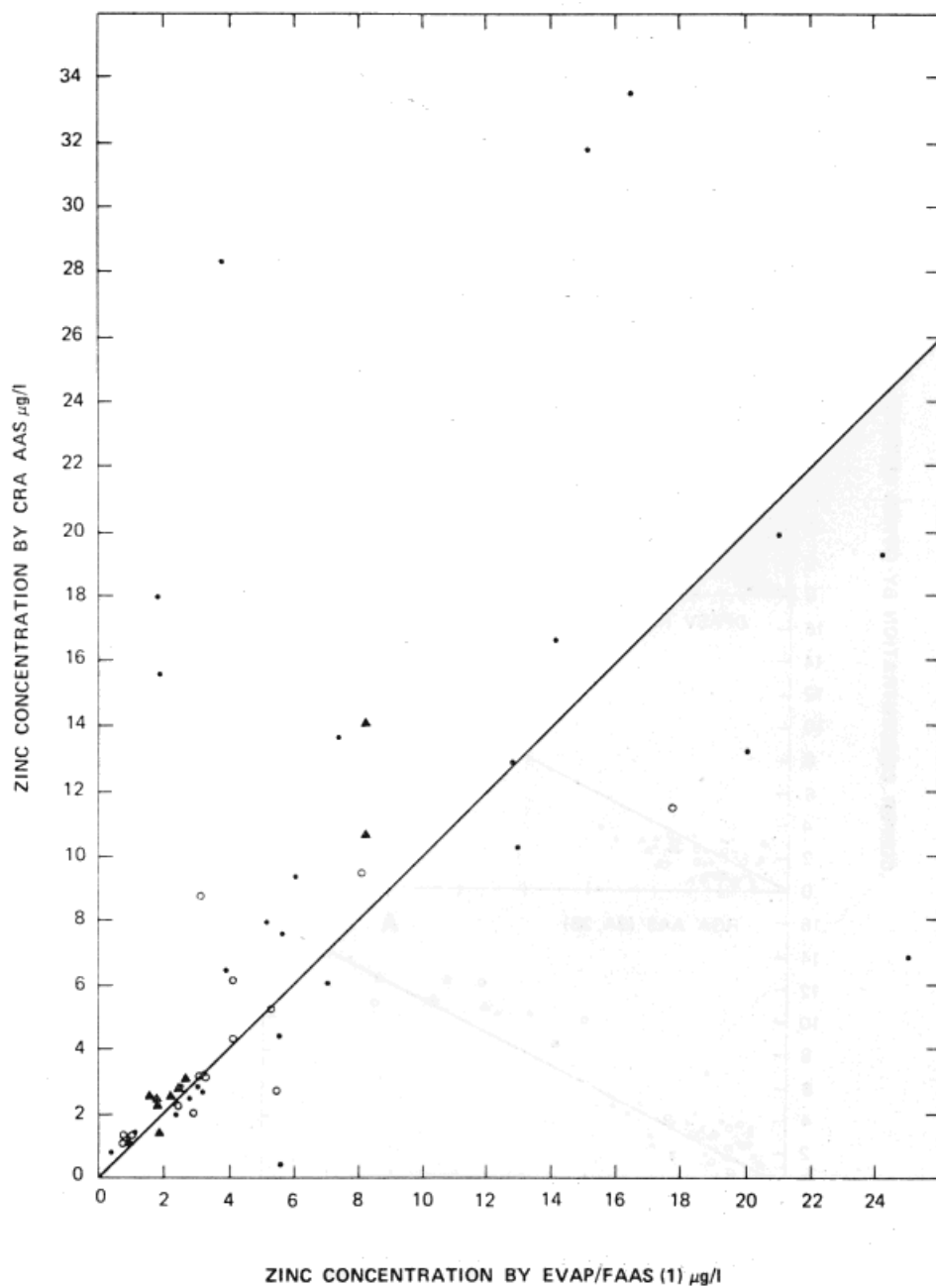


Figure 25. Relationship between zinc concentrations in unfiltered and filtered natural and distilled water samples measured directly by carbon rod atomization/AAS, and by evaporation/flame AAS. ●:unfiltered natural water; ○:filtered natural water; ▲:distilled water. The line represents a slope of unity.

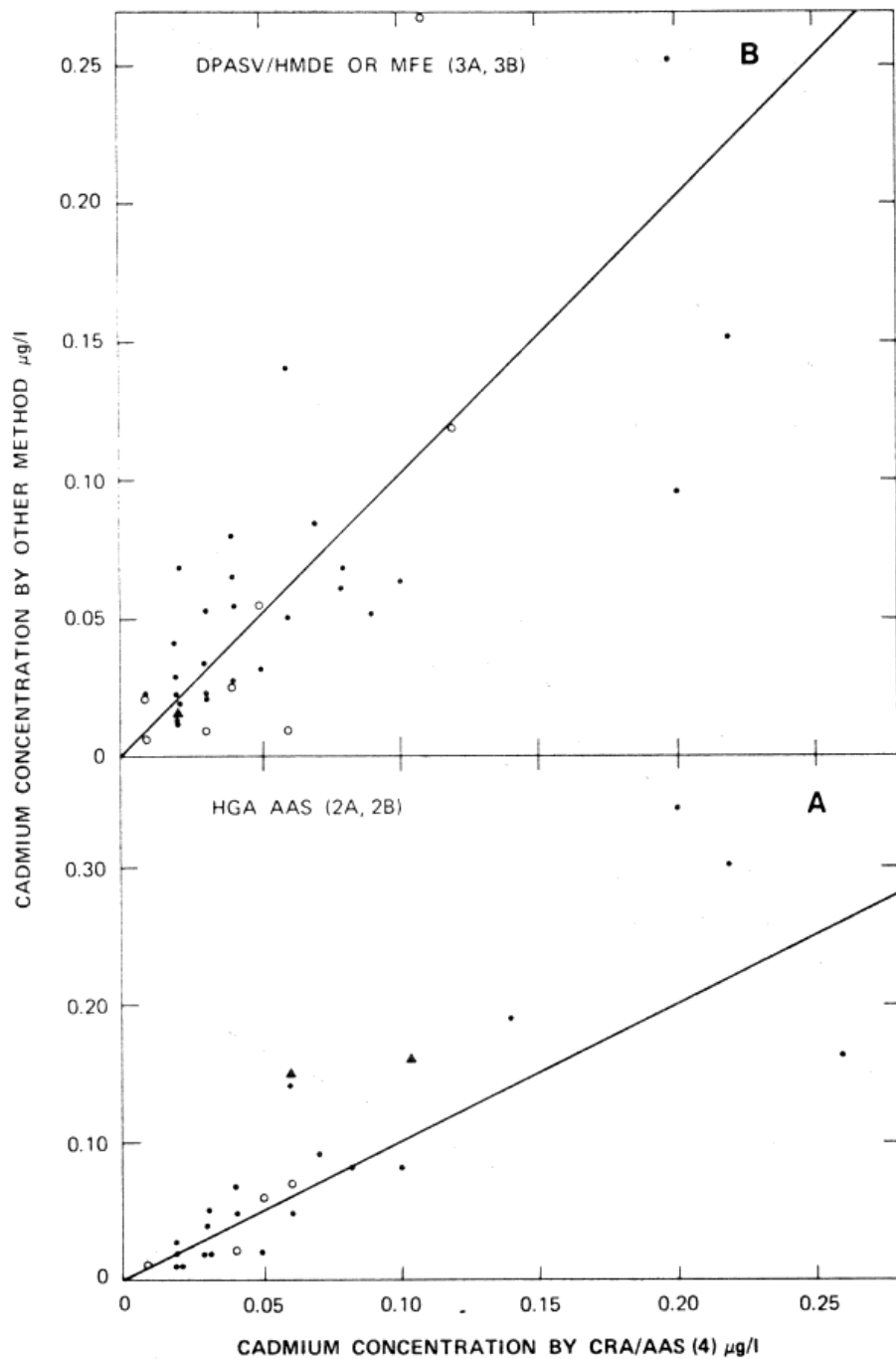


Figure 26. Relationships between cadmium concentrations in unfiltered and filtered natural and distilled water samples measured by different analytical methods, and values obtained by carbon rod atomization/AAS. ●:unfiltered natural water; ○:filtered natural water; ▲:distilled water. The lines represent unit slope.

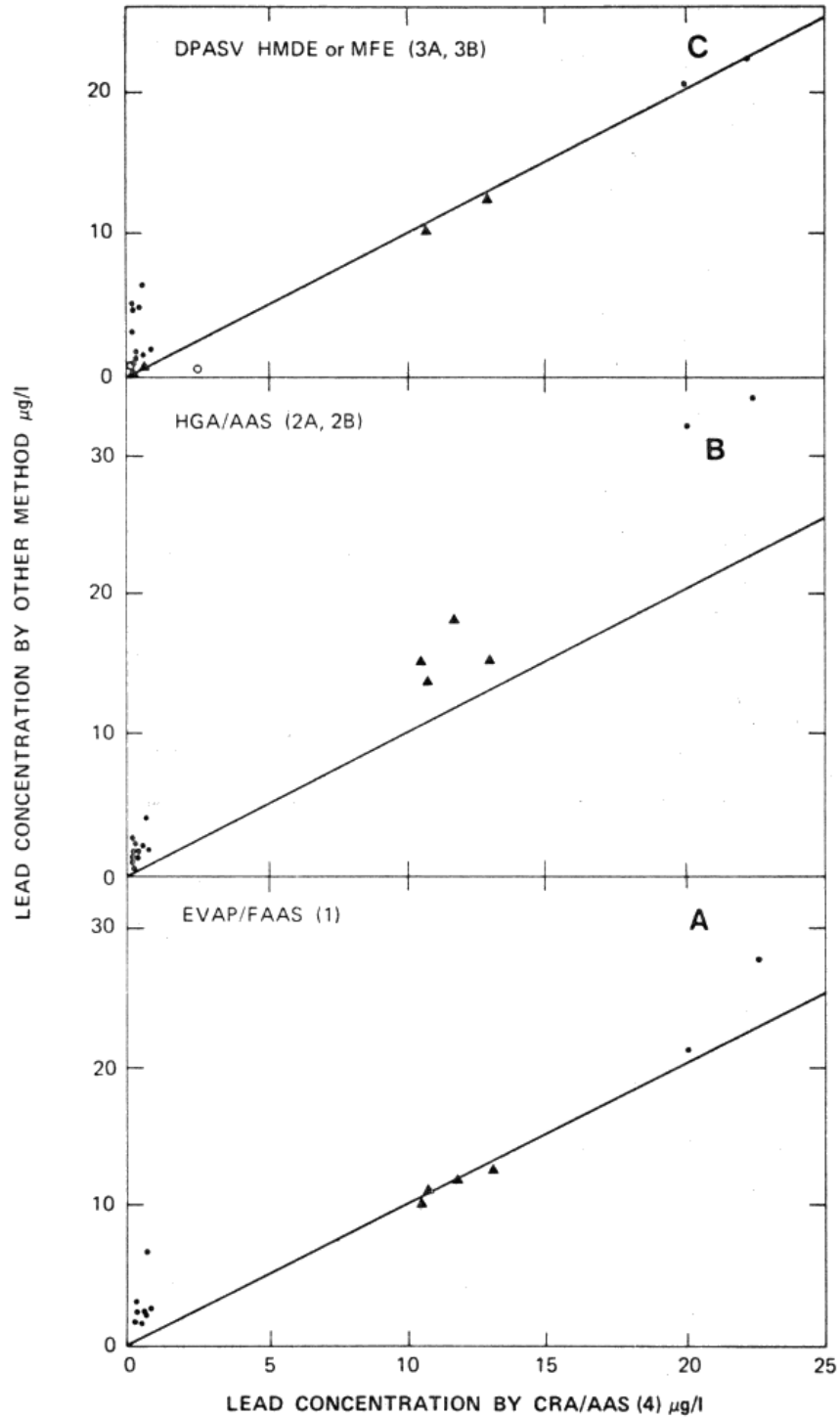


Figure 27. Relationships between lead concentrations in unfiltered and filtered natural and distilled water samples measured by different analytical methods, and values obtained by carbon rod atomization/AAS. ●:unfiltered natural water; ○:filtered natural water; ▲:distilled water. The lines represent unit slope.

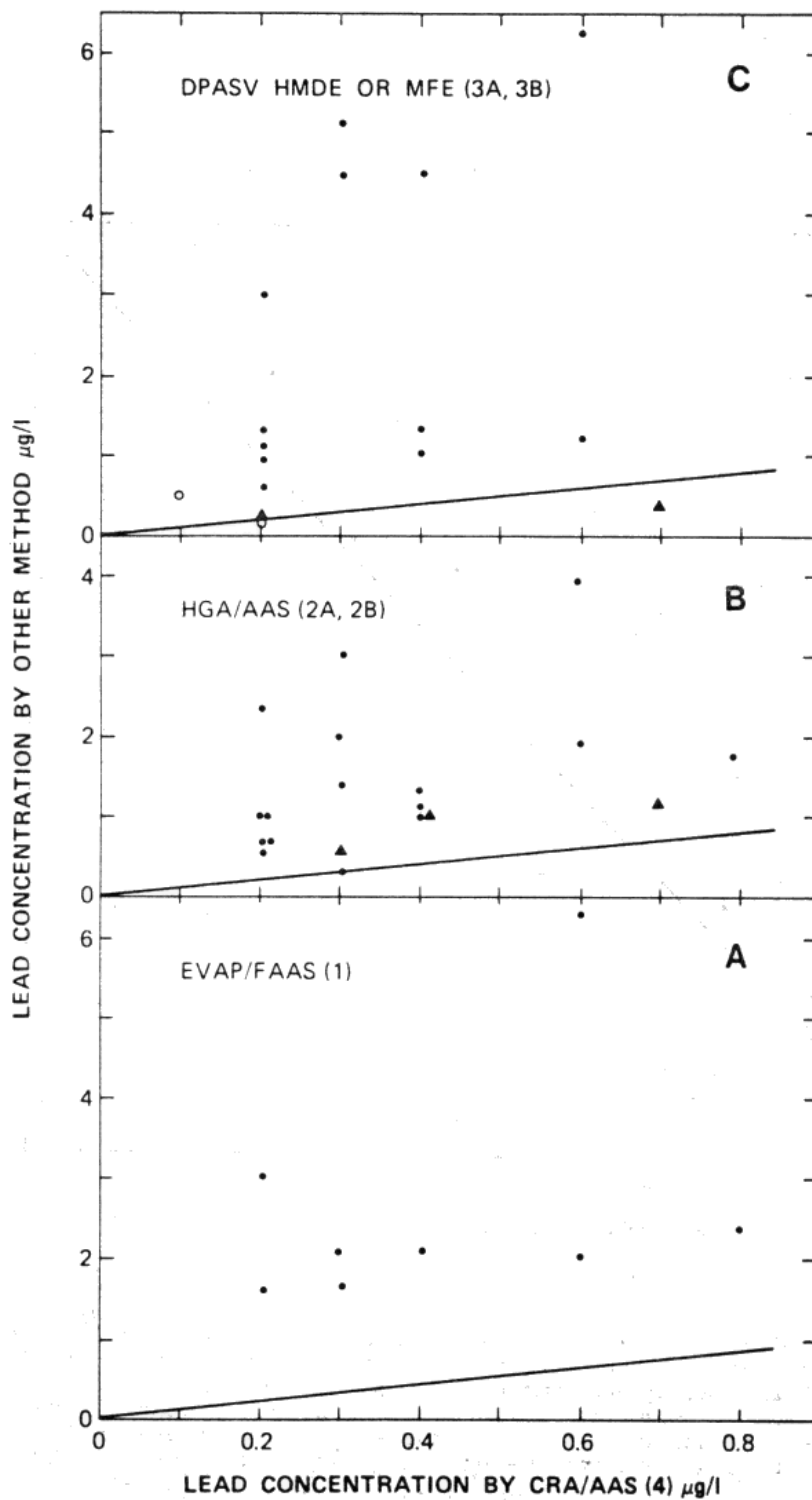


Figure 28. Relationships between low-level lead concentrations in unfiltered and filtered natural and distilled water samples measured by different analytical methods and values obtained by carbon rod atomization/AAS. ●:unfiltered natural water; ○:filtered natural water; ▲:distilled water. The lines represent unit slope.

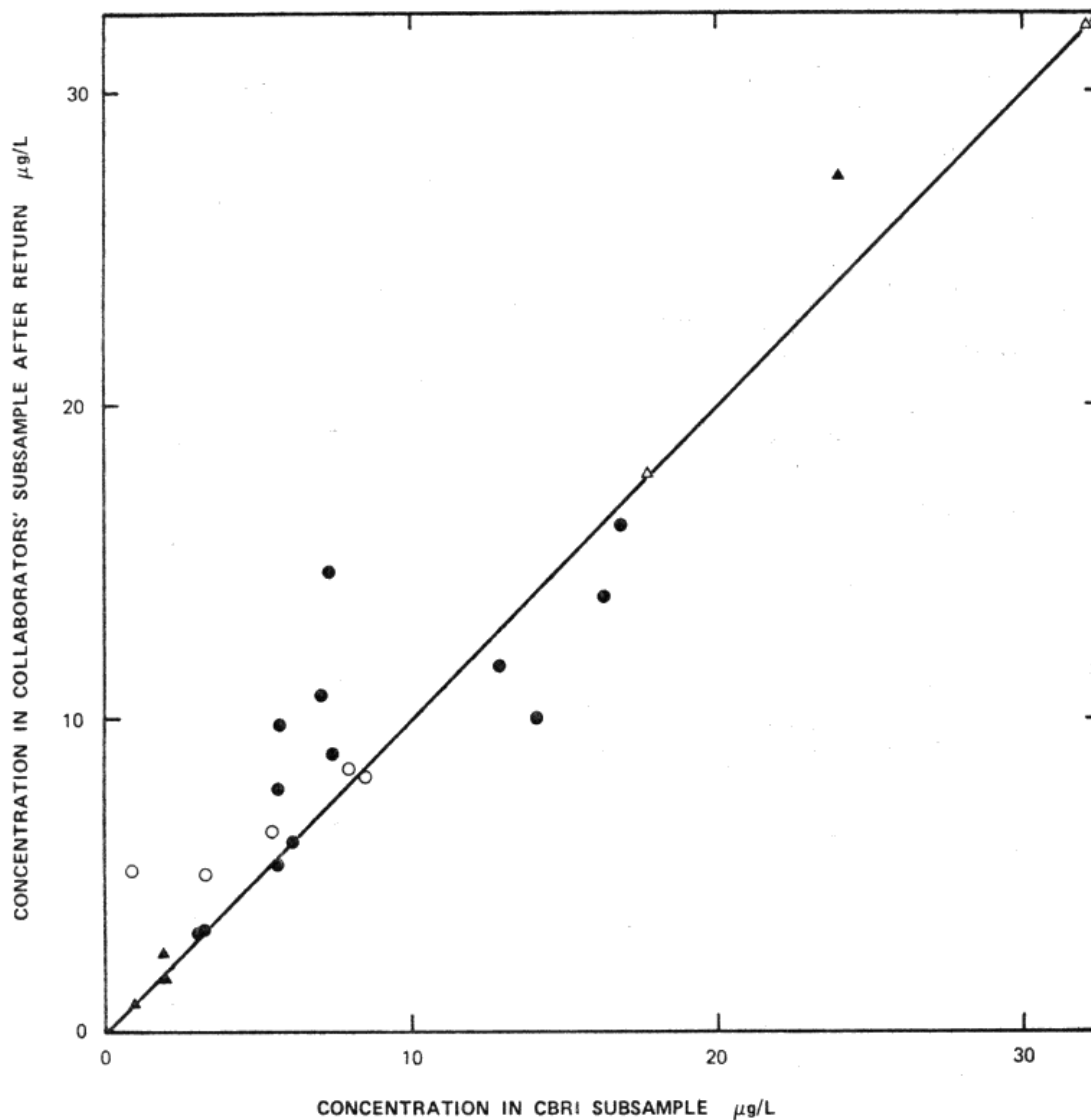


Figure 29. Concentration of Zn in subsamples returned from two collaborating laboratories as a function of concentration in initiating (CBRI) laboratory subsamples. All analyses were conducted by the initiating laboratory; collaborator subsamples were analyzed 38 months after analyses of CBRI samples. ●: unfiltered natural water; ○: filtered natural water; ▲: distilled water; △: EPA sample. The point for the EPA sample at *ca* 18  $\mu\text{g/L}$  represents a datum divided by 10 for plotting. Data have been converted to concentrations in the original samples. Analysis of EPA solutions was by direct aspiration/FAAS whereas all other solutions were subjected to concentration by evaporation prior to FAAS measurement.

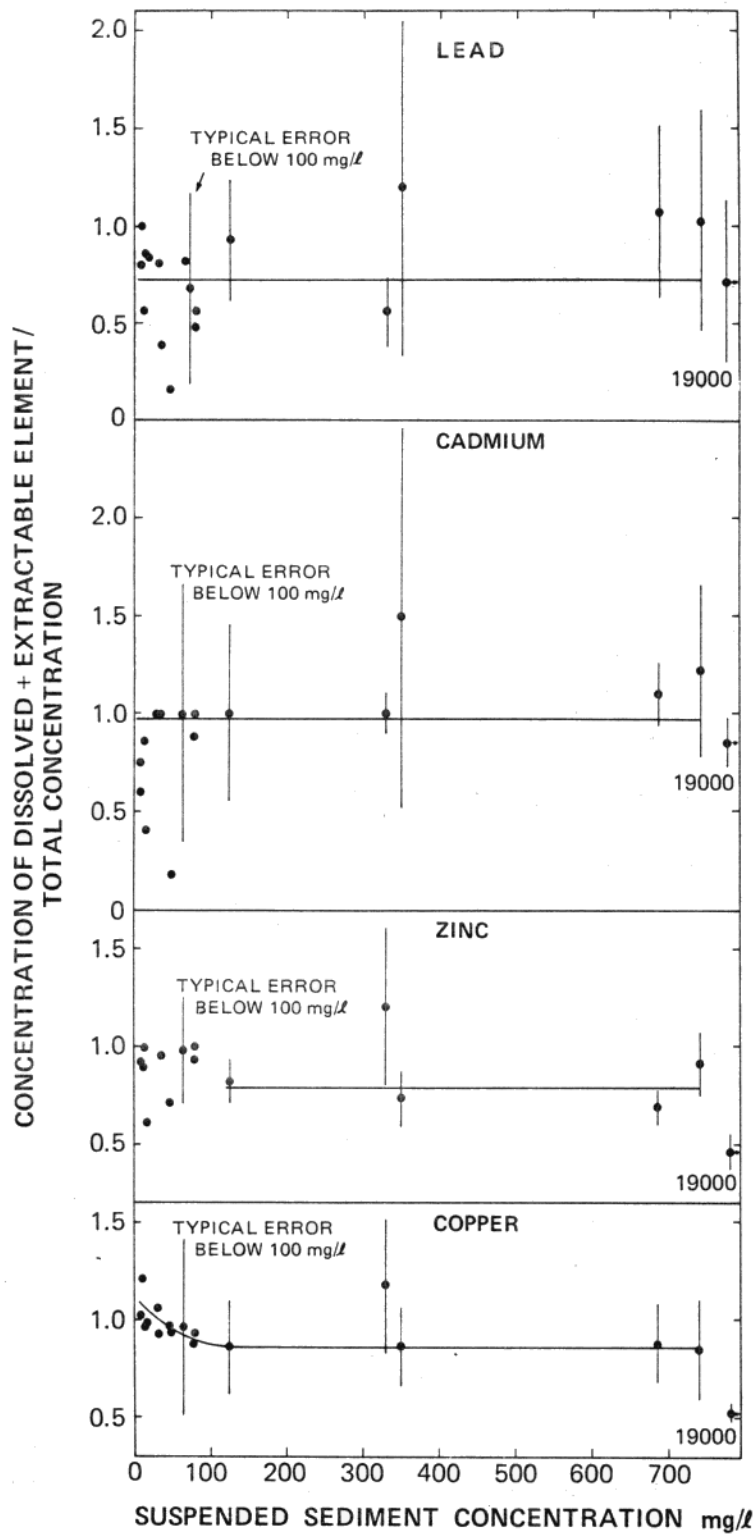


Figure 30. Relationships of the ratio: dissolved + extractable trace element concentration/total concentration, for Cu, Zn, Cd and Pb, to concentration of suspended sediment in the stream waters.

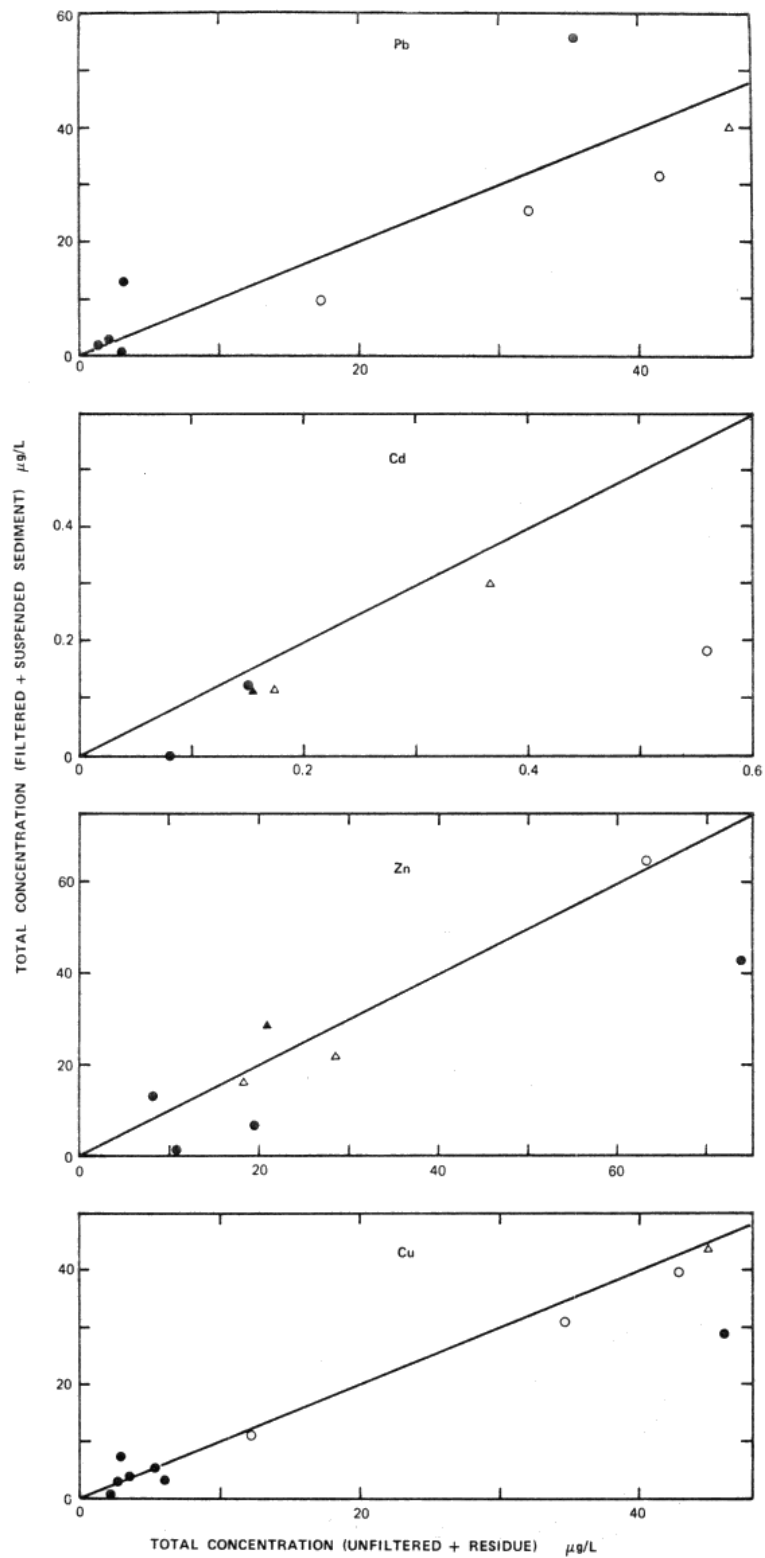


Figure 31. Relationships between total concentrations of Cu, Zn, Cd, and Pb in natural waters determined as (a) sum of concentrations in filtered water + suspended sediment and (b) sum of concentrations in unfiltered water + residue (acid-leached sediment). ●:1976 field-filtered samples; ○, △, ▲:1977 laboratory-filtered samples; △, ▲: actual total concentrations have been reduced 10- and 100-fold respectively for plotting. The straight lines represent slopes of unity.

## APPENDIX II: DETAILED DATA

This appendix contains the body of data pertaining to trace element characteristics of the agricultural watersheds, upon which rest the summary information and conclusions presented in the main part of this report. Although detailed, the information is not quite "raw" experimental data, but has already been subjected to some processing (averaging, smoothing of errors, and rejection of obviously aberrant values); it is, however, sufficiently detailed to form a basis for calculation of all information presented in this report. The appendix begins with a discussion of statistical treatments applied, and ends with tables of detailed comparisons of results from this study with those reported by other investigators of these watersheds and literature data for other "unpolluted" natural waters.

### STATISTICAL ANALYSIS

A small number of obviously aberrant data was omitted by inspection at the beginning of the task of data handling, and is not reported. Data reported by all cooperating laboratories were pooled over all field and laboratory subsamples for calculation of means and standard deviations. As far as possible, individual results rather than laboratory means were used if reported by the laboratories and additional few data were subjectively rejected as suspected outliers based on inspection and effects on standard deviations. Mean concentrations over all subsamples and methods,  $\bar{X}$ , and standard errors,  $s/\sqrt{n}$  were computed from the equations

$$\bar{X} = \sum \bar{X}_i/n \quad (1)$$

$$\bar{X}_i = \sum_k X_{ik}/k_i \quad (2)$$

$$s/\sqrt{n} = [(\frac{1}{n})^2 (ns_B^2 + \sum_i s_w^2/k_i)]^{\frac{1}{2}} \quad (3)$$

where  $\bar{X}$  is the unweighted overall mean (i.e. means from each method were weighted equally regardless of the number of analyses),  $\bar{X}_i$  is the mean of the  $i^{\text{th}}$  method,  $k_i$  is the number of replicate analyses on all subsamples for the given sampling date by the  $i^{\text{th}}$  method,  $n$  is the number of analytical methods, varying from 1 to 5, and  $s_w^2$  and  $s_B^2$  are

within-and between-method variances respectively. Data were pooled by element, type of sample (unfiltered or filtered natural or distilled water) and concentration range. Examples of analytical concentration data incorporated into means are listed in Table 29 to indicate the spread in data accepted. For this demonstration, data from two or more analytical methods were considered and were pooled over unfiltered and filtered natural water samples. For each element, nine ranges are given, reflecting three low extreme, three median and three high extreme ratios. As may be deduced from median ratios, Cu and Pb exhibit somewhat greater variability than Zn and Cd. The large high extreme ratios encountered for each element indicate the type of widely varying data retained because *a priori* it was impossible to judge which data were correct. Standard errors of the means, however, are independent of these ratios, as errors were calculated (eq. 3) from "smoothed" within-and between-method variances obtained from a large body of data. Standard deviations used in calculations of standard errors are listed in Table 30.

For calculations involving arithmetic manipulation of means referred to above, the following propagation of error equations were usually used to calculate standard errors.

$$\bar{W} = \bar{X} \pm \bar{Y} \quad S_{\bar{W}}^{-2} = S_{\bar{X}}^{-2} + S_{\bar{Y}}^{-2} \quad (4)$$

$$\bar{W} = \bar{X}/\bar{Y} \quad S_{\bar{W}}^{-2} = \left(\frac{\bar{X}}{\bar{Y}}\right)^2 \left(\frac{S_{\bar{X}}^{-2}}{\bar{X}^2} + \frac{S_{\bar{Y}}^{-2}}{\bar{Y}^2}\right) \quad (5)$$

$$\bar{W} = \bar{X} \bar{Y} \quad S_{\bar{W}}^{-2} = (\bar{X} \bar{Y})^2 \left(\frac{S_{\bar{X}}^{-2}}{\bar{X}^2} + \frac{S_{\bar{Y}}^{-2}}{\bar{Y}^2}\right) \quad (6)$$

where  $\bar{W}$  is the mean of arithmetic manipulations of  $\bar{X}$  and  $\bar{Y}$ , with corresponding standard errors  $S_{\bar{W}}$ ,  $S_{\bar{X}}$  and  $S_{\bar{Y}}$  respectively. Every datum reported thus has associated with it a standard error which, in the case of multi-method generated data, is precision-and accuracy-related, the latter due to the use of different analytical methodologies.

## DETAILED TABLES

Tables of detailed data follow; Tables 31-48 list analytical data from this study upon which were based results and conclusions presented in the main part of this report, whereas Tables 49-55 list comparisons of data obtained in this study with those reported by other investigators of these watersheds and other "unpolluted" natural waters. Often,

more figures are given than is warranted by precision of the data; these data were used in calculations, with rounding-off occurring at the final stages. The tables are fairly well self-explanatory, and only minor comments follow.

Data in Tables 35 and 40, mean concentrations in unfiltered and filtered waters, respectively, form the basis for calculation of total and dissolved levels. Calculations may be exemplified using data for Cu in sample AG1260776:

$$\begin{aligned}\text{Dissolved Cu } (\mu\text{g/L}) &= 4.35 \pm 1.04 \text{ (Table 40)} - 1.3 \pm 1.6 \text{ (Table 23)} \\ &= 3.1 \pm 1.9 \text{ (Table 7)}.\end{aligned}$$

$$\begin{aligned}\text{Total Cu}(\mu\text{g/L}) &= 3.1 \pm 1.9 \text{ (Table 7)} + 0.3 \pm 0.4 \text{ (Table 6)} \\ &= 3.4 \pm 1.9 \text{ (Table 41)}.\end{aligned}$$

Also,

$$\begin{aligned}\text{Total Cu}(\text{pg/L}) &= 5.79 \pm 0.75 \text{ (Table 35)} + 0.34 \pm 0.08 \text{ (Table 48)} \\ &= 6.13 \pm 0.75 \text{ (Table 41)}.\end{aligned}$$

Standard errors reported in these Tables were computed from  $S_w$  and  $S_b$  for populations of data from several laboratories whether the mean concentration was for one or more laboratories. Thus, the datum for Cd for AG10 300376 (Table 40) is reported as  $0.600 \pm 0.039 \mu\text{g/L}$ ; this datum results from one method (Evap/FAAS) and should be  $0.60 \pm 0.12 \mu\text{g/L}$  if reported on information based on that method. The former value, however, was used. At times, unreal standard errors of  $0.000 \mu\text{g/L}$  were realized due to negative  $S_b^2$ , and must be treated with caution.

Table 29 Examples of analytical concentration data incorporated into means, µg/L <sup>a</sup>

Element	Concentration Range	Ratio of extreme values in range <sup>b</sup>	No. of analytical methods	Total no. of analyses	Mean ± standard error
Cu	4.40-6.90	1.57	4	9	4.35 ±1.04
	7.80-13.0	1.67	4	18	9.21 ±0.81
	9.80-18.0	1.84	5	10	13.1 ±0.98
	2.24-8.00	3.57	5	11	5.23 ±0.77
	4.40-16.5	3.75	5	11	7.94 ±0.77
	1.73-6.50	3.76	4	9	4.40 ±1.45
	0.50-5.90	11.8	5	15	3.22 ±0.93
	0.70-10.0	14.3	5	16	3.43 ±0.73
	0.40-9.50	23.8	5	15	3.00 ±0.92
Zn	2.20-2.39	1.09	2	5	2.30 ±0.99
	3.20-3.54	1.11	2	6	3.31 ±0.88
	3.49-4.20	1.20	2	6	4.01 ±0.88
	2.54-3.54	1.39	2	10	3.10 ±0.74
	0.93-1.40	1.50	2	10	1.21 ±0.70
	0.79-1.20	1.52	2	6	1.06 ±0.88
	1.26-5.10	4.05	2	3	3.37 ±0.90
	0.27-1.20	4.44	2	9	0.80 ±0.70
	0.40-6.40	16.0	2	10	4.57 ±0.74
Cd	0.030-0.035	1.17	2	3	0.033 ±0.021
	0.050-0.065	1.23	3	8	0.056 ±0.020
	0.010-0.013	1.30	2	3	0.012 ±0.035
	0.010-0.021	2.10	2	4	0.013 ±0.027
	0.010-0.022	2.20	3	8	0.015 ±0.020
	0.050-0.12	2.40	3	12	0.077 ±0.000
	0.030-0.20	6.67	2	10	0.095 ± -
	0.0070-0.050	7.14	3	8	0.030 ±0.020
	0.010-0.27	27.0	4	13	0.114 ±0.010
Pb	0.20-0.22	1.09	2	4	0.21 ±0.03
	0.17-0.20	1.20	2	4	0.19 ±0.94
	0.16-0.20	1.27	2	4	0.19 ±0.03
	0.06-0.20	3.33	2	4	0.16 ±0.03
	0.80-3.31	4.14	4	11	1.79 ±0.65
	0.38-1.75	4.67	3	5	0.93 ±0.78
	0.20-3.00	15.0	3	9	1.27 ±0.67
	0.30-5.00	16.7	3	12	1.66 ±0.76
	0.30-5.12	17.1	3	10	2.06 ±0.66

<sup>a</sup> Only data from two or more analytical methods were considered; results for unfiltered and filtered natural water samples were pooled for these examples.

<sup>b</sup> For each element, nine ranges are given reflecting, in sequence, three low extreme, three median and three high extreme ratios for the pooled sets of data.

Table 30 Precisions used in calculations of standard errors of means,  $\mu\text{g/L}$  <sup>a</sup>

Element	Sample type	Concentration range <sup>b</sup>	$S_w$ <sup>c</sup>	Degrees of freedom	$S_B$ <sup>c</sup>	Degrees of freedom
Cu	UNW	1.6 -10.0	1.06	102	1.49	82
		13.9 -223	6.75	21	5.28	9
Zn	UNW	0.7 -23.5	1.61	42	1.70	57
		10.5 -47.0	2.33	24	4.76	9
		70 -1164	10.50	4	4.55	1
	FNW	1.0 -10.5	1.26	17	0.98 <sup>d</sup>	11
		10.2 -24.2	6.98	2	-12.40	3
Cd	UNW	0.01 -0.29	0.064	44	-0.0006 <sup>d</sup>	45
		0.5 -11.4	use above			
	FNW	0.01 -0.43	0.050	18	-0.0009 <sup>d</sup>	23
Pb	UNW	0.15 -4.0	0.71	51	1.22	48
		16 -305	7.69	16	6.55	3
	FNW	0.13 -13.3	0.18	12	-0.014 <sup>d</sup>	15

<sup>a</sup> Information is for unfiltered and filtered natural water samples designated UNW and FNW respectively.

<sup>b</sup> These are unweighted concentrations,  $\bar{X}$ , defined elsewhere in the appendix

<sup>c</sup>  $S_w$  and  $S_B$  listed here, calculated from pooled data as indicated, were used to calculate standard errors of mean concentrations;  $S_w$  -within method standard deviation;  $S_B$ -between method standard deviation.

<sup>d</sup>  $S_B^2$  was negative and is reported instead of  $S_B$ .

Table 31. Concentrations of copper in natural water samples - detailed data for unfiltered samples <sup>a</sup>

Sample code	Mean concentration (number of analyses) ± standard error, s/√n or ts/√n , µg/L <sup>b</sup>									
	Laboratory/method									
	1	±	2A <sup>c</sup>	±	2B <sup>c</sup>	3A	3B	4	±	5
Watershed AG1										
UA 290376	13.3	0.3	13.5 (2)	0.8				13.4 (4)	0.8	12.8
UB	15.5	0.3	14.8 (2)	0.8				14.2 (4)	0.7	14.0
UA 260776	5.2	0.3			4.8 (2)		3.1	8.6 (4)	0.9	6.4
UB	5.8 (2)	0.2								
UC	5.7	0.3					3.9			
UD	5.7 (2)	0.2								
UA 051176	4.4	0.3			4.9 (2)		3.1	8.5 (4)	0.8	5.4
UB	4.0	0.3					3.1			
UB 130377	27.8 (2)	0.2								
Watershed AG3										
UA 050476	1.1	0.3	3.3 (4)	0.5		1.6 (2)		1.6 (4)	0.8	0.8
UB	1.1	0.3	2.5 (2)	0.6				2.0 (4)	0.8	
UA 080676	1.1	0.3			3.0 (2)		0.6	3.7 (4)	0.9	2.7
UB	1.8	0.3					0.6			
UA 190776	2.0	0.3			2.1 (2)		1.0	2.7 (4)	0.9	2.9
UB	1.3 (2)	0.2								
UC	1.6	0.3					1.4			
UD	1.5	0.3								
UA 141076	1.5	0.3			1.5 (2)		0.6	2.5 (4)	0.9	2.3
UB	2.1 (2)	0.2								
UC	1.7	0.3					0.6	5.9 (4)	0.9	2.1
Watershed AG4										
UA 260376	46.4	1.1	36.3 (4)	0.6		55.1 (2)		41.9 (4)	1.6	
UB	42.1	1.1	39.3 (4)	0.6		45.8 (2)		44.3 (4)	1.6	
UA 010676	4.7	0.3			4.4 (2)		8.0	5.3 (4)	0.9	5.4
UB	2.2 (2)	0.2								
UA 120776	2.9	0.3			3.5 (2)		3.2	4.3 (4)	0.9	3.4
UB	2.6	0.3					6.9			
UA 071076	2.3	0.3			3.0 (3)		1.0	3.7 (4)	0.9	1.4
UB	2.2 (2)	0.2								
UC	1.6	0.3					0.6	3.8 (4)	0.9	1.7
UD	2.2	0.3								
Watershed AG5										
UA 310376	8.9	0.3	10.3 (3)	0.6				10.4 (4)	0.8	8.1
UB	7.8	0.3	10.3 (3)	0.6				10.0 (4)	0.8	7.8
UA 030676	2.8	0.3			4.0 (3)			4.8 (4)	0.9	2.1
UB	2.0	0.3					0.9			
UA 150776	2.3	0.3			1.8 (2)		0.9	2.6 (4)	0.9	3.4
UB	3.9	0.3			2.3 (2)		1.7	3.7 (4)	0.8	<1.0
UC	2.4	0.3					0.7	3.3 (4)	0.8	3.3
UD	6.2	0.3						4.9 (4)	0.9	5.2
UA 210776	4.0	0.3			2.9 (2)		2.6	4.2 (4)	0.9	3.5
UB	3.6 (2)	0.2								
UC	3.8	0.3					2.0			
UD	4.2 (2)	0.2								

Cont'd...

Table 31 Cont'd

	1	±	2A	±	2B	3A	3B	4	±	5
UA 250876	1.0	0.3			1.7 (2)		1.9	2.4 (4)	0.9	2.2
UB	1.6 (2)	0.2								
UC	1.1	0.3								
UD	1.6 (2)	0.2								
UA 051076	<0.8				1.9 (3)		2.5	2.1 (4)	1.0	3.4
UB	0.8 (2)	0.2								
UC	1.1	0.3					0.3	3.0 (4)	0.9	<1.0
UD	1.0	0.3								
UB 250377-1	223	1								
UB 250377-5	10.0 (2)	0.2								
Watershed AG10										
UA 300376	14.5 (3)	0.2								
UB					6.4 (2)		4.4	6.1 (4)	0.9	8.3
UA 020676	2.5	0.3			3.3 (2)		2.4	5.5 (4)	0.9	4.1
UB	2.4	0.3					1.0			
UA 140776	1.9	0.3			3.8 (2)		2.7	10.8 (4)	0.8	3.4
UB							0.7			
UA 121076	2.3	0.3			6.9 (3)		1.5	14.8 (4)	0.9	1.0
UB	2.1 (2)	0.2								
UC	2.5	0.3					0.7	5.7 (4)	0.8	1.4
UD	2.2	0.3								
Watershed AG13										
UA 290376	34.5	1.1			33.8 (3)		12.1	55.5 (4)	4.2	39.5
UB	11.0	0.3								
UA 270776	3.4	0.3			2.1 (2)		2.5	4.0 (4)	0.8	3.0
UB	2.4 (2)	0.2								
UC							1.7			
UD	2.4	0.3								
UA 041176	2.4	0.3			2.0 (2)		1.4	4.4 (4)	0.8	3.7
UB	2.1	0.3					2.8	3.3 (4)	0.9	3.5
UB 030377	36.4 (2)	0.8								

<sup>a</sup> These concentrations were determined under various conditions giving measures of dissolved + acid- or solvent-extractable levels. They are neither dissolved nor total Concentrations but intermediate estimates. Refer to the text for discussion and to other tables for dissolved, total and suspended sediment trace element concentrations. Mean Concentrations reported in Table 35 were Calculated from expanded versions of these data and individual values where possible, after rejection of a limited number of outliers.

<sup>b</sup> The standard error,  $s/\sqrt{n}$ , is reported for data in Columns 1 and 2A, whereas  $ts/\sqrt{n}$  for 95% confidence limits as reported by Dr. Berman is reported for data in Column 4. Standard deviations used here (for 1, 2A) were obtained from tables 14 and 22 respectively. Values listed for laboratory/method 2A were calculated by the author from data provided by Dr. Stoeppler. No error estimates are available for the other data.

<sup>c</sup> Results obtained by calibration curve and standard addition methods have been pooled. All data including first estimates provided by Dr. Stoeppler have been averaged in 2A as all appeared compatible. Inclusion of all data will have inflated the standard deviation; the real performance of the heated graphite method can be ascertained by reference to standard deviations and detection limits reported for method 2B in Tables 22 and 21 respectively.

Table 32 Concentrations of zinc in natural water samples - detailed data for unfiltered samples <sup>a</sup>

Sample Code	Mean Concentration(number of analyses) ± standard error, s/√n or ts/√n, µg/L <sup>b</sup>				5 <sup>c</sup>
	1		4		
		±		±	
Watershed AG1					
UA 290376	16.5 (2)	0.2	33.4 (4)	2.6	
UB	15.1 (2)	0.2	31.7 (4)	2.2	
UA 260776	14.2	0.3	16.6 (4)	0.9	
UB	13.8 (2)	0.2			
UC	14.2	0.3			
UD	14.3	0.3			
UA 051176	5.6	0.3	7.6 (4)	0.9	
UB	10.8	0.3			
UB 130377	228 (2)	≈0.4			
Watershed AG3					
UA 050476	3.2 (2)	0.1	2.7 (4)	0.2	
UB	3.1 (2)	0.1	2.9 (4)	0.2	
UA 080676	2.0	0.2	15.6 (4)	0.9	5.1
UB	1.3	0.2			
UA 190776	1.8	0.2	17.9 (4)	0.9	
UB	1.5 (2)	0.1			
UC	1.4	0.2			
UD	0.3	0.1			
UA 141076	3.9	0.2	28.3 (4)	1.0	20.7
UB	4.5 (2)	0.1			
UC	4.0	0.2	<0.1		
UD					
Watershed AG4					
UA 260376	74.7	0.3	84.8 (4)	6.0	
UB	54.1	0.3	65.0 (4)	5.2	
UA 010676	2.4	0.2	2.0 (4)	0.1	
UB	1.9 (2)	0.1			
UA 120776	5.6	0.3	4.4 (4)	0.3	
UB	5.9	0.3			
UA 071076	7.4	0.3	13.6 (4)	1.3	
UB	7.6 (2)	0.2			
UC	7.3	0.3	<0.1		
UD	7.1	0.3			
Watershed AG5					
UA 310376	3.5	0.2	3.4 (4)	0.3	<0.8
UB	2.5	0.2	2.9 (4)	0.2	
UA 030676	5.1	0.2	7.9 (4)	0.6	
UB	3.5	0.2			

Cont'd .....

Table 32 Cont'd

	1	±	4	±	5 <sup>c</sup>
UA 150776	6.1	0.3	9.3 (4)	0.7	
UB	7.0	0.3	6.0 (4)	0.3	
UC	5.2	0.3	<0.2		
UD	5.7	0.3	<0.2		
UA 210776	12.9	0.3	10.2 (4)	1.3	
UB	10.5 (2)	0.2			
UC	11.8	0.3			
UD	10.0 (2)	0.2			
UA 250876	1.1	0.2	1.4 (4)	0.1	
UB	1.0 (2)	0.1			
UC	1.0	0.2			
UD	1.1 (2)	0.1			
UA 051076	0.3	0.1	0.8 (4)	0.1	
UB	0.8 (2)	0.1			
UC	1.2	0.2	<0.2		
UD	1.0	0.2			
UB 250377-1	1160	-			
UB 250377-5	47.0 (2)	0.2			
Watershed AG10					
UA 300376	37.9 (2)	0.2			
UB	42.8	0.3	31.6 (4)	2.2	20.3
UA 020676	20.1	0.3	13.1 (4)	0.6	
UA 140776	21.0	0.3	19.8 (4)	1.1	
UA 121076	24.3	0.3	19.2 (4)	1.1	14.1
UB	21.6 (2)	0.2			
UC	25.0	0.3	6.8 (4)	1.0	30.1
Watershed AG13					
UA 290376	12.8	0.3	12.9 (4)	0.6	
UB	8.5	0.3			
UA 270776	2.8	0.2	2.5 (4)	0.1	
UB	2.8 (2)	0.1			
UD	3.5	0.2			
UA 041176	5.9	0.3	6.4 (4)	0.4	
UB	5.6	0.3	0.4 (4)	0.1	
UB 030377	121 (2)	0.3			

<sup>a</sup> Refer to footnote a to Table 31.

<sup>b</sup> Refer to footnote b to Table 31.

<sup>c</sup> Only selected data, compatible with other results are listed for this laboratory.

Table 33 Concentrations of Cadmium in natural water samples - detailed data for unfiltered samples<sup>a</sup>.

Sample Code	Mean Concentration (number of analyses) ± standard error, s/√n or ts/√n, µg/L <sup>b</sup>								
	Laboratory/method								
	1		2A <sup>c</sup>		2B <sup>c</sup>	3A	3B	4	5
	±		±					±	
Watershed AG1									
UA 290376	<0.4		0.16(3)	0.06				0.26 (4)	0.01 <0.7
UB	<0.4		0.19(3)	0.06				0.14 (4)	0.01 <0.7
UA 260776	<0.4				0.09(2)		0.084	0.07 (4)	0.01 <1.1
UB	<0.4								
UC	<0.4						0.050		
UD	<0.1								
UA 051176	<0.4				0.02(2)		0.020	0.03 (4)	0.01 <0.8
UB	<0.1						0.0		
UB 130377	1.7 (2)								
	0.1								
Watershed AG3									
UA 050476	<0.4		0.2	0.1		<0.05		0.03 (4)	0.01 <0.7
UB	<0.4		0.1	0.1				0.05 (4)	0.01
UA 080676	<0.4				0.01(2)		0.010	<0.01	<0.8
UB	<0.1						0.021		
UA 190776	<0.4				0.01(2)		0.013	0.02 (4)	0.01
UB	<0.1								
UC	<0.1						0.014		
UD	<0.1								
UA 141076	<0.4				0.08(2)		0.067	0.08 (4)	0.01
UB	0.10	0.04							
UC	<0.1						0.027	0.04 (4)	0.01 <0.8
Watershed AG4									
UA 260376	<0.4		0.34(4)	0.05		0.25		0.20 (4)	0.01
UB	0.4	0.1	0.30(4)	0.05		0.15		0.22 (4)	0.01
UA 010676	<0.4				0.01(2)		0.012	0.02 (4)	0.01 <1.1
UB	<0.4								
UA 120776	<0.4				0.02(2)		0.021	0.03 (4)	0.01
UB	<0.4						0.024		
UA 071076	<0.4				0.14(2)		0.140	0.06 (4)	0.01 <0.8
UB	0.5	0.1							
UC	<0.4						0.095	0.20 (4)	0.01
UD	0.09	0.04							
Watershed AG5									
UA 310376	<0.4		<0.05					0.04 (4)	0.01 <0.7
UB	<0.4		<0.05					0.03 (4)	0.01 <0.7
UA 030676	<0.4				0.02(2)		0.031	0.05 (4)	0.01 <0.8
UB	<0.4						0.007		

Cont'd ...

Table 33 Concl'd

	1		2A <sup>c</sup>	2B	3A	3B	4		5
		±	±					±	
UA 150776	<0.4			0.02 (2)		0.028	0.02 (4)	0.01	
UB	<0.4			0.02 (2)		0.018	0.02 (4)	0.01	<0.8
UC	<0.1					0.022	0.01 (4)	0.01	
UD	<0.4					0.040	0.02 (4)	0.01	<0.8
UA 210776	<0.4			0.05 (2)		0.050	0.06 (4)	0.01	
UB	<0.4								
UC	<0.4					0.065			
UD	<0.1								
UA 250876	<0.4			0.01 (2)			<0.01		
UB	<0.4								
UC	<0.1					0.013			
UD	<0.1								
UA 051076	<0.4			0.01 (2)		0.005	<0.01		
UB	<0.1								
UC	<0.1					0.022	0.02 (4)	0.01	<0.8
UD	<0.1								
UB 250377-1	11.4	0.2							
UB 250377-5	0.5 (2)	0.1							
Watershed AG10									
UA 300376	<0.1								
UB	<0.4			0.08 (2)		0.062	0.10 (4)	0.01	<0.8
UA 020676	<0.4			0.04 (2)		0.033	0.03 (4)	0.01	
UB	<0.1					0.045			
UA 140776	<0.4			0.07 (2)		0.055	0.04 (4)	0.01	
UB	<0.4					0.170			
UA 121076	<0.4			0.07 (2)		0.079	0.04 (4)	0.01	<0.8
UB	<0.4								
UC	<0.4					0.050	0.09 (4)	0.01	<0.8
UD	<0.1								
Watershed AG13									
UA 290376	<0.4			0.05 (2)		0.053	0.03 (4)	0.01	<0.8
UB	<0.4								
UA 270776	<0.4			0.03 (2)		0.068	0.02 (4)	0.01	
UB	<0.4								
UC	<0.4					0.029			
UD	<0.1								
UA 041176	<0.4			0.05 (2)		0.064	0.04 (4)	0.01	
UB	<0.1					0.060	0.08 (4)	0.01	
UB 030377	3.7 (2)	0.1							

<sup>a</sup> Refer to footnote a to Table 31.

<sup>b</sup> Refer to footnote b to Table 31.

<sup>c</sup> Refer to footnote c to Table 31.

<sup>d</sup> Refer to footnote c to Table 32.

Table 34 Concentrations of lead in natural water samples - detailed data for unfiltered samples<sup>a</sup>

Sample Code	Mean Concentration (number of analyses) ± standard error s/ $\sqrt{n}$ or ts/ $\sqrt{n}$ , µg/L <sup>b</sup>									
	Laboratory/method									
	1	±	2A <sup>c</sup>	±	2B <sup>c</sup>	3A	3B	4	±	5 <sup>d</sup>
Watershed AG1										
UA 290376	3.0	0.5	2.3 (3)	0.4				0.2 (4)	0.1	<2.3
UB	2.1	0.5	2.0 (3)	0.4				0.3 (4)	0.1	<2.3
UA 260776	2.0	0.5			1.9 (2)		1.19	0.6 (4)	0.1	
UB	<1.6									
UC	3.8	0.5					1.490			
UD	2.7	0.5								
UA 051176	<1.6				0.3 (2)		0.420	<0.1		
UB	3.0	0.5					0.910			
UB 130377	29.4 (2)	0.4								
Watershed AG3										
UA 050476	<1.6		1.1 (5)	0.3		0.80 (2)		<0.2		
UB	<1.6		<1					0.2 (4)	0.1	
UA 080676	<1.6				≤0.2 (2)		0.139	<0.1		<3.8
UB							0.142			
UA 190776	<1.6				≤0.2 (2)		0.168	<0.1		<3.8
UB	<1.6									
UC							0.202			
UA 141076	<1.6				0.6 (2)		0.375	<0.1		
UB	<1.6									
UC	1.8	0.5					0.517	<0.1		
Watershed AG4										
UA 260376	27.6	0.5	34 (5)	4		22.4 (2)		22.6 (4)	1.2	
UB	21.0	0.5	32 (5)	4		20.4 (2)		20.1 (4)	1.1	
UA 010676	<1.6				0.5 (2)		0.365	<0.1		
UB	<1.6									
UA 120776	<1.6				1.1 (2)		1.020	0.4 (4)	0.1	
UB	3.1	0.5					1.110			
UA 071076	2.1	0.5			1.3 (2)		1.280	0.4 (4)	0.1	<4.2
UB	<1.6									
UC	<1.6						1.290	<0.1		
Watershed AG5										
UA 310376	1.7	0.5	3.0 (3)	0.4				0.3 (4)	0.1	
UB	<1.6		<1					0.3 (4)	0.1	
UA 030676	<1.6				0.3 (2)		0.382	<0.1		
UB	<1.6						0.187			
UA 150776	<1.6				1.0 (2)		1.130	0.2 (4)	0.1	
US	1.6	0.5			1.0 (2)		1.260	0.2 (4)	0.1	
UC							0.888	<0.1		<2.1
UD	1.8	0.5					1.050	<0.1		

Cont'd .....

Table 34 Concl'd

	1	±	2A	±	2B	3A	3B	4	±	5
UA 210776	2.4	0.5			1.8 (2)		1.720	0.8 (4)	0.1	
UB	<1.6									
UC	3.3	0.5					1.980			
UD	2.6	0.5								
UA 250876	<1.6				0.2 (2)		0.068	<0.1		
US	<1.6									
UC							0.138			
UD	<1.6									
UA 051076	<1.6				≤0.2 (2)		0.130	<0.1		
UB	<1.6									
UC							0.203	<0.1		<4.2
UB 250377-1	305	-								
UB 250377-5	16 (2)	0.4								
Watershed AG10										
UA 300376	4.6 (2)	0.4								
UB	6.3	0.5			3.9 (3)		6.250	0.6 (4)	0.1	
UA 020676	<1.6				1.4 (3)		5.120	0.3 (4)	0.1	
UB							3.920			
UA 140776	<1.6				≤0.2 (2)		4.500	0.3 (4)	0.1	<3.8
UB							2.210			
UA 121076	<1.6				1.0 (3)		4.480	0.4 (4)	0.1	<4.2
UB	3.0 (2)	0.4								
UC	<1.6						3.350	<0.1 (4)		<4.2
Watershed AG13										
UA 290376	<1.6				0.6 (2)		0.935	0.2 (4)	0.1	
UB	<1.6									
UA 270776	<1.5				0.7 (3)		2.980	0.2 (4)	0.1	
UB	<1.6									
UC							0.730			
UA 041176	<1.6				0.7 (2)		0.633	0.2 (4)	0.1	<2.1
UB	3.0	0.5					1.760	<0.1 (4)		<3.8
UB 030377	39.1 (2)	0.4								

<sup>a</sup> Refer to footnote a to Table 31.

<sup>b</sup> Refer to footnote b to table 31.

<sup>c</sup> Refer to footnote c to Table 31.

<sup>d</sup> Refer to footnote c to Table 32.

Table 35. Concentrations of Cu, Zn, Cd and Pb in unfiltered natural water samples, averaged over field and laboratory subsampling and analytical methodologies <sup>a</sup>.

Watershed and sampling date	Mean concentration ± standard error (no. of field subsamples, no of analytical methods, total no. of analyses) µg/L <sup>b</sup>											
	Cu			Zn			Cd			Pb		
	±			±			±			±		
Watershed AG1												
290376	13.9	3.3	(2,4,16)	15.8	4.9	(2,1,4)	0.189	0.000	(2,2,14)	1.65	0.74	(2,3,16)
260776	5.79	0.75	(4,5,15)	15.3	4.9	(4,2,9)	0.076	0.020	(2,3,8)	1.67	0.65	(3,4,11)
051176	5.22	0.76	(2,5,11)	7.89	0.77	(2,2,6)	0.033	0.020	(2,3,8)	1.32	0.78	(2,3,5)
130377	27.8	7.1	(1,1,2)	228	9.0	(1,1,2)	1.75	0.039	(1,1,2)	29.4	8.5	(1,1,2)
Watershed AG3												
050476	1.65	0.75	(2,5,19)	2.97	0.69	(2,2,12)	0.095	-	(2,2,10)	0.69	0.76	(2,3,10)
080676	2.29	0.76	(2,5,11)	3.37	0.90	(2,2,3)	0.013	0.027	(2,2,4)	0.17	0.94	(2,2,4)
190776	2.09	0.75	(4,5,14)	1.32	0.98	(4,2,9)	0.015	0.020	(2,3,8)	0.19	0.94	(2,2,4)
141076	2.07	0.73	(3,5,18)	4.22	1.01	(3,1,4)	0.072	0.020	(3,4,13)	0.93	0.78	(2,3,5)
Watershed AG4												
260376	43.9	3.1	(2,4,22)	69.7	3.5	(2,2,10)	0.285	0.173	(2,4,19)	25.3	3.8	(2,4,24)
010676	5.23	0.77	(2,5,11)	2.04	0.73	(2,2,7)	0.014	0.025	(1,3,7)	0.43	0.97	(1,2,3)
120776	3.80	0.76	(2,5,11)	5.08	0.77	(2,2,6)	0.024	0.020	(2,3,8)	1.41	0.67	(2,4,9)
071076	2.24	0.72	(4,5,20)	10.5	3.46	(4,2,9)	0.119	0.020	(4,4,14)	1.20	0.67	(2,4,9)
Watershed AG5												
310376	9.21	0.81	(2,4,18)	3.10	0.74	(2,2,10)	0.035	-	(2,1,8)	1.66	0.76	(2,3,12)
030676	2.81	0.76	(2,5,12)	6.10	0.77	(2,2,6)	0.030	0.020	(2,3,8)	0.29	0.94	(2,2,4)
150776	2.89	0.71	(4,5,30)	6.82	0.69	(4,2,12)	0.022	0.020	(4,3,24)	0.99	0.64	(4,4,18)
210776	3.36	0.75	(4,5,15)	10.6	3.4	(4,2,10)	0.056	0.020	(2,3,8)	1.79	0.65	(3,4,11)
250876	1.92	0.77	(4,5,14)	1.21	0.70	(4,2,10)	0.012	0.035	(2,2,3)	0.15	0.94	(2,2,4)
051076	2.02	0.72	(4,5,18)	0.80	0.70	(4,2,9)	0.015	0.020	(2,3,8)	0.18	0.94	(2,2,4)
250377-1	223	9.0	(1,1,1)	1160	11.0	(1,1,1)	11.42	0.059	(1,1,1)	305	10	(1,1,1)
250377-5	9.96	1.68	(1,1,2)	47.0	5.0	(1,1,2)	0.545	0.039	(1,1,2)	16.2	8.5	(1,1,2)
Watershed AG10												
300376	7.94	0.77	(2,5,11)	30.5	2.9	(2,3,8)	0.081	0.025	(1,3,7)	3.96	0.66	(2,4,11)
020676	3.41	0.76	(2,5,11)	16.6	3.6	(1,2,5)	0.036	0.020	(2,3,8)	2.06	0.75	(2,3,9)
140776	2.71	0.89	(2,4,6)	20.4	3.6	(1,2,5)	0.074	0.020	(2,3,8)	1.30	0.76	(2,3,8)
121076	3.43	0.73	(4,5,16)	18.1	2.9	(3,2,12)	0.067	0.018	(2,3,12)	2.06	0.66	(3,4,10)
Watershed AG13												
290376	40.8	3.8	(2,4,9)	11.8	3.5	(2,2,6)	0.044	0.025	(1,3,7)	0.58	0.77	(1,3,7)
270776	2.77	0.75	(4,5,13)	2.74	0.72	(3,2,8)	0.033	0.020	(2,3,8)	0.90	0.75	(2,3,9)
041176	2.75	0.84	(2,5,16)	4.57	0.74	(2,2,10)	0.057	0.018	(2,3,12)	1.27	0.47	(2,4,9)
030377	36.4	0.71	(1,1,2)	121	9.0	(1,1,2)	3.66	0.039	(1,1,2)	39.1	8.5	(1,1,2)

<sup>a</sup> These concentrations were determined under various conditions giving measures of dissolved, acid- and solvent-extractable levels. They are neither dissolved nor total concentrations but intermediate estimates. Refer to the text for discussion and to other tables for dissolved, total, and suspended sediment trace element concentrations.

<sup>b</sup> Mean concentrations over all subsamples and methods,  $\bar{X}$ , and standard errors,  $s/\sqrt{n}$ , were computed from the equations:

$\bar{X} = \sum_i \bar{X}_i/n$ , and  $s/\sqrt{n} = [(1/n)^2(ns_B^2 + \sum_i s_w^2/k_i)]^{1/2}$ , where  $\bar{X}_i (= \sum_k X_{ik}/k_i)$  is the mean of the  $i^{\text{th}}$  method,  $k_i$  is the number of replicate analyses on all subsamples for the sampling date by the  $i^{\text{th}}$  method,  $n$  is the number of analytical methods (1-5), and  $s_w^2$ , and  $s_B^2$  are within- and between-method variances respectively. Data used in calculations of  $\bar{X}$  and  $s/\sqrt{n}$  correspond to those reported in Tables 31-34 with the following exceptions: (1) individual results rather than laboratory means and, where possible, expanded versions of these data were used, (2) actual values have been used for some data from laboratory 1, reported as below the detection limit, (3)  $\leq x$  reported for method 2B has been taken as  $x$ , (4) a small number of suspected outliers have been subjectively rejected prior to calculation. Analytical methods 2A and 2B, as well as 3A and 3B were respectively taken as identical.

Table 36 Concentrations of Copper in natural water samples - detailed data for filtered samples, uncorrected for filtration contamination.

Sample code	Mean concentration (no. of analyses) ± standard error, s/√ n or ts/√n, µg/L <sup>a</sup>									
	Laboratory/method									
	1	±	2A <sup>b</sup>	±	2B <sup>b</sup>	3A	3B	4	±	5
Watershed AG1										
FA 260776	2.7	0.3			3.1 (2)			6.9 (4)	0.9	4.4
FB	3.3	0.3								
FA 051176	2.9	0.3								
FA 130377	3.6 (2)	0.2								
Watershed AG3										
FA 050476	2.5	0.3	3.1 (2)	0.6				2.3 (4)	0.8	
FE	2.1	0.3	3.1 (2)	0.6				2.5 (4)	0.8	4.7
FA 080676	1.7	0.3			3.5 (2)			6.5 (4)	0.8	4.9
FB	3.7	0.3								
FA 190776	1.5	0.3			2.6 (2)		1.7	3.3 (4)	0.9	3.8
FB	2.0	0.3					2.3			
FA 141076	2.1	0.3			1.5 (2)		1.0	3.1 (4)	0.9	4.4
FB	2.7	0.3					1.6	6.4 (4)	0.9	3.5
Watershed AG4										
FA 260376	19.7	0.3								
FA 010676	3.5	0.3			4.1 (2)		3.4	4.4 (4)	0.9	2.4
FB	3.6	0.3					2.3			
FA 120776	2.4	0.3								
FB	1.8	0.3								
FA 071076	1.7	0.3								
Watershed AG5										
FA 310376	9.3	0.3	12.3 (4)	0.6		7.5 (2)		12.5 (4)	0.8	
FB	6.1	0.3	10.0 (3)	0.6				8.5 (4)	0.8	7.4
FA 030676	1.3	0.3			3.7 (3)			5.4 (4)	0.9	3.4
FB	2.7	0.3					1.8			
FA 250876	1.7	0.3			1.7 (2)		2.0	2.5 (4)	0.9	2.7
FB							1.2			
FA 051076	1.6	0.3			0.9 (2)		0.4	2.4 (4)	0.9	1.9
FB							9.5	4.4 (4)	0.9	6.3
FA 250377-1	2.0 (2)	0.3								
FA 250377-5	1.4 (2)	0.3								
Watershed AG10										
FA/FB 300376	23.5	0.3								
FA 020676	1.3	0.3			2.4 (2)		1.1	7.2 (4)	0.7	4.2
FE							3.0			
FA 140776	<0.8				3.2 (2)		1.9	9.6 (4)	0.8	3.5
FE	2.7 (2)	0.3					2.6			
FA 121076	<0.8									
Watershed AG13										
FA 290376	12.6	0.3			10.8 (2)		9.8	18.0 (4)	0.9	13.1
FB	14.9	0.3								
FA 270776	1.7	0.3			2.2 (2)		3.9	6.8 (4)	0.8	3.1
FB	1.9	0.3								
FA 041176	3.4	0.3			3.4 (2)		2.9	5.9 (4)	0.8	2.4
FB							0.5	3.3 (4)	0.8	3.7
FA 030377	5.6 (2)	0.2								

<sup>a</sup> Refer to footnote b to Table 31.

<sup>b</sup> Refer to footnote C to Table 31.

Table 37 Concentrations of zinc in natural water samples - detailed data for filtered samples, uncorrected for filtration Contamination.

Sample code	Mean concentration (no. of analyses) $\pm$ standard error, s/ $\sqrt{n}$ or ts/ $\sqrt{n}$ , $\mu\text{g/L}$ <sup>a</sup>			
	Laboratory/method		Laboratory/method	
	1	$\pm$	4	$\pm$
<b>Watershed AG1</b>				
FA 290376	11.0	0.3	40.8 (4)	5.2
FA 260776	1.0	0.2	1.3 (4)	0.1
FB	1.2	0.2		
FA 051176	3.4	0.2		
FA 130377	4.0	0.2		
<b>Watershed AG3</b>				
FA 050476	3.2 (2)	0.1	8.7 (4)	1.0
FB	4.2	0.2	6.1 (4)	0.5
FA 080676	3.5	0.2	3.2 (4)	0.1
FB	3.3	0.2		
FB 190776	10.5	0.3		
FA 141076	2.9	0.2	2.0 (4)	0.1
FB	3.3	0.2	<0.1	
<b>Watershed AG4</b>				
FA 260376	9.8	0.3		
FA 010676	4.1	0.2	4.2 (4)	0.3
FB	3.5	0.2		
FA 120776	9.2	0.3		
FB	3.6	0.2		
FA 071076	2.4	0.2		
<b>Watershed AG5</b>				
FA 310376	2.5	0.2	2.9 (4)	0.2
FB	3.3 (2)	0.1	3.3 (4)	0.3
FA 030676	5.3	0.3	5.2 (4)	0.3
FB	8.8	0.3		
FA 250876	0.8	0.1	1.1 (4)	0.1
FA 051076	2.4	0.2	2.2 (4)	0.1
FB			<0.2	
FA 250377-1	1.0 (2)	0.1		
FA 250377-5	5.4 (2)	0.2		
<b>Watershed AG10</b>				
FA/FB 300376	8.1	0.3		
FA 020676	17.1	0.3	11.4 (4)	0.5
FA 140776	5.4	0.3	2.7 (4)	0.1
FA 121076	3.9	0.2		
<b>Watershed AG13</b>				
FA 290376	8.0	0.2	9.4 (4)	0.4
FB	14.1	0.3		
FA 270776	0.8	0.1	1.2 (4)	0.1
FB	1.0	0.2		
FA 041176	27.4	0.4	27.3 (4)	1.1
FB			14.7 (4)	1.1
FA 030377	4.3 (2)	0.1		

<sup>a</sup> Refer to footnote b to Table 31.

Table 38 Concentrations of cadmium in natural water samples-detailed data for filtered samples, uncorrected for filtration contamination

Sample Code	Mean Concentration (no. of analyses) ± standard error, s/√n or ts/√n, µg/L							
	1		2A <sup>b</sup>	2B <sup>b</sup>	3A	3B	4	5 <sup>c</sup>
	±						±	
Watershed AG1								
FA 290376	0.4	0.1					0.15 (4)	0.01
FA 260776	<0.4			0.01 (2)		0.008	0.01 (4)	0.01 0.6
FB	<0.1					0.007		
FB 051176	<0.1							
FA 130377	0.13 (2)	0.3						
Watershed AG3								
FA 050476	<0.4		<0.05				0.04 (4)	0.01
FB	<0.4		<0.05				0.04 (4)	0.01 <0.7
FA 080676	<0.4							
FB	<0.1						<0.01	1.2
FA 190776	<0.4			0.05 (2)		0.010	0.03 (4)	0.01 1.2
FB	<0.1					0.055		
FA 141076	<0.4			0.07 (2)		0.010	0.06 (4)	0.01 2.2
FB	0.16	0.04				0.271	0.11 (4)	0.01 2.8
Watershed AG4								
FA 260376	<0.4							
FA 010676	<0.4			0.01 (2)		0.020	0.01 (4)	0.01 2.8
FE	<0.1					0.012		
FA 120776	<0.4							
FB	<0.4							
FA 071076	0.10	0.04						
Watershed AG5								
FA 310376	<0.4		<0.05		<0.05		0.04 (4)	0.01
FB	<0.4		<0.05				0.06 (4)	0.01 0.7
FA 030676	<0.4			0.01 (2)		0.016	0.02 (4)	0.01 <0.8
FB	<0.4					0.015		
FA 250876	<0.4			0.01 (2)		0.027	<0.01	1.8
FB						0.029		
FA 051076	<0.4			0.01 (2)		0.016	<0.01	2.6
FB							0.06 (4)	0.01 1.7
FA 250377-1	<0.1							
FA 250377-5	0.10 (2)	0.3						
Watershed AG10								
FA/FB 300376	0.6	0.1						
FA 020676	<0.4			0.02 (2)		0.014	0.03 (4)	0.01 1.8
FE	<0.4					0.006		
FA 140776	0.5	0.1		0.02 (2)		0.025	0.04 (4)	0.01 2.1
FB	0.3	0.04				0.033		
FA 121076	<0.4							
FE								
Watershed AG13								
FA 290376	<0.4			0.03 (2)		0.035	<0.01	<0.8
FB	<0.4							
FA 270776	0.5	0.1		0.02 (2)		0.017	<0.01	1.9
FB	<0.1					0.054		
FA 041176	<0.4			0.06 (2)		0.055	0.05 (4)	0.01 1.3
FE						0.118	0.12 (4)	0.01 1.2
FA 030377	0.43 (2)	0.03						

<sup>a</sup> Refer to footnote b to Table 31.

<sup>b</sup> Refer to footnote c to Table 31.

<sup>c</sup> Only selected low level data are listed for this laboratory

Table 39 Concentrations of lead in natural water samples - detailed data for filtered samples, uncorrected for filtration contamination.

Sample Code	Mean Concentration (no. of analyses) ± standard error, s/√n or ts/√n, µg/L <sup>a</sup>								
	Laboratory/method								
	1	±	2A <sup>b</sup>	2B <sup>b</sup>	3A	3B	4	±	5 <sup>c</sup>
Watershed AG1									
FA 290376	<1.6						0.2 (4)	0.1	
FA 260776	<1.6			≤0.2 (2)		0.062	<0.1		
FB						0.081			
FA 051176	<1.6								
FA 130377	<1.6								
Watershed AG3									
FA 050476	<1.6		<1				0.6 (4)	0.1	
FB	<1.6		<1				0.2 (4)	0.1	
FA 080676	1.6			≤0.2 (2)			<0.1		
FB									
FA 190776	<1.6			≤0.2 (2)		0.060	<0.1		<3.8
FB						0.169			
FA 141076	<1.6			0.4 (2)		0.268	<0.1		
FB	<1.6					0.256	<0.1		
Watershed AG4									
FA 260376	13.3	0.5							
FA 010676	<1.6			0.3 (2)		0.390	<0.1		
FB	<1.6					0.220			
FA 120776	1.9	0.5							
FB	<1.6								
FA 071076	<1.6								
Watershed AG5									
FA 310376	<1.6		<1		0.32(2)		2.5 (4)	1.1	
FB	<1.6		<1				0.3 (4)	0.1	<2.3
FA 030676	<1.6			≤0.2 (2)		0.195	<0.1		<3.8
FB	<1.6					0.158			
FA 250876	<1.6			≤0.2 (2)		0.213	<0.1		<2.1
FB						0.217			
FA 051076	<1.6			≤0.3 (2)		0.217	<0.1		
FB						0.364	<0.1		<2.1
FA 250377-1	<1.6								
FA 250377-5	<1.6								
Watershed AG10									
FB 300376	<1.6								
FA 020676	<1.6			≤0.2 (2)		0.580	0.1 (4)	0.1	
FB						0.140			
FA 140776	<1.6			≤0.2 (2)		0.114	0.2 (4)	0.1	<2.1
FB						0.253			
FA 121076	<1.6								
Watershed AG13									
FA 290376	<1.6			0.3 (2)		0.406	<0.1		<3.8
FB	<1.6								
FA 270776	<1.6			≤0.2 (2)		0.074	<0.1		
FB	<1.6					0.634			
FA 041176	<1.6			0.3 (2)		0.400	<0.1		
FB						0.453	<0.1		<2.1
FA 030377	0.9 (2)	0.4							

<sup>a</sup> Refer to footnote b to Table 31.

<sup>b</sup> Refer to footnote c to Table 31.

<sup>c</sup> Refer to footnote c to Table 38.

Table 40 Concentrations of Cu, Zn, Cd and Pb in filtered natural water samples averaged over field and laboratory subsampling and analytical methodologies, uncorrected for filtration contamination.

Watershed and sampling date	Mean Concentration ± standard error, (no. of field subsamples, no. of analytical methods, total no. of analyses) µg/L <sup>a</sup>											
	Cu			Zn			Cd			Pb		
	±		( )	±		( )	±		( )	±	( )	
Watershed AG1												
290376	-		( )	11.0	6.0	(1,1,1)	0.150	0.000	(1,1,4)	0.20	0.00	(1,1,4)
260776	4.35	1.04	(2,4,9)	1.18	0.88	(2,2,6)	0.009	0.006	(2,3,8)	0.13	0.03	(2,2,4)
051176	2.87	2.34	(1,1,1)	3.40	1.59	(1,1,1)	-		( )	-		( )
130377	3.61	2.05	(1,1,2)	3.96	1.59	(1,1,1)	0.130	0.017	(1,1,2)	0.26	0.04	(1,1,2)
Watershed AG3												
050476	3.11	1.01	(2,4,15)	5.46	0.81	(2,2,11)	0.040	0.000	(2,1,8)	0.40	0.00	(2,1,8)
080676	4.40	1.45	(2,4,9)	3.31	0.88	(2,2,6)	-		( )	0.20	0.04	(1,1,2)
190776	2.69	0.93	(2,5,11)	10.5	6.0	(1,1,1)	0.038	0.006	(2,3,8)	0.16	0.03	(2,2,4)
141076	2.78	0.89	(2,5,16)	2.57	0.88	(2,2,6)	0.114	0.010	(2,4,13)	0.33	0.03	(2,2,4)
Watershed AG4												
260376	19.7	2.3	(1,1,1)	9.76	1.59	(1,1,1)	-		( )	13.3	0.1	(1,1,1)
010676	3.46	0.93	(2,5,11)	4.01	0.88	(2,2,6)	0.012	0.006	(2,3,8)	0.30	0.03	(2,2,4)
120776	2.12	2.05	(2,1,2)	6.37	1.32	(2,1,2)	-		( )	1.86	0.13	(1,1,1)
071076	1.71	2.34	(1,1,1)	2.37	1.59	(1,1,1)	0.100	0.039	(1,1,1)	-		( )
Watershed AG5												
310376	8.87	0.90	(2,5,20)	3.06	0.81	(2,2,11)	0.050	0.000	(2,1,8)	0.31	0.11	(2,2,5)
030676	3.24	0.95	(2,5,11)	6.13	0.88	(2,2,6)	0.015	0.006	(2,3,8)	0.19	0.03	(2,2,4)
150776	-		( )	-		( )	-		( )	-		( )
210776	-		( )	-		( )	-		( )	-		( )
250876	2.04	0.96	(2,5,10)	0.96	0.99	(1,2,5)	0.019	0.012	(2,2,4)	0.21	0.03	(2,2,4)
051076	3.00	0.92	(2,5,15)	2.30	0.99	(2,2,5)	0.029	0.013	(2,3,7)	0.30	0.03	(2,2,4)
250377-1	2.04	2.05	(1,1,2)	1.01	1.32	(1,1,2)	0.050	0.017	(1,1,2)	0.00	0.04	(1,1,2)
250377-5	1.40	2.05	(1,1,2)	5.43	1.32	(1,1,2)	0.095	0.017	(1,1,2)	0.20	0.04	(1,1,2)
Watershed AG10												
300376	23.5	2.3	(2,1,1)	8.05	1.59	(2,1,1)	0.600	0.039	(2,1,1)	-		( )
020676	3.43	0.98	(2,5,10)	14.6	3.0	(1,2,5)	0.020	0.006	(2,3,8)	0.22	0.00	(2,3,8)
140776	4.24	0.98	(2,5,10)	4.06	0.99	(1,2,5)	0.030	0.006	(2,3,8)	0.20	0.00	(2,3,8)
121076	0.70	2.34	(1,1,1)	3.90	1.59	(1,1,1)	-		( )	-		( )
Watershed AG13												
290376	13.1	0.98	(2,5,10)	10.2	1.7	(2,2,6)	0.033	0.021	(1,2,3)	0.35	0.07	(1,2,3)
270776	3.56	0.98	(2,5,10)	1.06	0.88	(2,2,6)	0.028	0.012	(2,2,4)	0.28	0.03	(2,2,4)
041176	3.22	0.93	(2,5,15)	24.2	2.7	(2,2,9)	0.077	0.000	(2,3,12)	0.36	0.03	(2,2,4)
030377	5.57	2.05	(1,1,2)	4.26	1.32	(1,1,2)	0.430	0.000	(1,1,2)	0.94	0.04	(1,1,2)

<sup>a</sup> Refer to Table 35 footnote b for details. Data used in Calculations of  $\bar{X}$  and  $s/\sqrt{n}$  correspond to those reported in Tables 36-39. Values below the limit of detection (especially the Case for Cd and Pb) have generally been omitted from calculations.

Table 41 Total concentrations of Cu in natural water samples-detailed data

Watershed and sampling date	Total concentration $\pm$ standard error, $\mu\text{g/L}$ <sup>a</sup>					
	Calculated from level in filtered sample + suspended sediment		Calculated from level in unfiltered sample + residue		Selected data	
		$\pm$		$\pm$	$\pm$	
Watershed AG1						
290376	-	-	>13.9	>3.30	-	-
260776	3.43	1.91	6.13	0.75	4.78	1.69
051176	5.94	2.84	5.32	0.76	5.63	2.01
130377	31.0	4.24	34.6	7.18	32.8	5.08
Watershed AG3						
050476	>1.86	-	>1.65	-	-	-
080676	>3.15	-	>2.29	>0.76	-	-
190776	>1.44	-	>2.09	>0.75	-	-
141076	>1.53	-	2.16	0.73	2.16	0.73
Watershed AG4						
260376	29.0	2.99	46.0	3.15	37.5	10.7
010676	>2.21	>1.82	>5.23	>0.77	-	-
120776	3.93	2.63	>3.80	>0.76	3.93	2.63
071076	0.76	2.82	2.25	0.73	2.25	0.73
Watershed AG5						
310376	-	-	>9.21	>0.81	-	-
030676	>1.99	>1.83	>2.81	>0.76	-	-
150776	>1.90	>0.72	3.13	0.71	3.13	0.71
210776	>2.34	>0.47	3.73	0.75	3.73	0.75
250876	>0.79	>1.83	>1.92	>0.77	-	-
051076	>1.75	>1.81	>2.02	>0.72	-	-
250377-1	439	-	449	>25	445	>26
250377-5	10.9	2.71	12.2	1.74	11.6	1.92
Watershed AG10						
300376	>22.3	>2.81	9.24	0.80	9.24	0.80
020676	2.96	1.85	3.41	>0.76	3.19	1.31
140776	7.31	1.92	2.85	0.89	5.08	2.79
121076	>4.74	>0.54	3.64	0.73	3.64	0.73
Watershed AG13						
290376	-	-	>40.8	>3.79	-	-
270776	>2.31	>1.83	>2.77	>0.75	-	-
041176	2.78	1.92	2.75	>0.84	2.77	1.36
030377	39.8	4.02	42.8	7.17	41.3	5.07

<sup>a</sup> Data presented here are means over all subsamples and analytical methodologies; concentrations in filtered water samples have been corrected for estimated filtration procedure contamination. Standard errors have usually been computed using propagation of error formulae and standard errors in the following parameters: concentration of the element in unfiltered natural water, filtered natural water (uncorrected for filtration procedure contamination), distilled and deionized water control samples, suspended sediment and residue, and the concentration of the suspended sediment or residue in the water sample; standard errors of selected data were estimated as follows: when one of the two data was selected, its standard error was taken; when the mean of the two data was used, the standard error reported is the larger of (i) the larger standard error  $\sqrt{2}$  or (ii) the standard deviation of the mean (estimated as  $0.886 \times$  the difference of the two results)  $\sqrt{2}$ .

> indicates one datum for the summation is missing; - indicates no concentration data are available for both water samples and solids.

Table 42 Total Concentrations of Zn in natural water samples - detailed data

Watershed and sampling date	Total Concentration $\pm$ standard error, $\mu\text{g/L}^{\text{a}}$					
	Calculated from level in filtered sample + suspended sediment		Calculated from level in unfiltered sample + residue		Selected data	
		$\pm$		$\pm$		$\pm$
Watershed AG1						
290376	-	-	>15.8	>4.9	-	-
260776	-	-	17.2	4.9	17.2	4.9
051176	13.0	3.7	7.99	0.96	7.99	0.96
130377	218	29	286	23	252	43
Watershed AG3						
050476	>2.23	>2.5	>2.97	>0.69	-	-
080676	>0.08	>2.5	>3.37	>0.90	-	-
190776	>7.27	>6.5	>1.32	>0.98	-	-
141076	-	-	4.31	1.02	4.31	1.02
Watershed AG4						
260376	42.7	8.7	73.6	4.58	58.2	19.4
010676	>0.78	>2.5	>2.04	>0.73	-	-
120776	7.19	3.9	>5.08	>0.77	7.2	3.9
071076	1.0	3.0	10.6	3.46	10.6	3.46
Watershed AG5						
310376	-	-	>3.10	>0.74	-	-
030676	>2.90	>2.5	>6.10	>0.77	-	-
150776	>3.84	>1.7	11.1	1.12	11.1	1.12
210776	>6.60	>2.2	11.2	3.46	11.2	3.46
250876	-	-	>1.21	>0.70	-	-
051076	-	-	>0.80	>0.70	-	-
250377-1	2850	-	2100	>523	2500	500
250377-5	64.8	14	63.1	6.42	64.0	9.90
Watershed AG10						
300376	>4.82	>2.8	37.0	3.48	37.0	3.48
020676	12.9	3.9	>16.6	>3.61	-	-
140776	11.9	3.4	>20.4	>3.61	-	-
121076	6.99	3.5	19.4	2.95	19.4	2.95
Watershed AG13						
290376	>6.97	>2.9	>11.8	>3.51	-	-
270776	-	-	>2.74	>0.72	-	-
041176	-	-	5.01	0.77	5.01	0.77
030377	168	27	182	20.2	175	19.1

<sup>a</sup> Refer to footnote a to Table 41.

Table 43 Total Concentrations of Cd in natural water samples - detailed data

Watershed and sampling date	Total Concentration ± standard error, µg/L <sup>a</sup>					
	Calculated from level in filtered sample + suspended sediment		Calculated from level in unfiltered sample + residue		Selected data	
		±		±		±
Watershed AG1						
290376	0.56	0.10	>0.19	-	0.56	0.10
260776	0.00	0.05	0.08	0.02	0.04	0.04
051176	>0.09	>0.06	0.03	0.02	0.03	0.02
130377	1.14	0.74	1.74	0.04	1.44	0.52
Watershed AG3						
050476	>0.01	>0.04	>0.10	-	-	-
080676	-	-	>0.01	>0.03	-	-
190776	>0.01	>0.05	>0.01	>0.02	-	-
141076	>0.08	>0.05	0.07	0.02	0.07	0.02
Watershed AG4						
260376	>0.03	>0.03	0.29	0.02	0.29	0.02
010676	-	-	>0.01	>0.03	-	-
120776	-	-	>0.02	>0.02	-	-
071076	0.12	0.07	0.15	0.02	0.14	0.05
Watershed AG5						
310376	>0.02	>0.04	>0.04	-	-	-
030676	-	-	>0.03	>0.02	-	-
150776	>0.00	>0.00	0.05	0.02	0.05	0.02
210776	>0.00	>0.01	0.06	0.02	0.06	0.02
250876	-	-	>0.01	>0.04	-	-
051076	-	-	>0.01	>0.02	-	-
250377-1	11.43	>1.9	15.42	>1.34	13.4	2.50
250377-5	0.18	0.06	0.56	0.05	0.37	0.24
Watershed AG10						
300376	>0.57	>0.06	0.08	0.03	0.08	0.03
202676	-	-	0.04	0.02	0.04	0.02
140776	0.38	>0.07	>0.07	>0.02	0.40	>0.07
121076	>0.02	>0.02	0.08	0.02	0.08	0.02
Watershed AG13						
290376	>0.00	>0.05	>0.04	>0.03	-	-
270776	-	-	0.05	0.02	0.05	0.02
041176	>0.05	>0.05	0.08	0.02	0.08	0.02
030377	3.01	0.69	3.66	0.04	3.34	0.49

<sup>a</sup> Refer to footnote a to Table 41.

Table 44 Total Concentrations of Pb in natural water samples - detailed data

Watershed and sampling date	Total Concentration $\pm$ standard error, $\mu\text{g/L}$ <sup>a</sup>					
	Calculated from level in filtered sample + suspended sediment		Calculated from level in unfiltered sample + residue		Selected data	
		$\pm$		$\pm$		$\pm$
Watershed AG1						
290376	2.51	1.88	>1.65	>0.74	2.51	1.88
260776	0.22	0.47	3.01	0.75	3.01	0.75
051176	>6.00	>1.33	2.70	0.92	2.70	0.92
130377	25.3	19.2	32.1	9.56	28.7	13.6
Watershed AG3						
050476	>0.15	>0.21	>0.69	>0.76	-	-
080676	-	-	>0.17	>0.94	-	-
190776	-	-	>0.19	>0.94	-	-
141076	>0.08	>0.23	1.13	0.80	1.13	0.80
Watershed AG4						
260376	55.8	5.37	35.3	6.12	45.6	12.8
010676	>0.05	>0.23	>0.43	>0.97	-	-
120776	8.66	2.00	>1.41	>0.67	8.66	2.00
071076	>1.07	>0.67	1.42	0.68	1.42	0.68
Watershed AG5						
310376	>0.06	>0.26	>1.66	>0.76	-	-
030676	-	-	>0.29	>0.94	-	-
150776	>1.02	>0.69	1.22	0.66	1.22	0.66
210776	>0.76	>1.20	4.58	0.84	4.58	0.84
250876	-	-	>0.15	>0.94	-	-
051076	>0.05	>0.23	>0.18	>0.94	-	-
250377-1	399	364	466	>108	433	257
250377-5	9.84	9.12	17.2	8.74	13.5	6.45
Watershed AG10						
300376	-	-	4.31	1.15	4.31	1.15
020676	3.07	1.16	2.06	>0.75	2.57	0.82
140776	12.9	2.06	3.20	1.15	8.1	6.1
121076	>22.1	>2.57	3.67	1.01	-	-
Watershed AG13						
290376	>0.10	>0.24	>0.58	>0.77	-	-
270776	>0.03	>0.23	0.93	0.75	0.93	0.75
041176	1.91	1.46	1.37	0.68	1.64	1.03
030377	31.6	17.8	41.4	9.30	36.5	12.6

<sup>a</sup> Refer to footnote a to Table 41.

Table 45. Suspended sediment Concentrations in natural water samples

Watershed and sampling date	Mean suspended sediment Concentration (no. of determinations), mg/L					Mean of selected values $\pm s/\sqrt{n}$ (n) <sup>f</sup>
	A <sup>a</sup> (Direct)	B <sup>b</sup> (Direct)	C <sup>c</sup> (By Diff.)	D <sup>d</sup> (Direct)	E <sup>e</sup> (By Diff.)	
Watershed AG1						
290376				76 (1)	65	71 $\pm$ 8 (2)
260776		102 (2) <sup>g</sup>	256 <sup>g</sup>	11 (1)	66 <sup>g</sup>	11 $\pm$ 12 (1)
051176	99 (1)	95 (2)	68	70 (1)	67	80 $\pm$ 5 (5)
130377	740 (1)					740 $\pm$ 10 (1)
Watershed AG3						
050476					10	10 $\pm$ 12 (1)
080676		8 (1)	32		8	16 $\pm$ 7 (3)
190776		8 (1)	10		28	15 $\pm$ 7 (3)
141076		61 (2)	81		50	64 $\pm$ 7 (3)
Watershed AG4						
260376				343 (1)	304	329 $\pm$ 8 (2)
010676						
120776		36 (4)	42		62	47 $\pm$ 7 (3)
071076		18 (2)	41 <sup>g</sup>	12 (1)	10	13 $\pm$ 7 (3)
Watershed AG5						
310376				2 (1)		2 $\pm$ 12 (1)
030676			12		42 <sup>g</sup>	12 $\pm$ 12 (1)
150776		19 (2)	18	16 (1)	12	16 $\pm$ 6 (4)
210776		29 (2)	22	34 (1)	48	33 $\pm$ 6 (4)
250876		4 (4)	10			7 $\pm$ 8 (2)
051076					11	11 $\pm$ 12 (1)
250377-1	19.0 x10 <sup>3</sup> (1)					19.0 x10 <sup>3</sup> (1)
250377-5	350 (1)					350 $\pm$ 10 (1)
Watershed AG10						
300376				115 (1)	135	125 $\pm$ 8 (2)
020676		25 (3)		36 (1)	49	31 $\pm$ 8 (2)
140776		27 (4)	64	59 (1)	41	48 $\pm$ 6 (4)
121076		27 (2) <sup>g</sup>		75 (1)	82	79 $\pm$ 8 (2)
Watershed AG13						
290376				6 (1)	63 <sup>g</sup>	6 $\pm$ 12 (1)
270776		12 (2)	6		46 <sup>g</sup>	9 $\pm$ 8 (2)
041176		4 (1)	24		0	9 $\pm$ 7 (3)
030377	685 (1)					685 $\pm$ 10 (1)

- (a) Direct determination by the author; standard deviations are  $\pm 10$  mg/L for all values except  $19.0 \times 10^3$  mg/L
- (b) Determined in Dr. G.J. Wall's laboratory by weighing wet membrane filters containing the sediment.
- (c) Calculated by the author from total and dissolved solids Concentration s determined in Dr. Wall's laboratory.
- (d) Determined by Dr. L. Whitby Costescu by weighing dried sediment collected by centrifugation.
- (e) Calculated by the author from total and dissolved solids Concentration s determined by Dr. Costescu.
- (f) Values were selected by inspection. For the population of data in columns A to E, a standard deviation of 12 mg/L (32 degrees of freedom) over the range 0-340 mg/L was estimated by the author and used to calculate standard error,  $s/\sqrt{n}$ , where n is the number of data selected to give an unweighted mean (equal weight given to data in each column regardless of no. of determinations).
- (g) Rejected from mean and standard deviation calculations.

Table 46. Concentrations of Cu, Zn, Cd and Pb in suspended sediments - detailed data

Sample code <sup>a</sup>	Concentration (no. of analyses) ± standard error, s/√n, µg/g <sup>b</sup>									
	Cu		Zn				Cd <sup>e</sup>		Pb	
	A <sup>c</sup>	B	A <sup>c</sup>	B <sup>d</sup>	A <sup>c</sup>	B <sup>d</sup>	A <sup>c</sup>	B <sup>d</sup>		
	±		±		±		±		±	
Watershed AG1										
290376(LC)	94.0 (2)	2.7	280 (2)	15	6.2 (2)	1.0	36 (2)	3		
260776(LC)	348 (1)	4	430 (1)	21	6.2 (1)	1.0	570 (1)	-		
260776	25.3 (4)	1.9	40 (2)	170 (4)	10	25 (2)	0.4 (4)	0.1	14 (4)	2 65 (2)
A051176	49.4 (2)	2.7	45 (1)	180 (2)	15	25 (1)	1.2 (2)	1.0	53 (2)	3 100 (2)
B051176	70.6 (1)	3.9		240 (1)	21		2.0 (1)	1.4	67 (1)	4
A130377	37.3 (2)	2.7		290 (2)	15		1.4 (2)	1.0	34 (2)	3
Watershed AG4										
260376(LC)	36.2 (3)	2.2	25 (2)	150 (3)	12	45 (2)	0.1 (3)	0.1	15(3)	3 300 (2)
B120776			65 (1)			150 (1)				150 (1)
071076(LC)	20.9 (1)	3.9	25 (1)	260 (1)	21	20 (1)	3.8 (1)	1.4	74(1)	4 90 (1)
Watershed AG5										
150776(LC)	119 <sup>f</sup>			240 <sup>f</sup>			0.1 <sup>f</sup>		64 <sup>f</sup>	
210776(LC)	71			200			0.1		23 <sup>f</sup>	
A250377-1	22.5 (4)	1.9		150 (4)	10		0.6 (4)	0.1	21 (4)	2
A250377-5	27.3 (2)	2.2		170 (2)	15		0.3 (2)	0.1	28(2)	3
Watershed AG10										
A020676	- <sup>g</sup>			560 (1) <sup>g</sup>	21 <sup>g</sup>		- <sup>g</sup>		100 (1) <sup>g</sup>	-
B020676			25 (1)			50 (1)				100 (1)
140776(LC)	90 (2) <sup>g</sup>	3 <sup>g</sup>		230 (2) <sup>g</sup>	15 <sup>g</sup>		7.9 (2) <sup>g</sup>	1.0 <sup>g</sup>	270 (2) <sup>g</sup>	-
121076(LC)	30.0 (1)	3.9	30 (2)	230 (1)	21	30 (2)	0.2 (1)	0.2	340(1)	- 400 (2)
A121076			60 (1)			50 (1)				80 (1)
B121076			150 (1)			55 (1)				150 (1)
Watershed AG13										
A041176			90 (1)			200 (1)				200 (1)
A030377	50.0 (2)	2.7		240 (2)	15		3.8 (2)	1.0	45 (2)	3

<sup>a</sup> LC refers to suspended sediment provided by Dr. L. Whitby Costescu; the other 1976 samples were provided by K. LaHay whereas 1977 samples were prepared in the author's laboratory. A and B refer to the unfiltered A and B field-collected subsamples.

<sup>b</sup> Concentrations are expressed on a dry weight basis; values less than the detection limit are included.

<sup>c</sup> Analyses in the author's (M. Ihnat) laboratory of typically 5-30 mg samples using acid digestion-flame atomic absorption spectrometry.

<sup>d</sup> Analyses by D. S. Russell and P. Tymchuk of 1-10 mg samples using optical emission spectrography (ORS).

<sup>e</sup> By OES, Cd was below the detection limit (0.10 g corresponding to 10-100 µg/g for 1-10 mg samples) in all samples.

<sup>f</sup> Value provided by Dr. Costescu.

<sup>g</sup> Values are unreliable as only limited sample weights (<1 mg) were available for analysis.

Table 47. Concentrations of Cu, Zn, Cd and Pb in residues - detailed data <sup>a</sup>

Sample code	Concentration (no. of analyses) ± standard error, s/√n, µg/g <sup>b</sup>										
	Cu			Zn			Cd <sup>e</sup>		Pb		
	A <sup>c</sup>	±	B <sup>d</sup>	A <sup>c</sup>	±	B <sup>d</sup>	A <sup>c</sup>	±	A <sup>c</sup>	±	B <sup>d</sup>
Watershed AG1											
B260776	3.9 (2)	1.7		55 (2)	5		0.0 (2)	0.1	2 (2)	3	
D260776	3.5 (2)	1.7	6 (2)	10 (2)	5	10 (2) <sup>g</sup>	0.0 (2)	0.1	2 (2)	3	50 (2)
A051176	-		5 (1)	-			-				50 (1)
B051176	0.0 (1)	2.4	5 (2)	4 (1)	7		0.0 (1)	0.2	3 (1)	4	80 (2)
0130377	12.8 (2)	1.7		110 (2)	15		0.0 (2)	0.1	5 (2)	3	
Watershed AG3											
B141076	15 (2) <sup>f</sup>	2		15 (2) <sup>f</sup>	5		0.0 (2) <sup>f</sup>	0.1	33 (2) <sup>f</sup>	3	
C141076											
Watershed AG4											
0260376	7.4 (1)	2.4	10 (2)	30 (1)	7	10 (2) <sup>g</sup>	0.0 (1)	0.2	12 (1)	4	60 (2)
B071076	0.0 (2)	1.7		11 (2)	5		3.4 (2)	1.0	7 (2)	3	
D071076	2.9 (1)	2.4		0 (1)	7		0.0 (1)	0.2	35 (1)	4	
Watershed AG5											
C150776	16.5 (1)	2.4		300 (1)	21		1.8 (1)	1.4	16 (1)	4	
B210776	11.6 (1)	2.4	15 (1)	60 (1)	7	10 (2) <sup>g</sup>	0.0 (1)	0.2	2 (1)	4	90 (1)
D210776	-		12.5 (2)	-		10 (2) <sup>g</sup>	-		-		150 (2)
0250377-1	16.9 (2)	1.7		70 (2)	5		0.3 (2)	0.1	12 (2)	3	
8250377-5	8.9 (2)	1.7		65 (2)	5		0.1 (2)	0.1	4 (2)	3	
Watershed AG10											
A300376	11.0 (2)	1.7		55 (2)	5		0.0 (2)	0.1	3 (2)	3	
B020676	0.0 (1)	2.4		8 (1)	7		0.0 (1)	0.2	0 (1)	4	
A140776	-		6 (1)	-			-		-		80 (1)
8121076	6.1 (1)	2.4	6 (2)	30 (1)	7		0.2 (1)	0.2	9 (1)	4	70 (2)
D121076	3.3 (2)	1.7		30 (2)	5		0.2 (2)	0.1	3 (1)	4	
Watershed AG13											
D270776	780 (1) <sup>f</sup>	-		1100 (1) <sup>f</sup>	-		4.3 (1)	0.2	6 (1)	4	
A041176	0.0 (1)	2.4		0 (1)	7		2.8 (1)	0.2	15 (1)	4	
8041176	0.0 (1)	2.4		70 (1)	7		0.7 (1)	0.2	0 (1)	4	
B030377	13.7 (2)	1.7		130 (2)	15		0.0 (2)	0.1	5 (2)	3	

<sup>a</sup> Residue refers to solid material remaining after evaporation of acidified water sample to a small volume. All data are for unfiltered water samples and therefore relate to acid-leached suspended sediment; values less than the detection limit are included. A, B, C, D in sample codes refer to the unfiltered field-collected subsamples.

<sup>b</sup> Concentrations are expressed on a dry weight basis.

<sup>c</sup> Analyses in the author's (M. Ihnat) laboratory of typically 3-30 mg samples using acid digestion-flame atomic absorption spectrometry.

<sup>d</sup> Analyses by D. S. Russell and P. Tymchuk of 1-10 mg samples using optical emission spectrography (OES).

<sup>e</sup> By OES, Cd was below the detection limit (0.10 µg, corresponding to 10-100 µg/g for 1-10 mg samples) in all samples.

<sup>f</sup> Values are unreliable as only limited, sample weights (<2 mg) were available for analysis.

<sup>g</sup> Detection in doubt due to interference.

Table 48 .Contributions of residues to concentrations of Cu, Zn, Cd and Pb in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13<sup>a</sup>

Watershed and sampling date	Concentration of the trace element t standard error, s/ $\sqrt{n}$ , $\mu\text{g/L}$ <sup>b</sup>							
	Cu		Zn		Cd		Pb	
		$\pm$		$\pm$		$\pm$		$\pm$
Watershed AG1								
290376	-	-	-	-	-	-	-	-
260776	0.34	0.08	1.86	0.67	0.00	0	1.34	0.37
051176	0.10	0.03	0.10	0.57	0.00	0	1.38	0.48
130377	6.81	0.96	58.5	20.8	0.00	0	2.66	4.26
Watershed AG3								
050476	-	-	-	-	-	-	-	-
080676	-	-	-	-	-	-	-	-
190776	-	-	-	-	-	-	-	-
141076	0.09	0.01	0.09	0.10	0.00	0	0.20	0.16
Watershed AG4								
260376	2.07	0.33	3.88	2.97	0.00	0	10.0	4.80
010676	-	-	-	-	-	-	-	-
120776	-	-	-	-	-	-	-	-
071076	0.01	0.02	0.09	0.18	0.03	0.01	0.22	0.10
Watershed AG5								
310376	-	-	-	-	-	-	-	-
030676	-	-	-	-	-	-	-	-
150776	0.24	0.03	4.32	0.88	0.03	0.02	0.23	0.17
210776	0.37	0.04	0.57	0.29	0.00	0	2.79	0.52
250876	-	-	-	-	-	-	-	-
051076	-	-	-	-	-	-	-	-
250377-1	226	>24	938	>523	4.02	>1.34	161	>107
250377-5	2.20	0.44	16.06	3.97	0.02	0.03	0.99	1.98
Watershed AG10								
300376	1.30	0.21	6.49	1.89	0.00	0	0.35	0.94
020676	0.00	-	-	-	0.00	0	0.00	-
140776	0.14	0.06	-	-	-	-	1.90	0.87
121076	0.21	0.05	1.27	0.55	0.01	0.00	1.61	0.77
Watershed AG13								
290376	-	-	-	-	-	-	-	-
270776	-	-	-	-	0.02	0.01	0.03	0.07
041176	0.00	-	0.44	0.21	0.02	0.01	0.10	0.10
030377	6.38	0.84	60.6	18.2	0.00	0	2.33	3.73

<sup>a</sup> Residue refers to solid material remaining after evaporation of acidified water sample to a small volume. All data are for unfiltered water samples and therefore relate to acid-leached suspended sediments.

<sup>b</sup> Contributions of residues to the trace element levels in the streams were computed from concentrations of these solids in the water samples, and concentrations of trace elements found in the solids. Standard errors were calculated by propagation of error formulas.

Table 49 Suspended sediment concentrations in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13; comparison of data

Watershed and Sampling date	Suspended sediment concentration $\pm$ standard error, $s/\sqrt{n}$ , mg/L		
	This work <sup>a</sup>	Project 9A <sup>b</sup>	OME <sup>c</sup>
Watershed AG1			
290376	71 $\pm$ 8	76.2	19.0, 32.5, 26.0,
260776	11 $\pm$ 12	10.7	81.0
051176	80 $\pm$ 5	70.0	-
130377	740 $\pm$ 10	-	439
Watershed AG3			
050476	10 $\pm$ 12	-	6.6, 11.0, 5.9
080676	16 $\pm$ 7	-	8.0, 3.0
190776	15 $\pm$ 7	-	30.0, 5.3
141076	64 $\pm$ 7	-	50.0
Watershed AG4			
260376	329 $\pm$ 8	436.8	342.9, 130.0
120776	47 $\pm$ 7	-	30.0, 31.0
071076	13 $\pm$ 7	11.6	39.0
Watershed AG5			
310376	2 $\pm$ 12	1.8	1.5, 3.5, 2.5, 2.0
030676	12 $\pm$ 12	-	0.25, 41.0
150776	16 $\pm$ 6	16.2	1794
210776	33 $\pm$ 6	33.5	470
250876	7 $\pm$ 8	-	4.0
051076	11 $\pm$ 12	-	4.0, 10.0, 3.5, 5.0
250377-5	350 $\pm$ 10	-	-
Watershed AG10			
300376	125 $\pm$ 8	-	70.0
020676	31 $\pm$ 8	3.7	35.0, 35.7
140776	48 $\pm$ 6	59.0	4.5
121076	79 $\pm$ 8	74.8	74.8 <sup>d</sup>
Watershed AG13			
290376	6 $\pm$ 12	63.4	60.5, 28.0, 10.5
270776	9 $\pm$ 8	-	13.0, 46.0
041176	9 $\pm$ 7	-	5.0, 11.5
030377	685 $\pm$ 10	-	-

<sup>a</sup> These data are means of data including those of project 9A reported here, and are therefore not independent determinations in respect of project 9A data.

<sup>b</sup> Whitby *et al.* (1978).

<sup>c</sup> Data from NAQUADAT listed as "Ontario Ministry of the Environment monitoring data and estimates". Several values reflect different sampling times; no sampling times for sediment reported in this work, were chosen to coincide with OME sampling times.

Table 50. Contributions of suspended sediments to concentrations of Cu, Zn, Cd and Pb in waters of agricultural watersheds 1, 4, 5, and 10; comparison of data.

Watershed and sampling date	Concentration of the element $\pm$ standard error, s/ $\sqrt{n}$ , $\mu\text{g/L}$			
	Cu		Zn	
	This work	Project 9A <sup>a</sup>	This work	Project 9A
Watershed AG1				
290376	6.6 $\pm$ 0.8	6.9	19.9 $\pm$ 3.6	22.0
051176	4.3 $\pm$ 0.4	3.9	12.8 $\pm$ 2.4	10.2
Watershed AG4				
260376	10.5 $\pm$ 1.0	12.7	36.2 $\pm$ 8.3	46.3
Watershed AG5				
150776	1.9 $\pm$ 0.7 <sup>b</sup>	2.0	3.8 $\pm$ 1.7 <sup>b</sup>	3.9
210776	2.3 $\pm$ 0.5 <sup>b</sup>	2.4	6.6 $\pm$ 2.2 <sup>b</sup>	6.8
Watershed AG10				
020676	0.8 $\pm$ 0.3	0.2	1.6 $\pm$ 0.8	1.8
140776	4.3 $\pm$ 0.6	2.7	11.0 $\pm$ 2.3	21.5
121076	4.7 $\pm$ 0.5	1.8	6.3 $\pm$ 2.1	20.2
		Cd		Pb
Watershed AG1				
290376	0.44 $\pm$ 0.09	0.5	2.6 $\pm$ 1.9	4.1
051176	0.09 $\pm$ 0.06	0.1	6.0 $\pm$ 1.3	9.2
Watershed AG4				
260376	0.03 $\pm$ 0.03	0.1W	42.8 $\pm$ 5.4	11.1
Watershed AG5				
150776	0.00 $\pm$ 0.00 <sup>b</sup>	0.1W	1.0 $\pm$ 0.7 <sup>b</sup>	1.0
210776	0.00 $\pm$ 0.01 <sup>b</sup>	0.1W	0.8 $\pm$ 0.8 <sup>b</sup>	0.8
Watershed AG10				
020676	-		3.1 $\pm$ 1.1	0.1
140776	0.38 $\pm$ 0.07	0.1T	13.0 $\pm$ 2.0	7.2
121076	0.02 $\pm$ 0.02	0.1	-	

<sup>a</sup> Whitby *et al.* 1978. The T and W codes used in project 9A for reporting low level data are defined in the PLUARG Handbook.

<sup>b</sup> Based on data provided by Dr. L. Whitby Costescu and therefore not independent of data listed for project 9A.

Table 51. Concentrations of dissolved Cu, Zn, Cd and Pb in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13; comparison of data.

Watershed and sampling date	Concentration of the element $\pm$ standard error, s/ $\sqrt{n}$ , $\mu\text{g/L}$					
	Zn		Cd		Pb	
	This work	Project 9A <sup>a</sup>	This work	Project 9A	This work	Project 9A
Watershed AG1						
290376	-		0.12 $\pm$ 0.04	0.3	-	
260776	-		-		-	
051176	0.2 $\pm$ 2.8	9.5	-		-	
Watershed AG3						
050476	2.2 $\pm$ 2.5	7.2	0.01 $\pm$ 0.04	0.1	0.2 $\pm$ 0.2	3.0
080676	0.1 $\pm$ 2.5	6.6	-		-	
190776	7.3 $\pm$ 6.5	17.8	0.01 $\pm$ 0.05	0.2T	-	
141076	-		0.08 $\pm$ 0.05	0.5	0.1 $\pm$ 0.2	4.3
Watershed AG4						
260376	6.5 $\pm$ 2.8	3.8	-		13.1 $\pm$ 0.3	0.6
010676	0.8 $\pm$ 2.5	4.6	-		0.1 $\pm$ 0.2	3.6
120776	3.1 $\pm$ 2.7	10.0	-		1.6 $\pm$ 0.3	3.4
071076	-		0.07 $\pm$ 0.06	0.3	-	
Watershed AG5						
030676	2.9 $\pm$ 2.5	3.4	-		-	
051076	-		-		0.1 $\pm$ 0.2	6.9
Watershed AG10						
020676	11.4 $\pm$ 13.9	13.2	-		-	
140776	0.8 $\pm$ 2.5	14.6	-		-	
121076	0.7 $\pm$ 2.8	8.0	-			
Watershed AG13						
290376	7.0 $\pm$ 2.9	10.1	0.00 $\pm$ 0.05	0.1W	0.1 $\pm$ 0.2	6.3
270776	-		-		0.0 $\pm$ 0.2	3.5
041176	-		0.05 $\pm$ 0.05	<0.1	0.1 $\pm$ 0.2	4.6

<sup>a</sup> Whitby *et al.* (1978); as Cu data reported by these authors are very high and considered aberrant, no comparisons are listed.

Table 52. Total concentrations of Cu and Zn in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13; comparison of data.

Watershed and sampling date	Concentration of the element $\pm$ standard error, s/ $\sqrt{n}$ , $\mu\text{g/L}$				
	Cu		Zn		
	This work	OME <sup>b</sup>	This work	Project 9A <sup>c</sup>	OME <sup>b</sup>
Watershed AG1					
290376	13.9 $\pm$ 3.3*	7	15.8 $\pm$ 4.9*	22.2	23
260776	4.8 $\pm$ 1.7	-	17.2 $\pm$ 4.9	25.5	-
051176	5.6 $\pm$ 2.0	-	8.0 $\pm$ 1.0	14.1	-
Watershed AG3					
050476	1.7 $\pm$ 0.7*	3	3.0 $\pm$ 0.7*	8.0	1
080676	2.3 $\pm$ 0.8*	6	3.4 $\pm$ 0.9*	4.2	4
190776	2.1 $\pm$ 0.8*	-	1.3 $\pm$ 1.0	16.2	-
141076	2.2 $\pm$ 0.7	-	4.3 $\pm$ 1.0	2.8	-
Watershed AG4					
260376	37.5 $\pm$ 10.7	-	58.2 $\pm$ 19.4	45.9	-
010676	5.2 $\pm$ 0.8*	-	2.0 $\pm$ 0.7*	4.8	-
120776	3.9 $\pm$ 2.6	-	7.2 $\pm$ 3.9	12.6	-
071076	2.3 $\pm$ 0.7	-	10.6 $\pm$ 3.5	5.0	-
Watershed AG5					
310376	9.2 $\pm$ 0.8*	2	3.1 $\pm$ 0.7*	9.2	16
030676	2.8 $\pm$ 0.8*	-	6.1 $\pm$ 0.8*	4.1	-
150776	3.1 $\pm$ 0.7	-	11.1 $\pm$ 1.1	9.7	-
210776	3.7 $\pm$ 0.8	-	11.2 $\pm$ 3.5	12.4	-
051076	2.0 $\pm$ 0.7*	<1	0.9 $\pm$ 0.7*	5.3	<1
Watershed AG10					
020676	3.2 $\pm$ 1.3	-	16.6 $\pm$ 3.6*	13.8	-
140776	2.9 $\pm$ 0.9	-	20.4 $\pm$ 3.6*	38.3	-
121076	3.9 $\pm$ 2.0	-	19.4 $\pm$ 3.0	25.3	-
Watershed AG13					
290376	40.8 $\pm$ 3.8*	2	11.8 $\pm$ 3.5*	20.0	6
270776	2.8 $\pm$ 0.8*	6	2.7 $\pm$ 0.7*	8.4	4
041176	2.8 $\pm$ 1.4	<1	5.0 $\pm$ 0.8	9.7	6

<sup>a</sup> Where total concentration data are unavailable, dissolved + acid- or solvent-extractable concentrations (denoted \*) are included as estimates of total concentrations.

<sup>b</sup> Data from NAQUADAT listed as "Ontario Ministry of the Environment monitoring data and estimates". Analysis by nitric acid digestion - atomic spectrometry; levels are not strictly total concentrations.

<sup>c</sup> Whitby *et al.*, 1978; Cu data reported by these authors being very high and considered aberrant, are excluded.

Table 53. Total concentrations of Cd and Pb in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13; comparison of data.

Watershed and sampling date	Concentration of the element $\pm$ standard error, s/ $\sqrt{n}$ , $\mu\text{g/L}$				
	Cd		Pb		OME <sup>c</sup>
	This work <sup>a</sup>	Project 9A <sup>b</sup>	This work <sup>a</sup>	Project 9A <sup>b</sup>	
Watershed AG1					
290376	0.56 $\pm$ 0.10	1.7	2.5 $\pm$ 1.9	3.7	<2
260776	0.04 $\pm$ 0.04	0.1W	3.0 $\pm$ 0.8	6.9	-
051176	0.03 $\pm$ 0.02	0.3	2.7 $\pm$ 0.9	9.9	-
Watershed AG3					
050476	0.10 $\pm$ 0.0*	0.3	0.7 $\pm$ 0.8*	1.7	<2
080676	0.01 $\pm$ 0.03*	0.1W	0.2 $\pm$ 0.9*	8.5	<1
190776	0.02 $\pm$ 0.02*	0.1W	0.2 $\pm$ 0.9*	12.8	-
141076	0.07 $\pm$ 0.02	0.4	1.1 $\pm$ 0.8	1.8	-
Watershed AG4					
260376	0.29 $\pm$ 0.02*	0.1W	45.6 $\pm$ 12.8*	9.8	-
010676	0.01 $\pm$ 0.02*	0.1W	0.4 $\pm$ 1.0	3.3	-
120776	0.02 $\pm$ 0.02	0.1W	8.7 $\pm$ 2.0	4.3	-
071076	0.14 $\pm$ 0.05	0.3	1.4 $\pm$ 0.7	2.2	-
Watershed AG5					
310376	0.04 $\pm$ 0.00*	0.1W	1.7 $\pm$ 0.8*	3.3	<2
030676	0.03 $\pm$ 0.02*	0.3	0.3 $\pm$ 0.9*	1.4	-
150776	0.05 $\pm$ 0.02	0.2T	1.2 $\pm$ 0.7	6.5	-
210776	0.06 $\pm$ 0.02	0.1T	4.6 $\pm$ 0.8*	4.9	-
051076	0.02 $\pm$ 0.02	0.9	0.2 $\pm$ 0.9	2.8	<2
Watershed AG10					
020676	0.04 $\pm$ 0.02	0.1	2.6 $\pm$ 0.8	4.5	-
140776	0.04 $\pm$ >0.07	0.1W	8.1 $\pm$ 6.1	10.6	-
121076	0.08 $\pm$ 0.02	1.2	3.7 $\pm$ 1.0	13.8	-
Watershed AG13					
290376	0.04 $\pm$ 0.02*	0.1W	0.6 $\pm$ 0.8*	5.6	<2
270776	0.05 $\pm$ 0.02	1.3	0.9 $\pm$ 0.8	2.6	4, 7
041176	0.08 $\pm$ 0.02	0.2	1.6 $\pm$ 1.0	6.7	<2

<sup>a</sup> Where total concentration data are unavailable, dissolved + acid- or solvent extractable concentrations (denoted \*) are included as estimates of total concentrations.

<sup>b</sup> Whitby *et al.* 1978.

<sup>c</sup> Data from NAQUADAT listed as "Ontario Ministry of the Environment monitoring data and estimates". Analysis by nitric acid digestion - atomic spectrometry; levels are not strictly total concentrations. Levels of Cd were generally not detectable and typically reported as <0.00 mg/L.

Table 54 Comparison of total concentrations of Cu, Zn, Cd and Pb in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13 with literature data for these and other "unpolluted" fresh surface natural waters-detailed data.

Element	Concentration, µg/L				Water <sup>a</sup>	Reference
	This work		Literature <sup>b</sup>			
	Range (n/m) <sup>c</sup>	Median <sup>d</sup>	Range(n/m) <sup>c</sup>	Median <sup>e</sup> or mean		
Cu	2.2 - 445 (17/6)	3.9 ± 2.6	2-68 (146/1)	8	A	Gaynor 1977 <sup>f</sup>
			<1-230 (878/6)	5	A	OME <sup>g</sup>
			<1-150 (- /30)	3	O	Fisheries & Environment Can.1977 <sup>h</sup>
			1-33.0 (44/1)	4.7	O	Chan 1977 <sup>i</sup>
				2.0±1.8	O	Poldoski et al 1976 <sup>j</sup>
			4.5-9.6 (>12/2)	6.9	O	Philips et al 1975 <sup>k</sup>
				15	O	Chawla and Chan 1969 <sup>l</sup>
			0.4-5.0 (168/170)	1.2	O	Bradford et al 1968 <sup>m</sup>
			(439/ -)	1.16	O	Turekian & Kleinkopf 1956 <sup>n</sup>
				12	A	Gaynor 1977 <sup>f</sup>
Zn	4.3 - 2500(15/6)	17.2 ± 4.9	2-200 (146/1)	5.5	A	OME <sup>g</sup>
			<1-820 (882/6)	<10	O	Fisheries& Environment Can.1977 <sup>h</sup>
			1-620 (- /27)	7.8	O	Chan 1977 <sup>i</sup>
			4-18.0 (45/1)	8	O	Chawla and Chan 1969 <sup>l</sup>
				1.5	O	Bradford et al 1968 <sup>m</sup>
Cd	0.03 - 13.4(17/6)	0.08 ±0.02	0.3-100 (168/170)	<0.6	A	Gaynor 1977 <sup>f</sup>
			(- /1)	<1 or <10	A	OME <sup>g</sup>
			(123/6)	<1	O	Fisheries.& Environment Can.1977 <sup>h</sup>
			<1-6 (- /25)	<1	O	Chan 1977 <sup>i</sup>
			<1-2.0 (40/1)	1.0	O	Phillips et al 1975 <sup>k</sup>
			0.3-0.8 (12/2)	<0.5	O	Phillips et al 1975 <sup>k</sup>
Pb	0.9 - 433(19/6)	3.7 ±1.0	0.02-0.15 (10/3)	0.045	O	Doolan and Smythe 1973 <sup>o</sup>
				<11	A	Gaynor 1977 <sup>f</sup>
			<1-76 (902/6)	<2	A	OME <sup>g</sup>
			<1-200 (- /30)	<1	O	Fisheries& Environment Can. 1977 <sup>h</sup>
			<1-7.0 (45/1)	0.8	O	Chan 1977 <sup>i</sup>
				0.7±0.8	O	Poldoski et al 1976 <sup>j</sup>
			3.5-29.4 (>12/2)	5.4	O	Phillips et al 1975 <sup>k</sup>
				0.015	O	Hirao and Patterson 1974 <sup>p</sup>
			0.3-4 (168/170)	4	O	Chawla and Chan 1969 <sup>l</sup>
(439/ -)	0.5	O	Bradford et al 1968 <sup>m</sup>			
	0.26	O	Turekian and Kleinkopf 1956 <sup>n</sup>			

<sup>a</sup> A - PLUARG agricultural watershed; O - other natural water. All waters may not be truly unpolluted.

<sup>b</sup> All levels reported in the literature may not, strictly speaking, be total concentrations; some may reflect extractable concentrations. Ranges were either reported or estimated by this author, from the data reported.

<sup>c</sup> n is the total no. of samples (or observations) from one or more sampling locations on m different bodies of water; - indicates unknown quantity.

<sup>d</sup> Refer to footnote to Table 9 for details.

<sup>e</sup> Reported in the literature or estimated by this author. Median (or median of medians) of data reported by Gaynor, OME, Fisheries & Environment Canada, Bradford et al; means reported by the other authors.

<sup>f</sup> Five sites in AG13 were sampled between 11/04/75 and 10/03/76.

<sup>g</sup> Based on ca 100-200 samplings of each of the six watersheds 1, 3, 4, 5, 10 and 13 between ca 11/09/74 and 31/05/77 at the gauging stations near the outlet sites.

<sup>h</sup> Different rivers throughout Canada sampled in 1960-1975.

<sup>i</sup> 1974 survey of the Niagara river.

<sup>j</sup> Near-shore waters from Lakes Huron and Superior and waters from several incoming streams sampled in 1975.

<sup>k</sup> Two rivers passing through industrialized suburbs of Melbourne, Australia were sampled in 1974.

<sup>l</sup> Lake Erie sampled in 1967.

<sup>m</sup> High Sierra Lakes in California sampled in 1965.

<sup>n</sup> Stream and Lake waters from Maine

<sup>o</sup> Three rivers in New South Wales, Australia sampled in 1972.

<sup>p</sup> Stream runoff from Thompson Canyon, California.

Table 55 Comparison of concentrations of dissolved Cu, Zn, Cd and Pb in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13 with literature data for other "unpolluted" fresh surface natural waters - detailed data <sup>a</sup>.

Element	Concentration, µg/L				Reference
	This work		Literature		
	Range (n/m) <sup>b</sup>	Median <sup>c</sup>	Range(n/m) <sup>b</sup>	Median or mean <sup>d</sup>	
Cu	0.5-18.5 (21/6)	2.0 ±1.8	1-3.0 (60/1)	1.6	Chan 1977 <sup>e</sup>
			0.3-3		Florence & Batley 1977 <sup>f</sup>
			0.20-2.91		Nürnberg et al 1976 <sup>g</sup>
			10-50 (30/-)		Wahlgren et al 1971 <sup>h</sup>
			4.9,9.3 (-/1)		Wahlgren et al 1971 <sup>i</sup>
			1-280 (~1600/ ~130)	15	Kopp 1970 <sup>j</sup>
			0.72-27.5 (45/1)	2.24	Silker 1964 <sup>k</sup>
Zn	0.1-11.4 (17/6)	3.1 ±2.7	0.83-105 (≥57/15)	5.3	Durum & Haffty 1960,1963 <sup>l</sup>
			<1.0-8.0 (55/1)	3.5	Chan 1977 <sup>e</sup>
			2-10		Florence & Batley 1977 <sup>f</sup>
			6.2-600 (30/-)		Wahlgren et al 1971 <sup>h</sup>
			2-1183 (~1600/ ~130)	64	Kopp 1970 <sup>j</sup>
Cd	0.00-0.57 (13/6)	0.07 ±0.06	2.4-37.6 (40/1)	14.4	Silker 1964 <sup>k</sup>
			0-215 (≥59/15)	0	Durum & Haffty,1960,1963 <sup>l</sup>
			<1-12.0 (60/1)	0.2	Chan 1977 <sup>e</sup>
			0.1-0.5		Florence & Batley 1977 <sup>f</sup>
			0.004-0.082		Nürnberg et al 1976 <sup>g</sup>
Pb	0.0-13.1 (11/6)	0.1 ± 0.2	0-4.7 (30/-)		Wahlgren et al 1971 <sup>h</sup>
			1-120 (~1600/ ~130)	9.5	Kopp 1970 <sup>j</sup>
			<1-1.0 (60/1)	0.2	Chan 1977 <sup>e</sup>
			0.2-2		Florence & Batley 1977 <sup>f</sup>
			0.058-0.236		Nürnberg et al 1976 <sup>g</sup>
			0.1-6.2 (30/-)		Wahlgren et al 1971 <sup>h</sup>
			2-140 (~1600 / ~130)	23	Kopp 1970 <sup>j</sup>
			0-55 (≥59/15)	4.0	Durum & haffty,1960,1963 <sup>l</sup>

<sup>d</sup> Analyses of typically 0.45 µm filtered water samples gave "dissolved" concentrations; all waters may not be truly unpolluted.

<sup>b</sup> Refer to footnotes to Table 53 for details.

<sup>c</sup> Refer to footnotes to Table 9 for details.

<sup>d</sup> Reported in the literature or estimated by this author. Median of data reported by Silker, and Durum and Kaffty; means reported by Chan and Kopp.

<sup>e</sup> 1974 survey of the Niagara river.

<sup>f</sup> Ranges of levels in many "unpolluted" fresh water rivers throughout the world were obtained by these authors from Phillips et al 1975, Spencer et al 1970, and T.M. Florence (unpublished results on Northern Territory rivers, Australia); data reported by Spencer et al, seem to refer to the oceans.

<sup>g</sup> Weser river and Lake Constance.

<sup>h</sup> Tributaries to Lake Michigan.

<sup>i</sup> Two sites in Lake Michigan.

<sup>j</sup> Sampling of US surface waters 1958-1969.

<sup>k</sup> Columbia river (Washington, USA) sampled in 1962.

<sup>l</sup> Rivers in USA and Canada sampled in 1958-1959.

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