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### Analytical Approach to the Determination of Copper, Zinc, Cadmium and Lead in- Natural Fresh Waters

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# Analytical Approach to the Determination of Copper, Zinc, Cadmium and Lead in Natural Fresh Waters

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A description is given of a total analytical approach to the determination of copper, zinc, cadmium and lead in fresh natural waters of streams draining selected southern Ontario agricultural watersheds. Central to the attainment of accurate analytical information was the adoption of a data quality assurance program encompassing: (1) field and laboratory processing of control samples to establish filtration adsorption/contamination parameters, (2) performance evaluation of analytical methodology *via* recoveries of added analytes and use of reference samples, (3) systematic incorporation into the measurement scheme of quality control solutions, (4) participation in analytical round robin laboratory studies, (5) participation in the study of several other laboratories applying independently different analytical methodologies to the analysis of water and suspended sediment samples, and (6) other related considerations. Analytical methodologies based on atomic absorption spectrometry, optical emission spectrometry and differential pulse anodic stripping voltammetry gave satisfactory data in respect of dissolved, suspended and total concentrations of the trace metals in natural water samples.

KEY WORDS: Natural water, Trace metals, Analytical methodology.

## INTRODUCTION

A recent project<sup>1</sup> under the auspices of the International Reference Group on Great Lakes Pollution from Land Use Activities (PLUARG) of the International Joint Commission (IJC) dealt with the determination and assessment of relationships between selected heavy metals in stream waters and suspended sediments within six Ontario agricultural watersheds draining into the lower Great Lakes. The objectives of this study were:

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(1) to assess, develop and adapt analytical methodology for the reliable determination of trace and ultratrace levels of copper, zinc, cadmium and lead in waters and suspended sediments from six watersheds selected for intensive study, and (2) to assess relationships between metal concentrations in dissolved and particulate forms and to elucidate metal transport and storage mechanisms. Analytical chemical methodology played a dominant role in this undertaking, as reliable analytical information was a prerequisite to the formulation of meaningful conclusions. The very low  $\mu\text{g/l}$  and sub  $\mu\text{g/l}$  concentrations, at which the elements of interest normally occur in natural fresh waters, necessitated attention to detail in the executions of all facets of sampling and analysis.

Central to the attainment of accurate data was the adoption of a data quality assurance program dealing with assessment of sampling and sample preparation procedures, contamination, analytical method performances and the participation of several other laboratories bringing to bear on water and sediment analysis, independently different analytical methodologies. Descriptions and discussion of analytical methods used by cooperating laboratories, and the results of interlaboratory comparisons have been presented in the first paper in this series,<sup>2</sup> which together with this report, constitutes an integral part of the analytical considerations for this project. The ultimate use of the analytical data for delineation of storage and transport mechanisms of the elements within the agricultural watersheds is the topic of the final report.<sup>3</sup> In this paper, emphasis is placed on the detailed description and discussion of atomic absorption and other methodologies used in the author's laboratory and the overall analytical approach (cf objective 1). For details, the reader is referred to the IJC technical report.<sup>1</sup>

## EXPERIMENTAL

### Reagents and solutions

All reagents used were reagent grade or better. In the laboratory deionized water was used throughout. Acids used for sample processing and other procedures were of the highest purity available (Ultrex  $\text{HNO}_3$  from J. T. Baker, Chemical Co., double distilled  $\text{HNO}_3$  and  $\text{HClO}_4$  from G. Frederick Smith Chemical Co., and high purity HF courtesy of S. S. Berman, National Research Council, Ottawa). Reagents used in the field for sample preservation and processing-blank controls and by sampling personnel were reagent grade acids and distilled water (Guelph). Cu, Zn and Cd metals and  $\text{Pb}(\text{NO}_3)_2$  were used as sources of the elements for preparing composite standard solutions in an acid matrix matching that of the samples. Quality control standard solutions containing the four

elements at calibration curve mid-point levels of 500 and 600  $\mu\text{g/l}$  in 0.2 M  $\text{HNO}_3$ , designated Q1 and Q2 respectively, were prepared and used throughout this work (17 months), to monitor spectrometer performance.

A stock solution of 100-fold concentrated synthetic natural water was prepared from  $\text{CaCO}_3$ ,  $\text{MgSO}_4$ ,  $\text{NaCl}$ ,  $\text{HCl}$  and deionized water, to contain three of the most common inorganic cations found in fresh natural waters at levels of *ca* 10000 mg Ca/l, 2000 mg Mg/l and 1000 mg Na/l. The stock solution was diluted with water as required. The diluted solution, simulating a natural water sample, had a pH of *ca* 2.5, about the value for acid-preserved samples of real natural waters. Two 20-fold concentrated synthetic natural water quality control solutions (A-blank, B-containing added 100  $\mu\text{g/l}$  of each element) in 1.6 M  $\text{HNO}_3$ , simulating the typical 20-fold concentrated natural water sample, were used in conjunction with Q1 and Q2 to monitor data quality.

### Reference samples

US Environmental Protection Agency quality control water samples for trace metal analysis nos. 1-575, 2-575 and 3-575 (courtesy of J. A. Winter, EPA), and US Geological Survey rock samples G-2, BCR-1 and AGV-1 were used to assess the performance of water analysis and suspended sediment analysis methods respectively

### Atomic absorption spectrometric instrumentation

Atomic absorption spectrometric measurements were made with a Varian Techtron model AA5 spectrometer equipped with an IM6D amplifier and a BC6 background corrector module. Radiation from single element hollow cathode lamps operated at 2mA (Cu), 5mA (Zn) and 3mA (Cd and Pb) was directed through the air/acetylene flames at a height of 5 mm above the surface of the 100 mm single slot AB51 burner head. Absorbances were measured at wavelengths for Cu, Zn, Cd and Pb of 324.8, 213.9, 228.8 and 217.0 nm respectively, with corresponding spectral band passes of 0.2, 0.3, 0.5 and 1.0 nm, and read on the digital read-out meter using a 10-50 $\times$  scale expansion and a 3-10 sec integration period. All readings were corrected for non-atomic absorbance by simultaneous use of a  $\text{H}_2$  hollow cathode lamp.

### Water handling and processing apparatus

Water samples were collected using either a US DH-48 hand-held sampler fitted with a *ca* 450 ml glass bottle or an electric-powered peristaltic pump with tygon tubing, and stored in leak-proof typically 1 l white, linear polyethylene (LPE) bottles with polypropylene (PP) screw closures

(Nagle Co.). Filtration was carried out with 250 ml Sartorius polycarbonate filtering apparatuses (no. SM 16510) fitted with Sartorius 47 mm diameter, 0.45  $\mu\text{m}$  pore size cellulose acetate membrane filters (no. SM 11106.047) for field work, and 47 mm diameter, 0.4  $\mu\text{m}$  pore size polycarbonate membrane filters (no. N040, Nuclepore Corp.) for laboratory application. Water samples were heat-concentrated, and sediments digested in 600 ml and 30 ml respectively, polytetrafluoroethylene (PTFE) beakers (Bel-Art Products).

### **Cleaning of glassware and plasticware**

All glass and plasticware used in collection and analysis (with the exception of membrane filters used in the field) were cleaned by contacting with 1 M  $\text{HNO}_3$  for at least 24 hr and thoroughly rinsing with deionized water. PTFE beakers were cleaned by contacting with hot 1:1  $\text{HNO}_3$  for 24 hr, rinsing with water, and thereafter rinsing with water before each use. Membrane filters used in the laboratory were cleaned by filtering through, 1 M  $\text{HNO}_3$  to fill pores, and soaking in 1 M  $\text{HNO}_3$  for two days. They were then rinsed with water, by filtration, and soaked in water until used.

### **Sample collection and preparation (field)**

Unfiltered water samples were collected by filling stream water-rinsed containers, directly from the DH-48 sampler or from a 20 l conventional polyethylene carboy used as a temporary storage vessel and were acidified with 2 ml/l of (1 + 1)  $\text{HNO}_3$  or (1 + 1) HCl. Efforts were made to provide for vertical and lateral integration of the streams by making a number of transects across the stream. Field-filtered water samples were prepared by vacuum-filtration (hand pump) and likewise acid-preserved immediately thereafter. Membrane filters were placed (in pairs from the same sample, with sediment sides in contact) in polyethylene-lined bags. The several samples collected in 1977 were shipped unacidified and processed and acidified in the Ottawa laboratory.

Aliquots of distilled water were similarly treated to provide unfiltered and filtered quality control blanks in order to monitor the collection–filtration–storage procedure. All samples were stored at 4° until shipment to the author, and again until analysis. Typically, each sampling provided a total of 8 to 10 samples: two to four unfiltered natural water samples, two filtered natural water samples, two each unfiltered and filtered distilled water samples, eight filters with suspended sediment and eight filters from the duplicate filtration of distilled water. Samples of the two acids used for field preservation, added to aliquots of deionized water supplied by the author 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 samples were obtained during the 1977 spring runoff.

### Sample preparation (laboratory)

Suspended sediments in water samples collected in the Spring of 1977 were isolated in this laboratory by vacuum filtration of the unacidified samples through  $0.4\ \mu\text{m}$  Nuclepore membrane filters, dried at *ca*  $70^\circ$  and transferred to glass vials. Upon completion of spectrometric analysis of the supernatant liquid phases of heat-concentrated water solutions, those with visible solid residues were similarly filtered. 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.

Water samples were subsampled as described previously<sup>2</sup> for submission to cooperating laboratories for analysis. Sediment and residue samples with masses of 10's of mg were retained for analysis by acid digestion/flame atomic spectrometry. Solid samples of only several mg were forwarded to the National Research Council, Ottawa.

### Filtration studies

A supply of Sartorius cellulose acetate filters used in field work together with the Nuclepore filters used in the CBRI laboratory, and another common filter type manufactured by Millipore Corp. (Bedford, MA,  $0.45\ \mu\text{m}$ , 47 mm diameter, cellulose acetate/nitrate, type HA) were tested as possible sources of trace metal contamination. Each of the 12 filters (two each acid-cleaned and as-received) was separately rinsed with 250 ml of deionized water. This was followed by consecutively filtering two 500 ml portions of deionized water which were then acidified with 0.5 ml  $\text{HNO}_3$  and retained for analysis.

Several additional experiments with Nuclepore filters were conducted using unacidified centrifuged natural water, simulating  $0.45\ \mu\text{m}$ -filtered water, to evaluate the filtration behaviour of real samples. Five hundred ml of natural water was filtered through a prerinsed filter, followed by re-filtering 250 ml of the filtrate through a second prerinsed filter. Duplicate tests gave four 250 ml filtrates which were acidified with 0.25 ml  $\text{HNO}_3$  prior to analysis. Five hundred ml of acidified, unprocessed, natural water was set aside as a control.

### **Water analysis by evaporation/flame atomic absorption spectrometry (Evap/FAAS)**

Nitric acid- and HCl-preserved unfiltered and filtered natural water and distilled water control samples were heat-concentrated by a factor of 10–50 fold. Typically, 500 ml of sample was measured into a 600 ml PTFE beaker followed by the addition of 2 ml or 0.5 ml of HNO<sub>3</sub> for reduction to 25 ml (20×) or 10 ml (50×), respectively. The sample volume was reduced by sub-boiling evaporation for *ca* 15 hr in a clean microenvironment, after the design of Thiers,<sup>4</sup> to less than 25 or 10 ml, transferred (inclusive of residue) to a volumetric flask and made up to volume with water.

Other samples processed in this way were deionized water for estimation of laboratory processing reagent blanks, EPA quality control solutions, and deionized water, synthetic natural water and selected natural water samples spiked with different levels of metals to test recoveries. Appropriate quantities of HNO<sub>3</sub> were added prior to evaporation to end up with 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 volume reduction. Five to 20% of the natural water samples were analyzed in duplicate. Some samples such as the EPA solutions and several natural water samples for Zn, were also analyzed without preconcentration.

Concentrated sample solutions, together with quality control solutions Q1, Q2, A and B and six 0–1000 µg/l standard solutions were run in duplicate on the atomic spectrometer. Element concentrations were computed by reference to standard response (absorbance)-concentration 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.

### **Suspended sediment and residue analysis 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. In a typical analysis scheme, 3–30 mg (occasionally  $\geq 1$  mg) of dry suspended sediment or residue was refluxed for 2 hrs in a 30 ml PTFE beaker with 2 ml conc. HNO<sub>3</sub> + 2 ml 70% HClO<sub>4</sub>. 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, brought to a mass of 0.340 g with 70%  $\text{HClO}_4$ , and diluted with water to 2 ml. 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. Element concentrations were determined by flame atomic absorption spectrometry by reference to standard solutions in an identical bulk acid matrix after correction for procedural reagent blanks.

### **Water and solids analysis by cooperating laboratories**

Subsamples of unfiltered and filtered natural and distilled waters were analyzed by analysts in three cooperating laboratories using methods centering on atomic absorption spectrometry and electrochemistry.<sup>1,2</sup> Methods based on electrothermal atomization/atomic spectrometry were used by M. Stoeppler and S. S. Berman-A. Desaulniers, a solvent extraction/flame atomic absorption spectrometry-based method was followed by J. D. Gaynor, whereas M. Stoeppler and P. Valenta applied the technique of differential pulse anodic stripping voltammetry. Sediment and residue samples were analyzed by optical emission spectrography (OES) by D. S. Russell and P. Tymchuk.

### **Calculations**

Processing and statistical analysis of data from the laboratories conducting trace metal on water samples has been previously described.<sup>2</sup> These data yielded mean concentrations over all subsamples, methods and replicate analyses, representing measures of dissolved + extractable concentrations of the trace metals. Analyses of filtered natural water samples, corrected for filtration contamination, gave levels of dissolved metals. Analyses of unfiltered waters augmented by analyses of suspended sediments gave total concentrations. Standard errors of data resulting from arithmetic manipulations were estimated from standard propagation of error formulas. Every datum reported in this study thus has associated with it a standard error  $\pm s/\sqrt{n}$ , where  $s$  is the standard deviation and  $n$  is the no. of observations, which is often accuracy-related stemming from the application of independently different analytical methodologies. Typically, each datum in this study is an average over 2 subsamples for each watershed and sampling time, and in respect of dissolved, suspended, and total metal concentrations is the result of a total of (2, 4), (2, 2) and (4, 8) analytical methods and total analyses, respectively.



## RESULTS AND DISCUSSION

Concentration ranges of Cu, Zn, Cd and Pb found in waters of the watersheds studied are summarized in Table I. For the reliable determination of elements at the  $\mu\text{g/l}$  and sub  $\mu\text{g/l}$  levels, positive and negative contamination of the sample during sampling, sample treatment and measurement together with errors from other sources are problems of continual concern. Steps must therefore be taken to ensure that the analytical approach yields reasonably reliable information in order to get a grasp of the partition of trace elements between suspended and soluble forms. In particular, should one be interested in comparisons of future data with the present information to monitor effects of changed land uses

TABLE I  
Concentrations of Cu, Zn, Cd and Pb found in waters of southern Ontario agricultural watersheds,  $\mu\text{g/l}$

Element	Dissolved		Total	
	Range	Median $\pm$ standard error	Range	Median $\pm$ standard error
Cu	0.5-18.5	2.0 $\pm$ 1.8	2.2-445	3.9 $\pm$ 2.6
Zn	0.1-11.4	3.1 $\pm$ 2.7	4.3-2500	17.2 $\pm$ 4.9
Cd	0.0-0.57	0.07 $\pm$ 0.06	0.03-13.4	0.08 $\pm$ 0.02
Pb	0.0-13.1	0.1 $\pm$ 0.2	0.9-433	3.7 $\pm$ 1.0

and pollution, then very accurate data indeed is a prerequisite for any serious comparisons. It is very difficult if not impossible to follow trends with time using information with a spotty reliability record. 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  $0.01-0.1 \mu\text{g/l}$ . Careful execution of experimentation is essential to provide a good data base for firm conclusions and comparisons.

### Data quality assurance and methodology considerations

Considerable 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:

- 1) Field filtration and processing of distilled water control samples to establish filtration contamination corrections.
- 2) Conduction of laboratory filtration experiments with deionized water and natural waters to estimate adsorption/contamination.
- 3) Duplicate-quadruplicate collection of unfiltered and filtered natural water samples and duplicate analyses.

4) Consideration of acid trace element levels and testing of acids used for field-preservation of water samples.

5) Performance studies of analytical methodologies *via* determination of recoveries of trace elements, at concentrations expected in real systems, from deionized water, synthetic natural water and natural water samples, and use of the reference samples, EPA Trace Metals Quality Control Samples, and USGS rocks.

6) Systematic incorporation of quality control solutions Q1, Q2, A and B simulating standard solutions and real water samples into the FAAS measurement scheme.

7) Systematic and frequent determinations of appropriate reagent blanks under conditions of analysis of water and solid samples.

8) Participation in PLUARG-sponsored round robin studies for trace metals in water.

9) Participation in the study of other laboratories applying independently different analytical methodologies.

10) Estimation of sample solution stability.

These aspects of data quality assurance and the methodological approach are discussed below.

*Sample filtration controls and laboratory filtration studies (items 1 and 2).* The desire to measure levels of dissolved elements required filtration of water samples, preferably in the field immediately after collection, and necessitated the determination of blanks for this processing step. Estimates of filtration procedural blanks were made by taking distilled water through filtration and processing steps at times and locations identical to those for natural samples using identical equipment (Table II). Field filtration corrections were computed as differences between trace metal levels in paired unfiltered and filtered distilled waters and were applied under the assumption that filtered control and natural waters both suffered identical contamination. As field-filtration raised trace element levels, sometimes substantially as exemplified by the ubiquitous problem with Zn, these data proved very useful in correcting trace element concentration data for field-filtered natural water samples. Unfortunately, corrections for field-filtering were large compared to dissolved trace element levels in the natural waters, resulting in large uncertainties in corrected data. 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.

As a follow-up to the large contaminations observed during field processing, and to further assess the role of the filter material in contamination, laboratory filtration studies were conducted and these data

TABLE II

Concentrations of Cu, Zn, Cd and Pb in distilled and deionized water control samples and corrections for filtration procedure contamination

Sample or Item	Mean concentration $\pm$ standard deviation, $\mu\text{g/l}^{\text{a}}$			
	Cu	Zn	Cd	Pb
Unfiltered distilled water used in the field	$4.2 \pm 4.0$	$0.9 \pm 0.7$	$0.02 \pm 0.02$	$1.1 \pm 1.6$
Contribution of field-filtration procedure	$1.3 \pm 1.6$	$3.2 \pm 2.3$	$0.03 \pm 0.05$	$0.3 \pm 0.2$
Laboratory deionized water <sup>b</sup>	$0.14 \pm 0.23$	$0.14 \pm 0.13$	$<0.024$	$0.21 \pm 0.40$
Contribution of laboratory-filtration procedure <sup>c</sup>	$0.0 \pm 0.2$	$0.17 \pm 0.12$	$0.02 \pm 0.04$	$0.16 \pm 0.49$

<sup>a</sup>No of samples associated with field water: 18–28 (Cu, Zn); 5–6 (Cd, Pb); 22–38 samples associated with laboratory water analyses.

<sup>b</sup>Analytical procedure (Evap/FAAS) reagent blanks determined in the author's 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>c</sup>Results from the author's laboratory averaged over tests with 11–12 Nuclepore, Sartorius and Millipore filters.

are also included in Table II. Compared to levels of Cu and Zn in deionized water produced in the author's laboratory, distilled water used in the field contained substantially 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). It should be noted that the values reported for deionized water represent levels actually present in the water, plus contributions from reagents, processing procedure, etc; they represent upper limits and are in fact blanks used as corrections for the analytical procedure.

As trace element levels in the deionized water filtrates varied neither with filter type nor cleaning, concentrations were averaged over all filters and conditions. Results for control as well as filtered deionized water were all below the limits of detection, indicating undetectable contamination from the filters. These mean values, taken as corrections for the laboratory-filtration procedure, are substantially lower than the corresponding ones 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 cleaned Nucleopore filters were conducted using a sample of unacidified centrifuged natural water to evaluate the behaviour of real samples and deal, at least superficially, with the question of adsorption of trace elements by the filter, a possibility reported by Davies<sup>5</sup> and Marvin *et al.*<sup>6</sup>. Data in Table III show a decrease in Cu and Zn levels following filtration whereas Cd and Pb concentrations were near or below limits of detection of the Evap/FAAS method. At first glance, this decrease 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 differences between unfiltered and filtered water may result from retention by the filter of traces of suspended solids present in the starting water rather than the phenomenon of adsorption of dissolved metal species

TABLE III  
Effect of filtration through membrane filters on levels of Cu, Zn, Cd and Pb in centrifuged natural water<sup>a</sup>

Sample	Concentration $\pm$ standard deviation, $\mu\text{g/l}$			
	Cu	Zn	Cd	Pb
Natural water, first filtration	$4.7 \pm 0.3$	$7.6 \pm 0.3$	$0.2 \pm 0.1$	$0.2 \pm 0.5$
Natural water, second filtration	$4.4 \pm 0.3$	$7.6 \pm 0.3$	$0.1 \pm 0.1$	$0.0 \pm 0.5$
Unfiltered natural water	$5.3 \pm 0.3$	$10.2 \pm 0.3$	$0.0 \pm 0.1$	$0.4 \pm 0.5$

<sup>a</sup>Means of duplicate filtrations through  $0.4 \mu\text{m}$  Nucleopore filters.

*Replicate analysis (item 3).* The reasoning behind duplicate or quadruplicate sampling of streams was to further minimize errors arising from vertical and lateral dependence of trace element concentrations, and all other aspects of the sampling, collection and manipulation steps. Replicate filtration of independently-collected samples served to reduce variability resulting from this important source of contamination. Replicate chemical analyses in this and cooperating laboratories yielded estimates of method precisions; together, all replication steps served to provide average values with improved precisions.

*Acid purity (item 4).* With such low trace element concentrations in natural waters, the purity of acids used for sample preservation and analysis must be considered. Impurity levels in reagent grade  $\text{HNO}_3$  from various commercial sources, as specified by the manufacturer varied widely. Considering, in five brands, the highest levels of Cu, Zn, Cd and Pb of 100, 40, 5 and  $200 \mu\text{g/l}$  of concentrated acid, the incorporation of

1 ml of acid/l of sample for preservation, and 4 ml of acid/l for sample preparation, and median levels in natural waters of dissolved Cu, Zn, Cd and Pb of 2, 3, 0.07 and 0.1  $\mu\text{g/l}$  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. Use of a high purity acid for both preservation and analysis, such as Ultrex  $\text{HNO}_3$ , which generally contains the lowest impurity levels of Cu, Zn, Cd and Pb of 3, <1, <1 and 2  $\mu\text{g/l}$  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 down to a minimum. Although reagent grade acid was used for field-preservation of samples, high purity acids were employed in the analytical laboratory for virtually all work.

From actual analyses, possible contributions of 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 0  $\mu\text{g/l}$  respectively for  $\text{HNO}_3$ , and 0.14, 0.08, 0 and 0.13  $\mu\text{g/l}$  respectively for HCl. The estimated contamination levels experienced were thus entirely negligible in respect of Cu and Zn and small in respect of Cd. Only in the case of Pb was there indication of the possibility of substantial contribution from the preserving acid and that only for filtered water samples. No corrections for preserving acid contamination were applied.

*Performance of analytical methodology (item 6): water analysis by evaporation/flame atomic absorption spectrometry.* Performance characteristics—detection limits, recoveries of added analytes and accuracy determined with EPA reference solutions—of the Evap/FAAS method are presented in Tables IV–VI. These characteristics were measured at various times during the course of this project and reflect actual analytical performance for the PLUARG study; they refer solely to the analytical procedure and do not include sampling and sub-sampling variances. The convenient 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. Detection limits (Table IV), taken as 3  $\times$  standard deviations of blanks and low level samples as advocated by Kaiser<sup>7</sup> and IUPAC,<sup>8</sup> were adequate for the measurement of Cu and Zn in all natural water samples, but the method was insufficiently detective for most water samples with low natural levels of Cd and Pb.

Mean recoveries of 1.00–40.0  $\mu\text{g/l}$  of Cu, Zn, Cd and Pb added from composite standard solutions, to deionized, synthetic natural and natural

TABLE IV  
Detection limits of flame atomic absorption spectrometric methods for analysis of water and suspended sediments/residues

Element	Detection limit <sup>a</sup>	
	Evap/FAAS method for water, $\mu\text{g/l}$	Digestion/FAAS method for solids, $\mu\text{g/g}^c$
Cu	0.8	7
Zn	0.3	22
Cd	0.1-0.4 <sup>b</sup>	0.5
Pb	1.6	13

<sup>a</sup>3  $\times$  the standard deviation of low level samples based on 44-109 and 9-18 degrees of freedom for water and solid analysis methods respectively.

<sup>b</sup>Detection limit dependent on concentration factor 50 and 20 fold, respectively.

<sup>c</sup>Limited quantities (1-30 mg) of samples used.

waters prior to taking the samples through the Evap/FAAS procedure (Table V) ranged from 83% to 114% with an excellent overall mean of 100.2% (108 analyses). Fairly respectable performance was obtained even at 0.20  $\mu\text{g/l}$  added element, a level at or below detection limits.

Results of analyses of EPA Trace Metals Quality Control Samples shown in Table VI are in excellent agreement with EPA values, with an overall deviation (this work minus EPA) of  $-1 \mu\text{g/l}$ . As 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 in

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

<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.

<sup>b</sup>Data are at or below detection limits reported in Table IV.

TABLE VI

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, $\mu\text{g/l}^a$							
	Cu		Zn		Cd		Pb	
	This work	EPA	This work	EPA	This work	EPA	This work	EPA
1-575	16.2 $\pm$ 0.1	16	11.2 $\pm$ 0.1	11	5.1 $\pm$ 0.2	5.2	22.1 $\pm$ 0.2	22
2-575	67.8 $\pm$ 2.6	72	32.1 $\pm$ 0.7	30	24.1 $\pm$ 0.9	23	297 $\pm$ 6	298
3-575	96.3 $\pm$ 2.6	102	177.2 $\pm$ 1.3	174	71.2 $\pm$ 0.9	73	346 $\pm$ 6	352

<sup>a</sup>Five analyses of solution 1-575 by evaporation/flame atomic absorption spectrometry; 8-9 analyses of solutions 2-575 and 3-575 by direct aspiration/flame atomic spectrometry.

natural waters found in this work, and in addition, as these three solutions are not natural water samples but pure solutions of trace elements in acidified distilled water, measurements made on the EPA 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 during the study.

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 should be considered. Although distilled water solutions exhibited no non-atomic absorption, concentrated solutions of natural waters did (Figure 1), and operation of the spectrometer in the corrected mode was imperative for accurate analyses.

*Performance of analytical methodology: suspended sediment and residue determination and their analysis by acid digestion/flame atomic absorption spectrometry.* The sediment-on-filter samples received from the field were intended to be analyzed 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 water samples. It was also intended to determine suspended sediment concentrations independently of measurements carried out at the sampling laboratory. The total attainment of these two objectives was precluded by the following experimental difficulties. (1) The high mass (*ca* 80 mg) and variability (standard deviation *ca* 4 mg) of each 47 mm 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 sediment concentration determinations

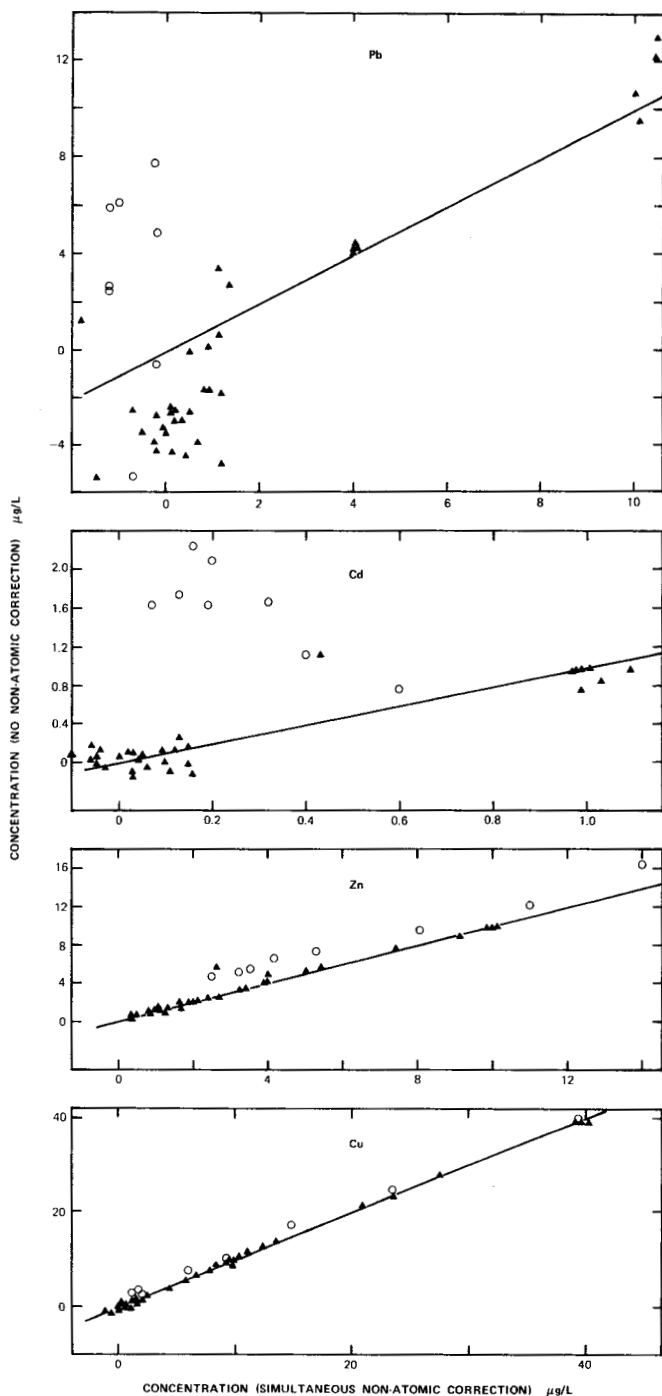


FIGURE 1 Effect of non-atomic absorption on determination of Cu, Zn, Cd and Pb, by flame atomic absorption spectrometry, in concentrated natural and distilled water samples, with or without added analytes in the latter matrix. Data have been converted to concentrations in the original samples.  $\circ$ : filtered natural water;  $\blacktriangle$ : 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



of any decent accuracy impossible. (2) 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. (3) 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 respect of (3), considering even as much as 10 mg of suspended sediment with observed median concentrations of Cu and Zn of 52 and 165  $\mu\text{g/g}$  respectively, and estimated levels in the filter of Cu and Zn of 0.8, and 0.2  $\mu\text{g}$  per 47 mm diameter filter respectively,<sup>9,10</sup> the filter would be the source of 60% and 10% of the Cu and Zn respectively in the analytical sample.

All of these problems were obviated by the use of Nucleopore membrane filters for experiments in the author's laboratory. These filters have a smaller mass and variability (mean mass and standard deviation =  $15.93 \pm 0.15$  mg,  $n=11$ ), 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 removed easily, conveniently, and almost quantitatively from the filters, permitting digestion of the sample alone.

With Nucleopore filters, the detection limit for the determination of solids by filtration, reflecting uncertainties from all facets of the procedure (filtration, drying and weighing) and subsampling, was 2.0 mg/l, and applies to determination in this laboratory of suspended sediment concentrations in 1977 water samples and residue levels in all samples. The bulk of the suspended sediment information, however, was calculated from 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 standard deviation of 1–9 mg/l, for 0–500 mg/l sediment and residue concentrations obtained in the author's laboratory. Difficulties in precisely determining suspended sediment in natural waters have been discussed by McGirr<sup>11</sup> who reported standard deviations from interlaboratory 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 Nucleopore filters<sup>10,12</sup> 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  $\mu\text{g/g}$  respectively, and levels of these elements in the filter of *ca* 0.04, 0.07, <0.001 and <0.001  $\mu\text{g}/47$  mm diameter filter respectively, the filter would contribute 7, 4, <10, and 0.2%

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 and even these considerations were precluded in this work.

Performance characteristics of the acid dissolutions/FAAS procedure for determining total trace element levels in milligram quantities of suspended sediment and residue samples are listed in Tables IV and VII. Detection limits (Table IV) reflect uncertainties from subsampling and analysis of

TABLE VII  
Accuracy of acid digestion/flame atomic absorption spectrometry in determining Cu, Zn, Cd and Pb in limited quantities of USGS rocks<sup>a</sup>

Element	Concentration $\pm$ standard error, $\mu\text{g/g}$ (triplicate analyses)					
	G-2		BCR-1		AGV-1	
	This work	Lit	This work	Lit	This work	Lit
Cu	$6 \pm 1$	$10 \pm 0.6^b$ $11^c$ $11.7^d$	$16 \pm 1$	$18.4^d$ $19^c$	$57 \pm 1$	$59.7^d$ $63^c$
Zn	$102 \pm 4$	$77 \pm 1^b$ $85^{c,d}$	$160 \pm 12$	$120^{c,d}$	$113 \pm 12$	$84^{c,d}$
Cd	$< 0.5$	$0.039^c$	$< 0.5$	$0.12^d$	$< 0.5$	$0.09^d$
Pb	$28 \pm 3$	$23 \pm 17^b$ $29^c$ $31.2^d$	$5 \pm 3$	$15^c$ $17.6^d$	$31 \pm 3$	$35.1^d$ $36^c$

<sup>a</sup>30 mg sample masses.

<sup>b</sup>Concentration  $\pm$  standard deviation reported by Rantala and Loring.<sup>13</sup>

<sup>c</sup>"Usable" values listed by Abbey.<sup>14</sup>

<sup>d</sup>Recommended values listed by Flanagan.<sup>15</sup>

small samples. Accuracy of the procedure in measuring the four trace elements in USGS rocks, G-2, BCR-1 and AGV-1, is shown in Table VII. For two of the three samples, our values for Cu and Pb agreed closely with those reported in the literature by Rantala and Loring,<sup>13</sup> Abbey,<sup>14</sup> and Flanagan,<sup>15</sup> whereas a negative bias was evident for Cu in G-2 and Pb in BCR-1. 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.

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  $\text{HNO}_3\text{-HClO}_4\text{-HF}$  met with difficulty due to the large

amount of dissolved and suspended solids. It was convenient, however, to analyze separately, the four components, supernatant liquid, residue, filtered water and suspended sediment, and get total metal concentrations by separately summing results from the former two and the latter two.

*Quality control solutions and reagent blanks (items 6 and 7).* Quality control standard solutions Q1 and Q2 and simulated natural water solutions A and B were routinely and systematically included into the sample measurement scheme when using the Evap/FAAS method, to monitor spectrometer performance. Charts of measured concentration sums and differences were plotted to follow measurement precision and systematic error throughout the study, with any large deviations from mean or expected values signalling the need for corrective measures. Procedural reagent blanks (reagents devoid of sample) were determined systematically, frequently and simultaneously with water and solid samples to gauge possible contributions from reagents, procedures and vessels used for sample processing, by virtue of endogenous content and retention from processed samples.

It was felt that blank measurements on A rather than on the unprocessed acid reagent blank (RBA) were more appropriate to use in calculations of trace element concentrations in water samples, as solution A more closely approximated sample matrices. These blank considerations are in addition, of course, to procedural reagent blanks. Solution A would have provided an excellent reagent blank for all determinations had 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 A could not be measured with certainty. An estimate, however, of *ca* 60  $\mu\text{g/l}$  was made for Cu. Solution RBA thus served as the reagent blank for Cu and also Zn, but it was decided to use A in conjunction with Cd and Pb analyses, the assumption being that Cd and Pb levels, in A were zero. Later independent analyses by optical emission spectrography for Cu and Pb and by spark source mass spectrometry for Pb revealed *ca* 40 and 30  $\mu\text{g/l}$  for Cu and Pb respectively in solution A. The former is in very good agreement with our estimate of 60  $\mu\text{g/l}$ ; these concentration estimates supported the decision not to use A as a blank for Cu. On the other hand, the estimated 30  $\mu\text{g Pb/l}$  being less than the FAAS detection limit for Pb, justified the choice of A as a blank for Pb. No independent analyses were available for Zn and Cd.

*Round robin studies for water analysis (item 8).* This laboratory participated in two trace metals round robins sponsored by PLUARG.

Compared to median levels of dissolved trace metals found in natural waters, the six non-blank samples submitted contained metal and acid concentrations 40–10000, and 100 times respectively as high. Hence although our performance was good, the fact that the samples did not approximate natural waters precluded strict estimation of method performance in respect of natural waters.

*Intercomparison of data obtained by different methodologies and analysts (item 9).* The participation of other laboratories in water and solid analyses, using independently different analytical methodologies was considered to be a cornerstone in the data quality assurance program. The philosophy behind this approach was that agreement of data generated by different analysts and techniques leads to analytical results with enhanced validity. Including the author's laboratory, four laboratories applied four different analytical methods to the analysis of water samples, whereas two laboratories analyzed suspended sediment and residue samples. In addition, data was available from three laboratories determining suspended sediment concentrations in waters.

A discussion of the intercomparison of results for water analyses has already been presented.<sup>1,2</sup> In respect of analyses of small quantities of solid samples by FAAS and OES, good agreement was observed among data for Cu, whereas FAAS data showed relative positive and negative biases for Zn and Pb respectively. It was possible, however, to extract decent mean data (e.g. blocks d and e of Table VIII). Overall, good agreement among analysts and the diverse approaches was found, with the result being a population of satisfactory analytical data.

*Sample solution stability (item 10).* Subsamples of unfiltered and filtered natural water returned from two collaborators were analyzed for Zn by the author. Comparison of this information with analyses on the author's subsamples 3–8 months previously (a mean deviation of 0.6  $\mu\text{g/l}$  for 16 solutions with a median concentration of 6  $\mu\text{g/l}$ ) suggested that, at least insofar as Zn was concerned, solution instability was not of consequence. It must be emphasized that, as the two sets of analyses refer to different subsamples, the observed behaviour reflects both solution stability *and* any possible subsampling variability, inadvertant contamination, effects of transportation, etc.

### **Total and extractable trace elements in natural waters**

It is evident when dealing with accurate analytical trace element concentration data for natural waters containing two phases, the question of analysis for total levels must be considered. Most published

TABLE VIII  
Examples of typical trace metal concentration data in respect of natural water analyses<sup>a</sup>

Block	Sample	Mean concentration of solids, mg/l	suspended sediment	residue			
a	A		9 ± 7(3)	13 ± 1(2)			
	B		80 ± 5(5)	26 ± 2(1)			
	C		329 ± 8(2)	228 ± 9(1)			
Mean concentrations of dissolved + extractable trace metals in unfiltered waters, µg/l							
b	A		2.8 ± 0.8(2, 5, 16)	4.6 ± 0.7(2, 2, 10)	0.06 ± 0.02(2, 3, 12)	Pb	1.3 ± 0.7(2, 4, 9)
	B		5.3 ± 0.8(2, 5, 11)	7.9 ± 0.8(2, 2, 6)	0.03 ± 0.02 (2, 3, 8)		1.3 ± 0.8(2, 3, 5)
	C		44 ± 3 (2, 4, 22)	70 ± 4 (2, 2, 10)	0.29 ± 0.02(2, 4, 19)		25 ± 4(2, 4, 24)
Mean concentrations of trace metals in filtered waters, uncorrected for filtration contamination, µg/l							
c	A		3.2 ± 0.9(2, 5, 15)	—	0.08 ± 0.00(2, 3, 12)	Pb	0.36 ± 0.03(2, 2, 4)
	B		2.9 ± 2.3 (1, 1, 1)	3.4 ± 1.6(1, 1, 1)	—		—
	C		20 ± 2 (1, 1, 1)	9.8 ± 1.6(1, 1, 1)	—		13.3 ± 0.1(1, 1, 1)
Mean concentrations of trace metals in suspended sediments, µg/g							
d	A		90 ± 6(1)	200 ± 55(1)	—	Pb	200 ± 36(1)
	B		54 ± 3(4)	160 ± 28(4)	1.1 ± 0.8(3)		75 ± 16(5)
	C		32 ± 3(5)	110 ± 25(5)	0.1 ± 0.1(3)		130 ± 16(5)

Mean concentrations of trace metals in residues, $\mu\text{g/g}$						
		Cu	Zn	Cd	Pb	
e	A	$0 \pm 2(2)$	$35 \pm 16(2)$	$2 \pm 1(2)$	$8 \pm 8(2)$	
	B	$4 \pm 1(4)$	$4 \pm 22(4)$	$0.0 \pm 0.2(1)$	$53 \pm 18(4)$	
	C	$9 \pm 1(3)$	$17 \pm 13(3)$	$0.0 \pm 0.2(1)$	$44 \pm 21(3)$	
Mean concentrations of dissolved trace metals, $\mu\text{g/l}$						
		Cu	Zn	Cd	Pb	
f	A	$2 \pm 2$	—	$0.05 \pm 0.05$	$0.1 \pm 0.2$	
	B	$2 \pm 3$	$0.2 \pm 2.8$	—	—	
	C	$19 \pm 3$	$7 \pm 3$	—	$13.1 \pm 0.3$	
Mean concentrations of suspended trace metals, $\mu\text{g/l}$						
		Cu	Zn	Cd	Pb	
g	A	$0.8 \pm 0.6$	$2 \pm 2$	—	$2 \pm 1$	
	B	$4.3 \pm 0.4$	$13 \pm 2$	$0.09 \pm 0.06$	$6 \pm 1$	
	C	$11 \pm 1$	$36 \pm 8$	$0.03 \pm 0.03$	$43 \pm 5$	
Mean total concentrations of trace metals, $\mu\text{g/l}^b$						
		Cu	Zn	Cd	Pb	
h	A	$3 \pm 1$	$5 \pm 1$	$0.08 \pm 0.02$	$2 \pm 1$	
	B	$6 \pm 2$	$8 \pm 1$	$0.03 \pm 0.02$	$3 \pm 1$	
	C	$38 \pm 11$	$58 \pm 19$	$0.29 \pm 0.02$	$46 \pm 13$	

<sup>a</sup>These data are representative of low, median and higher values determined in this work and are presented with associated standard errors; (n): no. of analyses; (n<sub>1</sub>, n<sub>2</sub>, n<sub>3</sub>): no. of field subsamples, no. of analytical methods, total no. of analyses.

<sup>b</sup>Selected data; see text.

methodologies for determination of "total" trace element levels in natural water samples advocate treatment of the sample with acid, typically  $\text{HNO}_3$  followed by  $\text{HCl}$ , prior to determination.<sup>16-19</sup> 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<sup>20</sup> and Bradshaw *et al.*<sup>21</sup> 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.

Based on analytical data amassed in this study, graphs of the ratio, concentration of dissolved+extractable trace element/total concentration of trace element, versus suspended sediment concentration, presented in Figure 2 demonstrate some interesting relationships. 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 high sediment. 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 0. 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 19000 mg/l, showed ratios ranging from 0.46 to 0.85 for the different metals, in general lower than samples in the 0-740 mg/l suspended sediment range. Thus we find methodology not involving complete destruction of particulate material, giving possible inaccurate total trace element concentrations.

### Discussion of data

Examples of typical concentration data, depicting low, median and high levels of the trace metals in three natural water samples are summarized in Table VIII, which together with Table II contains all information required for the step by step calculations. Data in blocks a-e is primary information leading to final data in blocks f-h. Trace metal concentrations in blocks b and c are means of extensive interlaboratory analyses,<sup>2</sup> and present dissolved+extractable levels. Concentrations in the solid suspended sediment and residue components (blocks d and e) reflect total analyses also based on interlaboratory cooperation. Application of filtration contamination corrections to the data in block c yielded concentrations of dissolved species listed in block f. Concentrations of metals occurring in suspended form (block g) were obtained directly from suspended sediment concentrations in the stream waters and trace metal

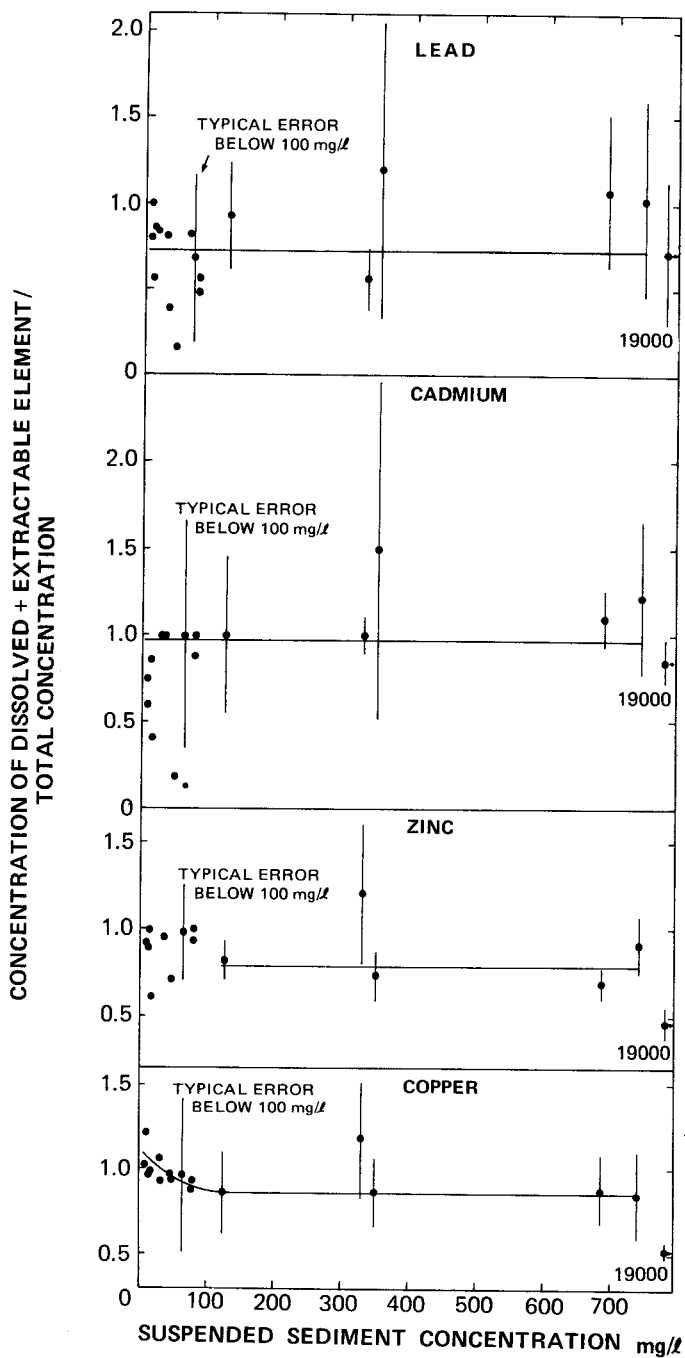


FIGURE 2 Relationships of the ratio: dissolved + extractable trace element concentration/total concentration, for Cu, Zn, Cd and Pb, to concentration of suspended sediment in the stream waters.



levels in the sediment (blocks a and d respectively). Total levels of the trace metals are given in block h and are discussed below.

Total concentrations of Cu, Zn, Cd and Pb in natural water samples were arrived at in two distinctly different ways, viz (1) summation of trace element concentrations obtained by analysis of unfiltered samples and contributions of residues, and (2) summation of dissolved concentrations in filtered water samples and contributions of suspended sediments. Importantly, one technique (1) does *not* involve filtration. Total concentrations thus obtained are compared in Table IX for the same three samples. The last column lists selected data calculated or chosen from the two independently calculated concentrations; these are also the data presented in block h of Table VIII. 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

TABLE IX  
Examples of typical total concentrations of Cu, Zn, Cd and Pb in natural water samples

Sample	Total concentration $\pm$ standard error, $\mu\text{g/l}^a$		
	Calculated from levels in filtered sample + suspended sediment	Calculated from levels in unfiltered sample + residue	Selected data <sup>b</sup>
	Copper		
A	2.8 $\pm$ 1.9	2.8 $\pm$ > 0.8	2.8 $\pm$ 1.4
B	5.9 $\pm$ 2.8	5.3 $\pm$ 0.8	5.6 $\pm$ 2.0
C	29 $\pm$ 3	46 $\pm$ 3	38 $\pm$ 11
	Zinc		
A	—	5.0 $\pm$ 0.8	5.0 $\pm$ 0.8
B	13 $\pm$ 4	8 $\pm$ 1	8 $\pm$ 1
C	43 $\pm$ 9	74 $\pm$ 5	58 $\pm$ 19
	Cadmium		
A	> 0.05 $\pm$ > 0.05	0.08 $\pm$ 0.02	0.08 $\pm$ 0.02
B	> 0.09 $\pm$ > 0.06	0.03 $\pm$ 0.02	0.03 $\pm$ 0.02
C	> 0.03 $\pm$ > 0.03	0.29 $\pm$ 0.02	0.29 $\pm$ 0.02
	Lead		
A	1.9 $\pm$ 1.5	1.4 $\pm$ 0.7	1.6 $\pm$ 1.0
B	> 6.0 $\pm$ > 1.3	2.7 $\pm$ 0.9	2.7 $\pm$ 0.9
C	56 $\pm$ 5	35 $\pm$ 6	46 $\pm$ 13

<sup>a</sup>Data presented here are means over all subsample and analytical methodologies; > indicates one datum for the summation is missing; — indicates no concentration data are available for both water samples and solids.

<sup>b</sup>Refer to text.

error reported is the larger of (a) the larger standard error/ $\sqrt{2}$  or (b) the standard deviation of the mean (estimated as  $0.886 \times$  the difference of the two results)/ $\sqrt{2}$ .

Total concentrations calculated in these two ways should obviously agree. Where data in Table IX appear for both methods of determination, agreement is indeed quite acceptable. A comparison of all available pairs of data made in Figure 3, shows reasonably good agreement between the two methods of calculation.

### Concluding remarks

The outcome of extensive experimental deliberations described in this report was a body of data from which were extracted fairly reliable estimates of dissolved, suspended sediment-contributed and total trace metal concentrations in waters of streams draining selected agricultural watersheds. 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 undergoing comparative analyses. This suggests that analytical information on the samples *analyzed* can be accepted with a good degree of confidence. Whether this confidence can be extrapolated to the *actual* stream water is another question dependent on sampling and sample manipulation considerations prior to chemical analysis. Keeping this in mind, Cu and Zn data are deemed reliable due to the easily measurable levels present in the natural systems and because corrections for sample manipulations could be applied where required. Information on Cd and Pb is considered to be less reliable due to the much lower natural concentrations of these metals and the attendant analytical uncertainties. For Cd, even though the comparative performances of the various electrochemical and electrothermal-AAS methodologies was good (cf Figure 3 in ref. 2) over concentration ranges encompassing levels found in the stream waters, possible contamination from acids and contamination and losses during sample manipulations not accounted for, suggest the indicated concentrations be accepted with reserve. In the case of Pb, uncertainty in the data results from identical sample manipulation considerations as for Cd. In addition, although good intermethod agreement was observed at high Pb levels (cf Figure 4 in ref. 2), weak agreement was found at low levels (cf Figure 5 in ref. 2), among the electrochemical and electrothermal-AAS methods capable of quantitating the low natural levels of this element. As a matter of fact, conclusions regarding Pb, arising from investigations not applying the essential techniques and careful execution followed by laboratories specializing in Pb determinations, must be treated with caution.<sup>22</sup>

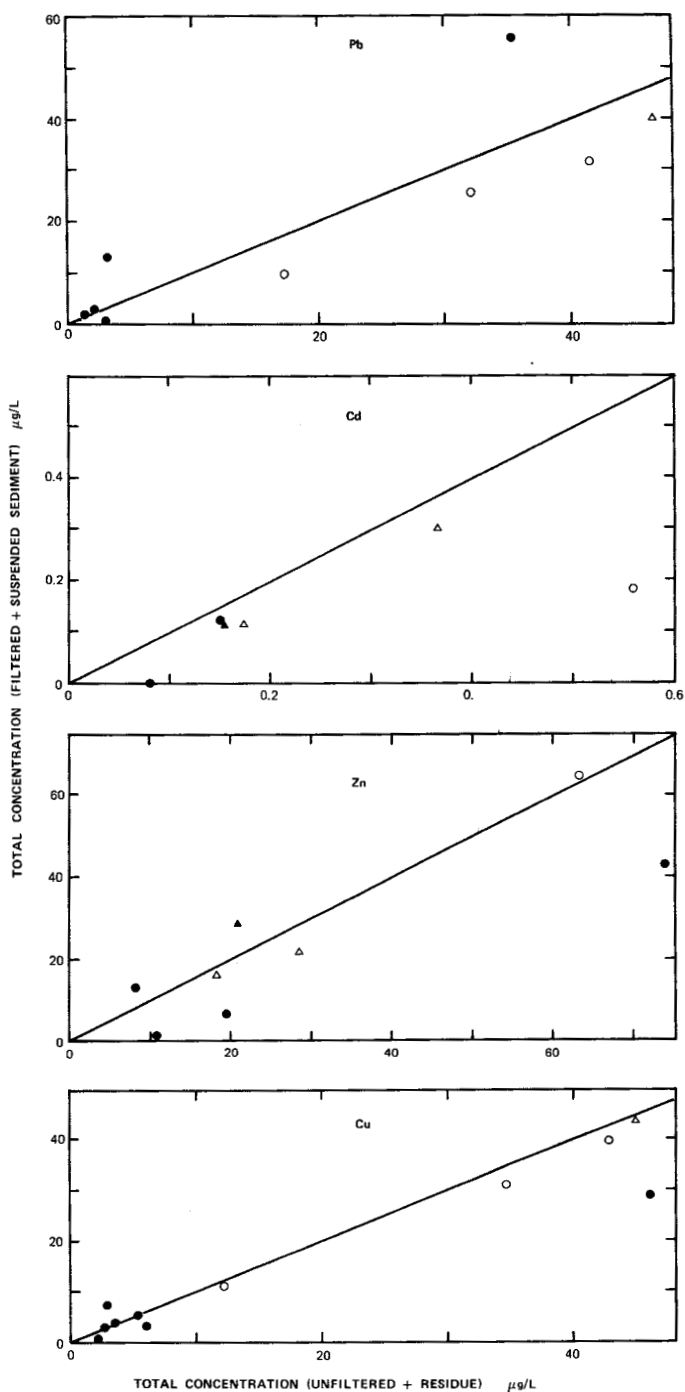


FIGURE 3 Relationships between total concentrations of Cu, Zn, Cd and Pb in natural waters determined as (a) sum of concentrations in filtered water + suspended sediment and (b) sum of concentrations in unfiltered water + residue (acid-leached sediment). ●: 1976 field-filtered samples; ○, △, ▲: 1977 laboratory-filtered samples; △, ▲: actual total concentrations have been reduced 10- and 100-fold respectively for plotting. The straight

Virtually every datum has associated with it a standard error giving a measure of precision. Since the typical datum is also the mean over different subsamples and particularly over several independently different analytical methodologies, the standard error may also be construed as an indication of accuracy. Although considerable effort and diligence were directed to the generation of analytical information regarding trace element concentrations in stream waters, it may be observed from Table VIII that somewhat large imprecisions are associated with some data. This stems from normal procedural errors augmented by some unusually large errors arising from the use of limited quantities of material, the application of analytical methods near detectivity limits, together with the propagation of error during arithmetic manipulation. The data compares very well with counterpart literature data available for these and other "unpolluted" natural fresh waters<sup>3</sup> and is considered to provide a realistic data base for consideration of metal transport and storage mechanisms discussed in the final report on this study.<sup>3</sup>

### **Critique and proposals for future studies**

As a consequence of the quality assurance program, it was possible to enhance the reliability of the information over that which would have resulted from a less thorough undertaking. The quality assurance approach was also instrumental in identifying weak points in the study and in leading to proposals for future protocols for similar studies. Some of the weak points defined were: high and variable field filtration blanks, poor quality distilled water used in the field for manipulation controls, high acid blanks for some sample-element combinations, and suboptimal performance of some analytical methodologies due to biases or insufficient detectivities.

The following are experimental details which should be considered for incorporation into future studies:

- 1) Replicate sampling and replicate preparation of unfiltered and filtered waters is pertinent to assessment of variability of the sampling/field processing procedures, and should be continued. Several sets of blind replicates should also be provided throughout the study period to further assess sampling/analysis variability.

- 2) That the high and variable field-processing correction factors could be reduced substantially was demonstrated by filtration experiments in the laboratory. Whether the contamination problem is specific to the field, or the result of other factors must be ascertained to determine whether field-filtration be specified for future studies. Filtration must, however, be carried out as soon as possible after sample collection. Distilled water

utilized for control of field processing contained high and variable quantities of trace elements of interest. Water, either multiple distilled or deionized, of much better quality must be used in the sampling protocol. Pressure-filtration rather than vacuum-filtration should be considered to reduce evaporation losses.

3) Nuclepore filters were found to be superior to Sartorius filters and their use for field and laboratory filtration should be continued. With careful filtration, suspended sediment concentrations can be determined by weighing the dry filters and contents, with superior precision and accuracy. Use of Nuclepore filters also permits analysis of filter-free solids, precluding the question of contamination by the filter matrix.

4) 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. Similarly, little can be said concretely concerning the behaviour of Cd and Pb in filtration studies of natural waters. 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.

5) Use of preservative acid volumes greater than 1 ml/l should be considered especially for samples with high suspended sediment loads 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. 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.

6) 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. 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.

Application of more detective methodologies would cut down on sample volume requirements and make easier the task of sampling.

7) As the collaboration in the project of other laboratories 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 solutions, and sediment reference materials should be monitored throughout the study. Subsamples should be circulated among the laboratories to provide a check on laboratory performance with real samples, sub-sampling 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 samples, should reduce errors in overall means.

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