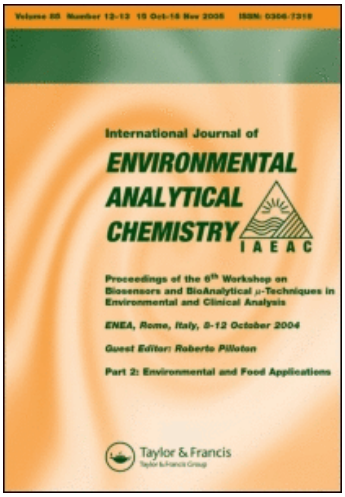

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Interlaboratory Analysis of Natural Fresh Waters for Copper, Zinc, Cadmium and Lead

M. Ihnat[a]; A. D. Gordon[a]; J. D. Gaynor[b]; S. S. Berman[c]; A. Desaulniers[c]; M. Stoeppler[d]; P. Valenta[d]
[a] Chemistry and Biology Research Institute, Ottawa, Ontario, Canada [b] Research Station, Agriculture Canada, Harrow, Ontario, Canada [c] Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada [d] Institute for Chemistry, Institute 4, Nuclear Research Centre, Juelich, Juelich, Federal Republic of Germany

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Interlaboratory Analysis of Natural Fresh Waters for Copper, Zinc, Cadmium and Lead

M. IHNAT AND A. D. GORDON

Chemistry and Biology Research Institute, Agriculture Canada, Ottawa, Ontario K1A 0C6, Canada

J. D. GAYNOR

Research Station, Agriculture Canada, Harrow, Ontario N0R 1G0, Canada

S. S. BERMAN AND A. DESAULNIERS

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

M. STOEPPLER AND P. VALENTA

Institute for Chemistry, Institute 4, Nuclear Research Centre, Juelich, D-5170 Juelich, Federal Republic of Germany.

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Disclaimer

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A multitechnique, multilaboratory approach was pursued for the analysis of natural fresh waters for selected trace elements as one important facet of a data quality assurance program

to generate reliable analytical information. Unfiltered and filtered natural water samples were analyzed for dissolved and extractable levels of Cu, Zn, Cd annd Pb by four laboratories employing four independently different analytical methodologies centering on evaporation- and solvent extraction- flame atomic absorption spectrometry, electrothermal atomization atomic absorption spectrometry and differential pulse anodic stripping voltammetry. Considering the different laboratories and methodologies, subsampling steps and low element levels, good agreement of analytical results was realized yielding a population of satisfactory data useful for computation of reliable estimates of total and dissolved trace element concentrations.

KEY WORDS: Natural water, Trace metals, Interlaboratory analysis, Atomic absorption spectrometry, Anodic stripping voltammetry.

INTRODUCTION

The undertaking of a project[1] on the determination and assessment of relationships between selected heavy metals in stream waters, suspended sediments, bottom sediments and soils within six selected Ontario agricultural watersheds draining into the lower Great Lakes, necessitated reliable analytical information regarding concentrations of Cu, Zn, Cd and Pb in waters and suspended sediments. The very low concentrations (μg/L and sub μg/L) at which these trace elements are normally found in natural waters required careful execution of sampling and analysis. In the absence of certified natural water reference samples, of all the steps taken to insure analytical data of some reliability, the participation of four laboratories using four independently different (a total of five) approaches to sample treatment and trace metal measurement was deemed the most important. The premise was that suitable agreement of results generated by different analysts and analytical methodologies brought to bear on subsamples of the same sample leads to analytical results with an enhanced degree of confidence over that for results from one technique or laboratory.

The primary objective of independent analyses was to arrive at improved estimates of trace metal concentrations in natural water samples. Intercomparison of analytical results from the different laboratories presented in this report is thus, in the main, from this viewpoint; discussion of method characteristics and performance is secondary.

EXPERIMENTAL

Sampling and sample preparation

Sampling procedures are detailed elsewhere.[1,2] In brief, typically 1L water samples were collected either with a manual or peristaltic pump sampler, transferred to acid-cleaned linear polyethylene bottles, preserved with

2 mL/L of (1+1)HNO_3 or (1+1)HCl, shipped to the laboratory of the senior author (MI) and stored at 4° until analysis. Nitric acid was the preservative for solutions scheduled for analysis by atomic spectrometry, whereas HCl was the required matrix for anodic stripping voltammetry. Filtered natural water samples (0.45 μm cellulose acetate membrane) together with unfiltered and filtered distilled water samples were also prepared in the field.

Some time after receipt from the field, water samples were subsampled by the senior author to provide aliquots of identical samples for analysis by the four participating laboratories. Samples were removed from cold storage, sediments resuspended by shaking, and suitable portions were transferred into 60 to 200 mL acid-cleaned, sample-rinsed linear polyethylene bottles. Five hundred + mL of each sample was retained, usually in the original container, for analysis by the central laboratory; the other subsamples were shipped to the three cooperating laboratories. Samples for interlaboratory analysis were thus unfiltered and filtered, natural fresh and distilled waters.

Analytical measurement procedures

Analytical methodologies used and analysts involved are listed in Table I,

TABLE I
Analytical methods for water analysis

Method description	Code	Principal investigators
Heat evaporation/flame atomic absorption spectrometry	Evap/FAAS	M. Ihnat and A. D. Gordon
Electrothermal atomization/ atomic absorption spectrometry with Perkin-Elmer heated graphite atomizer	HGA/AAS	M. Stoeppler
Differential pulse anodic stripping voltammetry with hanging mercury electrode and mercury film electrode	DPASV/HMDE DPASV/MFE	M. Stoeppler and P. Valenta
Electrothermal atomization/ atomic absorption spectrometry with Varian Techtron carbon rod atomizer	CRA/AAS	S. S. Berman and A. Desaulniers
Solvent extraction/flame atomic absorption spectrometry	Solv. ext/FAAS	J. D. Gaynor

and are described below. Analytes determined were acid-or acid-and solvent-extractable Cu, Zn, Cd and Pb, with median concentrations in the natural waters investigated of 2, 3, 0.1 and 0.1 μg/L respectively, in dissolved form, and 4, 17, 0.1, 4 μg/L respectively as total levels.[1,2]

Evaporation/Flame Atomic Absorption Spectrometry. Details of this method are presented elsewhere.[1,2] In summary, typically 500 mL of acid-preserved unfiltered, and filtered natural and distilled water was heat concentrated 20–50 fold in a polytetrafluoroethylene beaker within a clean microenvironment after the design of Thiers.[3] Metal concentrations were determined by comparing absorbances in air-acetylene flames of sample solutions with those of suitable standard solutions in identical acid matrices, using a Varian Techtron AA5 atomic absorption spectrometer equipped with an IM6D amplifier with digital readout. Absorbances were measured at wavelengths for Cu, Zn, Cd and Pb of 324.8, 213.9, 228.8 and 217.0 nm respectively, corrected for non-atomic absorption by simultaneous use of a H_2 hollow cathode lamp.

Electrothermal Atomization/Atomic Absorption Spectrometry-Perkin-Elmer Heated Graphite Atomizer. 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.[4] Fifty μl aliquots of 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 solution 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 measurements were carried out on a Jarrell-Ash 811 atomic absorption spectrometer in conjunction with the above systems at a wavelength of 283.3 nm, using the 282 nm non-absorbing line for non-atomic absorption compensation. After analyses 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.

Differential Pulse Anodic Stripping Voltammetry with Hanging Mercury Drop Electrode and with Mercury Film Electrode. Concentration data for early analysis of a small number of samples were obtained using the DPASV/HMDE technique. All other (the bulk) analyses were done with

the technique of DPASV/MFE[5,6] using an adapted Polarographic Analyzer Model 174A (Princeton Applied Research) in connection with a Hewlett-Packard X-Y recorder Model 7004B. The rotating mercury film-coated glassy carbon electrode was a modified construction of Sipos, Magjer and Branica.[7] Both HNO_3- and 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.

Electrothermal Atomization/Atomic Absorption Spectrometry-Varian Techtron Carbon Rod Atomizer. Measurements for all four elements were conducted with a Varian Techtron electrothermal atomizer, CRA 63, with a modified Model AA5 spectrometer using 5 μl injections. All solutions were analyzed with no treatment except dilution of those too concentrated for this technique. 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_3. 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 linear regression lines whereas 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 D_2 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. For low element levels, multiple 5 μl injections were made with drying in-between, and concentrations were calculated from calibration curves prepared in an identical manner.

Solvent Extraction/Flame Atomic Absorption Spectrometry. The organic extraction procedure for Cu, Cd, Pb and Zn was modified from Sachdev and West.[8] A 100 ml aliquot of the sample was pre-conditioned with 20 ml 5% ammonium tartrate and adjusted in the presence of *p*-nitrophenol indicator to pH 6 with (1+1) NH_4OH or tartaric acid crystals. The sample was saturated with 2 ml *n*-butyl acetate then extracted 1 min with 8 ml of extractant, which contained 0.4 g dithizone, 6.0 g quinolinol, and 200 ml acetylacetone in 1 L n-butyl acetate. The aqueous phase was discarded after separation for 20 min and the organic phase was brought to 10 ml with extractant. Organic standards were prepared by adding metal standard solutions to 100 ml of deionized water and extracting as indicated for samples. Organic solutions were aspirated into an air/acetylene flame of an Instrumentation Laboratory 251 spectrometer

and absorbances were read after four sec integration. Standards and instrument drift were checked after analysis of five samples. Air/acetylene ratios, and aspiration rates were optimized for each element prior to measurement. Nonatomic absorption was corrected simultaneously by a hollow cathode H_2 lamp. Concentrations of elements in samples were calculated from linear regression equations of absorbances against concentrations of standards.

RESULTS AND DISCUSSION

If a reference natural fresh water sample, certified for dissolved and either suspended or total concentrations of the trace metals of interest, had been available, it could have been incorporated into the analytical scheme to transfer accuracy from it to the results generated. It would have been thus conceivable for all analyses to have been performed by one laboratory with some estimate of reliability. This not being the case, the next best, and perhaps the only satisfactory, approach was chosen, that of having analyses performed by completely independent analytical methods and in addition, by different analysts. Concordance in results thus obtained, would indicate more confidence in the data than otherwise obtained.

Intercomparison of data obtained by different methodologies

Detection limits of the five analytical methods presented in Table II were either provided by the investigators or estimated by the senior author from data supplied. Different definitions of detection limit were used, and

TABLE II

Detection limits of analytical methods

Method	Detection limit[a], μg/L			
	Cu	Zn	Cd	Pb
Evap/FAAS	0.8	0.3	0.1 – 0.4	1.6
HGA/AAS	0.5	—	0.01	0.2
DPASV/HMDE	0.1	—	0.05	0.05
DPASV/MFE[b]	0.05	—	0.001	0.005
CRA/AAS	0.1	0.05	0.005	0.05
Solv. ext/FAAS	0.5 – 1.6	0.3 – 1.1	0.5 – 1.1	2.1 – 5.1

[a]Detection limits usually defined as 2 or 3x standard deviation of replicate analyses of reagent blanks and low level samples; ranges reflect differences in technique (Evap/FAAS) or different runs (Solv. ext/FAAS).

[b]Detection limits are based on analyses of real samples; Stoeppler reports that with standard solutions, detection limits are μg/L (element): 0.002 (Cu), 0.0001 (Cd) and 0.0002 (Pb).

no attempt was made to bring all to a common basis. The data presented should, however, demonstrate the relative capabilities. Flame AAS methods, preceded by concentration had the highest (poorest) detection limits followed 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 clearly have superior detection capabilities. Stoeppler[4] reported impressive detection limits by DPASV/MFE of 0.0001 and 0.0002 μg/L for Cd and Pb respectively in standard solutions.

Intercomparisons of data from the different methods, for unfiltered and filtered natural and distilled water subsamples are presented in Figures 1–5. Because analytical methodologies were not standardized, it was recognized that, in principle, different forms of the metals would have been measured by the various methods. It is conceivable that different combinations of several different metal parameters such as dissolved ionic, dissolved complexed, colloidal, acid- or acid-and solvent-extractable species would have been amenable to detection depending on the nature of the sample, sample treatment and measurememt technique. The Evap/FAAS procedure involved hot (concentrated, $\gtrsim 1.6\,M\,HNO_3$) acid leaching during the evaporation step. The electrothermal techniques (HGA and CRA) measured total elements in the supernatant solution, occurring naturally and leached-out by the 0.016 M preserving acid. The electrochemical methods responded to free metals in the same supernatant liquid, whereas solvent extraction relied on the extraction, via chelation, of metals from suspended and dissolved water components. Thus, in general, the different methodologies applied as described in this report, may be said to measure dissolved + extractable trace metal levels. In the Figures, dissolved + extractable concentrations determined by different techniques are plotted against levels determined by either Evap/FAAS or CRA/AAS and are related to lines of unit slope to gauge relative performances of the methods under the conditions of this study.

Copper. Copper concentrations in natural water samples were sufficiently high to permit analysis by all techniques and generally good agreement was observed among all the five methods (Figure 1). 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

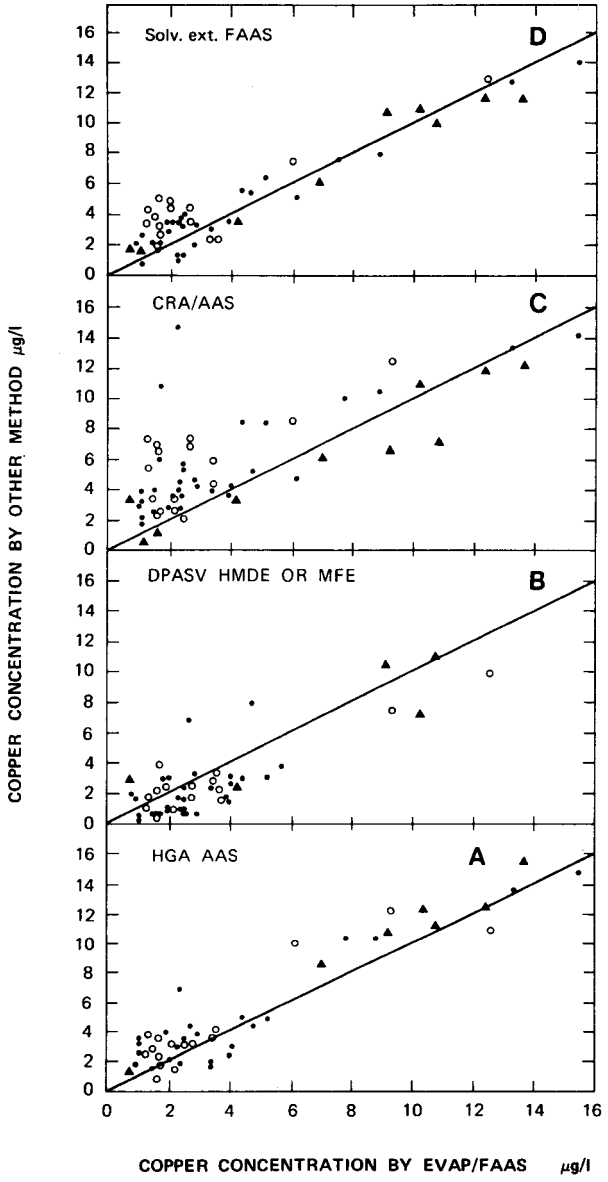

FIGURE 1 Copper concentrations in unfiltered and filtered natural and distilled water samples measured by different analytical methods, compared with values determined by evaporation/flame atomic absorption spectrometry. In this and other figures, ●: unfiltered natural water; ○: filtered natural water: ▲: distilled water: the lines represent unit slope.

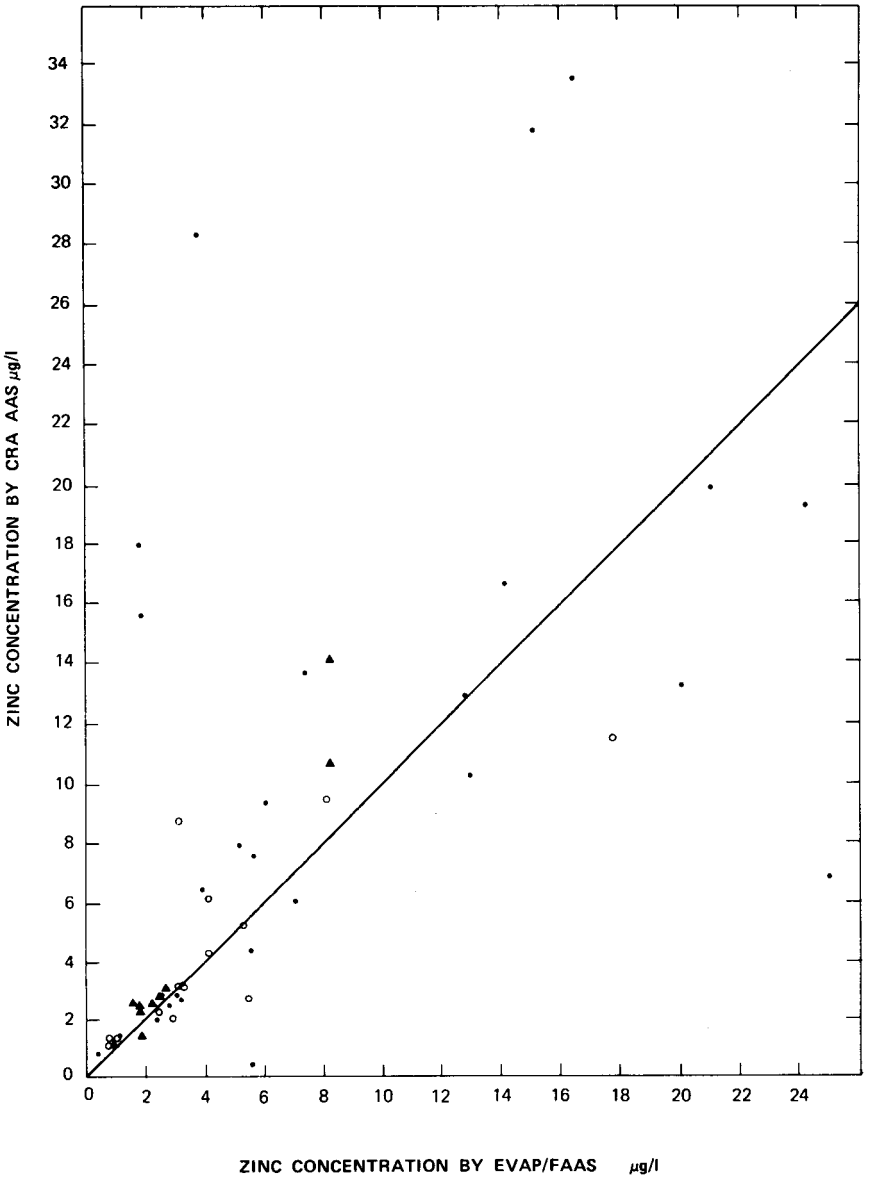

FIGURE 2 Zinc concentrations in unfiltered and filtered natural and distilled water samples measured directly by carbon rod atomization/AAS, and by evaporation/flame AAS.

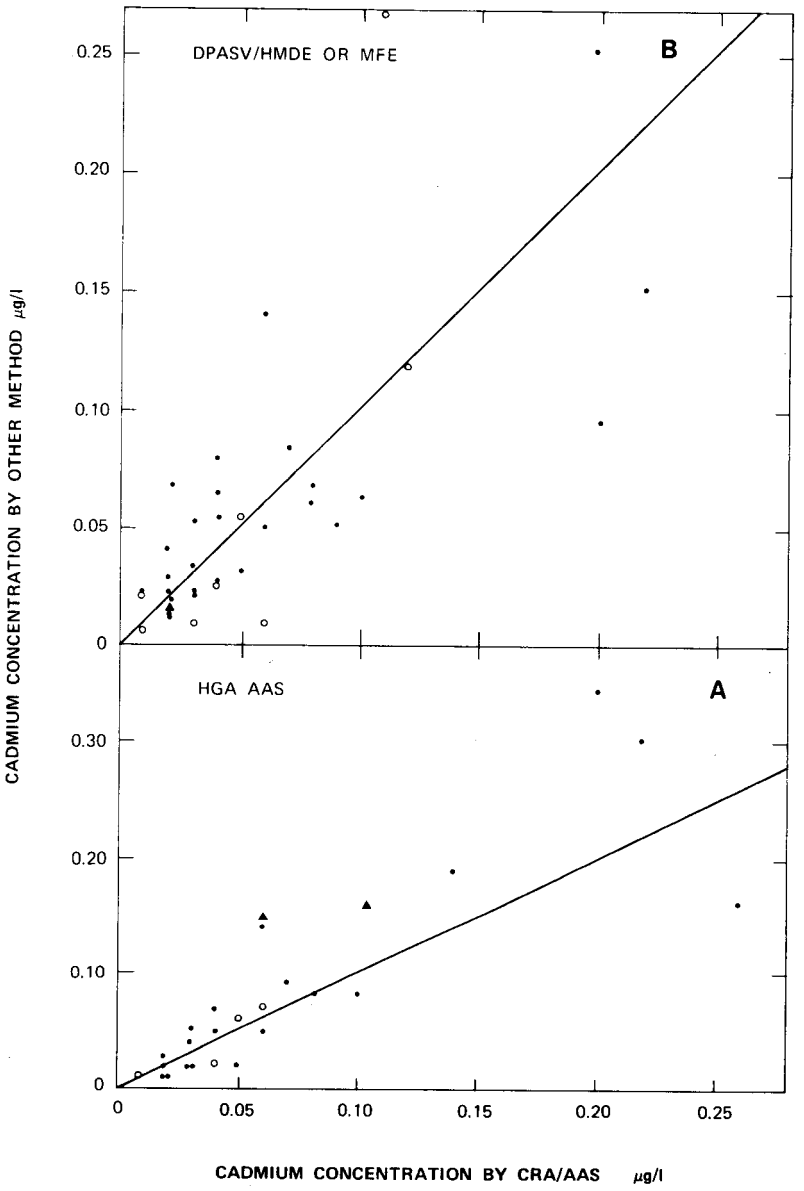

FIGURE 3 Cadmium concentrations in unfiltered and filtered natural and distilled water samples measured by different analytical methods, compared with values obtained by carbon rod atomization/AAS.

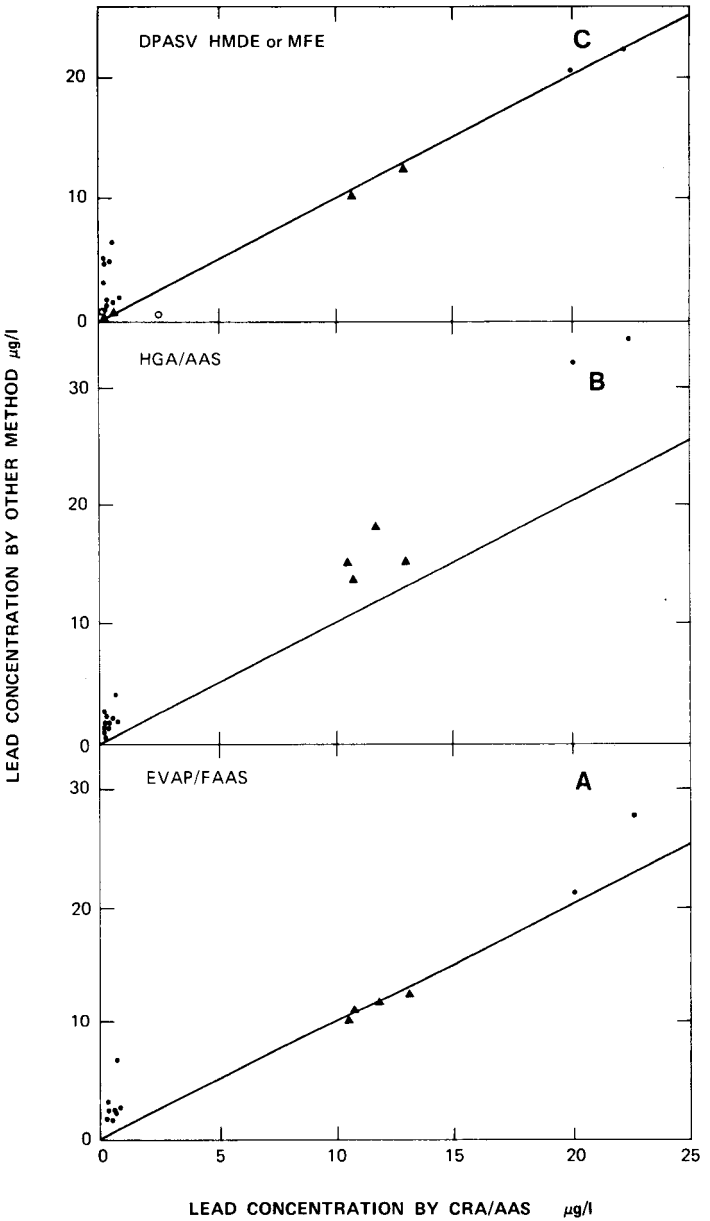

FIGURE 4 Lead concentrations in unfiltered and filtered natural and distilled water samples measured by different analytical methods, compared with values obtained by carbon rod atomization/AAS.

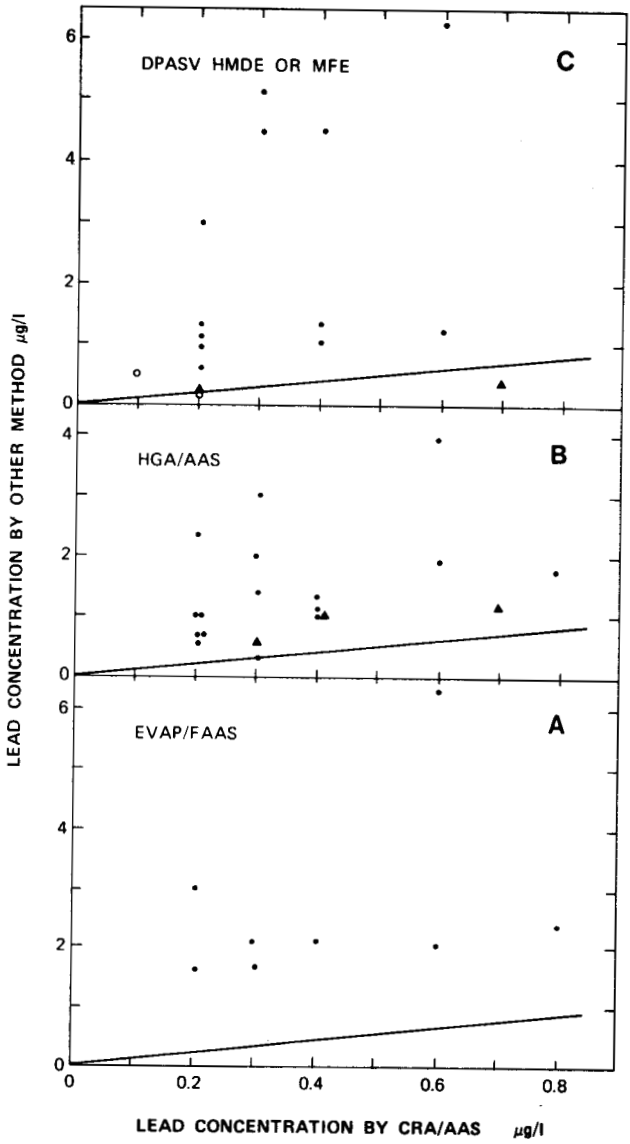

FIGURE 5 Low-level lead concentrations in unfiltered and filtered natural and distilled water samples measured by different analytical methods, compared with values obtained by carbon rod atomization/AAS.

concentrations. The generally more concordant behaviour with distilled water as opposed to natural water suggests that the biases observed with natural water samples reflect the measurement of different copper species and/or result from matrix interferences.

Zinc. Three laboratories determined zinc using the methods Evap/FAAS, CRA/AAS and Solv. ext/FAAS. Due to high values produced by the last technique resulting from instrument malfunction, only data from Evap/FAAS and CRA/AAS were considered for comparison (Figure 2). The graph of CRA/AAS-generated versus Evap/FAAS-generated data is characterized by highly scattered points. Although reasonable agreement seems evident for distilled and filtered natural water samples, electrothermal analysis of several unfiltered natural waters indicates a positive bias relative to Evap./FAAS. Whether this stems from natural sample effects (interferences) in CRA/AAS or spurious contamination by zinc is unknown. It should, however, be remembered that contamination by zinc is an ubiquitous problem in analytical chemistry as attested to by the occasional high values (again usually for unfiltered natural waters) also experienced by the Evap/FAAS technique and excessive scatter evident in Figure 2.

Cadmium. The two electrothermal atomization/AAS procedures and DPASV were sufficiently detective to measure the low concentrations of cadmium in natural water samples but FAAS techniques were not. Considering the sub part per 10^9 levels of cadmium present (median total cadmium level $= 0.08\,\mu g/L$) in the natural water samples and the divergent analytical methodologies employed, agreement among the techniques is good (Figure 3).

Lead. Data on lead were provided by Evap/FAAS, the electrothermal and electrochemical techniques. With the majority of natural water samples containing lead below $2\,\mu g/L$, flame AAS techniques lack sufficient detection capabilities. With reference to lead in the higher concentration regions ($> 10\,\mu g/L$) depicted in Figure 4, 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 lead 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 (Figure 5). 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 be explained as a con-

tamination artifact; the fact that all values reported are near the detection limit might also have a bearing. That similar biases occurred for methods without sample processing and operating well above detection limits is surprising. The possibility that blanks were not under control must be considered.

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 metal species. With the possible exception of performances with low level lead samples, however, 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. It thus appeared that questions of subsampling and responses to different metal species had no significant bearing on method performances. An attempt made to correlate performance of the methods with natural and distilled water samples discussed here, with performance with EPA solutions demonstrated no consistent correlations among method biases.

The data presented here are indicative of interlaboratory performance, in 1977, under conditions of "routine analysis" or "standard operation". That is, only the usual careful approach and good laboratory practice regularly adhered to by the participating analysts was exercised in this study. The analytical results together with variabilities and biases documented here thus reflect routine performance by some very experienced analytical chemists in water analysis and are the best we could conveniently accomplish.

Data treatment and utilization

A small number of obviously aberrant data was omitted by inspection at the beginning of the task of data handling, and these data have not been reported here. 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

$$\bar{X} = \Sigma \bar{X}_i / n \tag{1}$$

$$\bar{X}_i = \Sigma_k X_{ik} / k_i \tag{2}$$

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

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 ith method, k_i is the number of replicate analyses on all subsamples for the given sampling date by the ith 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 III to indicate the spread in data accepted and magnitudes of standard errors. 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, three ranges are given, reflecting low extreme, median and 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. Examples of standard deviations used in calculations of standard errors are listed in Table IV.

Every averaged datum has an associated standard error reflecting not only precision but also a measure of accuracy since independent methods were used in generating results leading to the mean. Some standard errors seem rather large (see also a further report[2] on this work in which even larger errors generally result from additional processing of the data). This is due to the combined effects of individual method imprecisions (s_w) and systematic errors (s_B) among the different methodologies. Although the latter error term inflates the error of the mean, amalgamation of data from different methodologies would be expected to give results closer to the truth. Agreement of results from diverse methodologies suggests confidence in the reliability of the data for *the sample analyzed.* Whether the same confidence could be transferred to the actual stream is a separate question dependent on sampling and sample handling prior to analysis.

This cooperative venture yielded a population of satisfactory analytical data (with perhaps the exception of lead), representing concentrations of selected dissolved + extractable trace metals in unfiltered and filtered natural waters. Analyses of field-filtered natural waters gave levels of

TABLE III

Examples of analytical concentration data incorporated into means, μg/L[a]

Element	Range of concentrations reported	Ratio of extreme values in range[b]	No. of analytical methods	Total no. of analyses	Mean ± standard error
Cu	7.80 – 13.0	1.67	4	18	9.21 ± 0.81
	4.40 – 16.5	3.75	5	11	7.94 ± 0.77
	0.70 – 10.0	14.3	5	16	3.43 ± 0.73
Zn	3.20 – 3.54	1.11	2	6	3.31 ± 0.88
	0.93 – 1.40	1.50	2	10	1.21 ± 0.70
	0.27 – 1.20	4.44	2	9	0.80 ± 0.70
Cd	0.050 – 0.065	1.23	3	8	0.056 ± 0.020
	0.010 – 0.022	2.20	3	8	0.015 ± 0.020
	0.0070 – 0.050	7.14	3	8	0.030 ± 0.020
Pb	0.17 – 0.20	1.20	2	4	0.19 ± 0.94
	0.80 – 3.31	4.14	4	11	1.79 ± 0.65
	0.30 – 5.00	16.7	3	12	1.66 ± 0.76

[a]Only data from two or more analytical methods were considered; results for unfiltered and filtered natural water samples have been pooled for these examples.

[b]For each element, three ranges are given reflecting, in sequence, low extreme, median and high extreme ratios for the pooled sets of data.

TABLE IV

Precisions used in calculations of standard errors of means[a]

Element	Sample type	Concentration range[b] μg/L	Within-method std. devn. s_w[c] μg/L	Degrees of freedom	Between-method std. devn. s_B[c] μg/L	Degrees of freedom
Cu	UNW	1.6 – 10.0	1.06	102	1.49	82
	FNW	0.7 – 23.5	1.61	42	1.70	57
Zn	UNW	0.8 – 7.9	1.09	37	0.85	12
	FNW	1.0 – 10.5	1.26	17	0.98	11
Cd	UNW	0.01 – 0.29	0.064	44	−0.0006[d]	45
	FNW	0.01 – 0.43	0.050	18	−0.0009[d]	23
Pb	UNW	0.15 – 4.0	0.71	51	1.22	48
	FNW	0.13 – 13.3	0.18	12	−0.014[d]	15

[a]Information is for unfiltered and filtered natural water samples designated UNW and FNW respectively.

[b]These are unweighted concentrations, $\bar{X}$, defined in the text.

[c]s_w and s_B listed here, calculated from pooled data as indicated, were used to calculate standard errors of mean concentrations.

[d]s_B^2 was negative and is reported instead of s_B.

dissolved metals; analyses of unfiltered natural waters, augmented by separate determinations of trace element levels in suspended sediments, reported elsewhere[1,2] gave *total concentrations* in natural water samples. These data were central to deliberations regarding mechanisms of storage and transport of Cu, Zn, Cd and Pb in fresh natural waters within agricultural watersheds draining into the great lakes.[1,2]

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