Copper, Zinc, Cadmium and Lead in Waters of Selected Southern Ontario Agricultural Watersheds

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Concentrations of Cu, Zn, Cd and Pb were determined in stream waters of six agricultural watersheds in Southern Ontario draining into the lower Great Lakes. Over all watersheds, samples collected during 1976 and the spring of 1977, had median concentrations ± analytical standard error, of elements in dissolved form of 2.0 ± 1.8 (range 0.5–18.5), 3.1 ± 2.7 (range 0.1–11.4), 0.07 ± 0.06 (range 0–0.57) and 0.1 ± 0.2 (range 0–13.1) µg/l for Cu, Zn, Cd and Pb respectively. Respective median total concentrations were 3.9 ± 2.6 (range 2.4–445), 17.2 ± 4.9 (range 4.3–2500), 0.08 ± 0.02 (range 0.03–13.4) and 3.7 ± 1.0 (range 0.9–433) µg/l for Cu, Zn, Cd and Pb. Concentrations of elements in dissolved form were invariable with, whereas total concentrations were proportional to suspended sediment levels whose range was from 10 to 19,000 mg/l with a median of 20 mg/l. Mode of transport was found to depend on suspended sediment level. In waters with low suspended sediment levels, below *ca* 20 mg/l, the majority of Cu and Zn was transported in dissolved form, whereas the suspended sediment accounted for most of the transport of these trace elements at higher particulate loads. Agricultural activities were estimated not to result in any gross contribution of these trace metals to the waters of these drainage systems.

KEY WORDS: Natural water, trace metals.

INTRODUCTION

Current widespread interest in the roles and effects of trace elements in respect of environmental pollution has been extended to the domain of agriculture. In this context, a large scale research program initiated by the International Reference Group on Great Lakes Pollution from Land Use Activities (PLUARG) of the International Joint Commission (IJC) had as its main objective the gathering of data on the inputs of pollutants into the Great Lakes Drainage System by agricultural activities. Within this scope, an investigation was undertaken to determine and assess the relationships between concentrations of the selected heavy metals, copper,
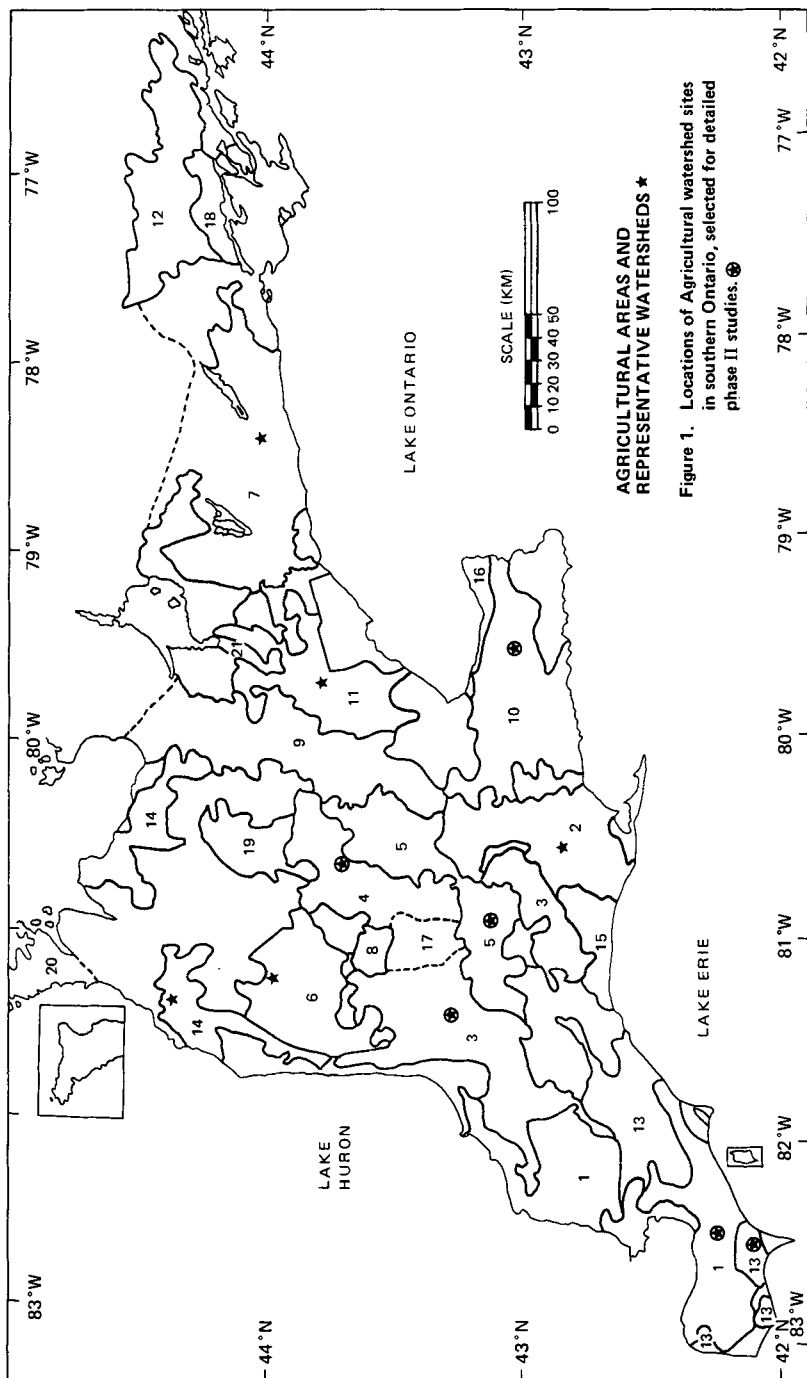
zinc, cadmium and lead in stream waters and suspended sediments within six selected agricultural watersheds draining into the Lower Great Lakes (Ontario, Erie and Huron). The objectives of this investigation were: (1) to assess, develop and adapt analytical methodology for the determination of trace levels of copper, zinc, cadmium and lead in water and suspended sediment samples, (2) to obtain reliable analytical information regarding concentrations of these elements in waters and suspended sediments, and (3) to assess relationships between metal concentrations in dissolved and particulate forms thus elucidating metal transport mechanisms. A detailed description of the analytical approach taken in this study,[1,2] and a discussion of interlaboratory analysis,[1,3] as an important contribution toward the acquisition of reliable analytical information, have been reported previously. This report presents the essential information and discussion concerning levels of copper, zinc, cadmium and lead in the stream waters and assessment of their modes of transport. Complete tabulation of data is available in the IJC report.[1]

EXPERIMENTAL

Watershed locations and descriptions

The six representative agricultural watersheds (Figure 1) chosen by PLUARG in southern Ontario for intensive study were: AG1 (draining the west branch of Big Creek, a tributary of the lower Thames River, Essex County), AG3 (Little Ausable River, Huron County) A64 (Canagagigue Creek, tributary of the Grand River, Wellington County), AG5 (Holiday Creek, tributary of the Upper Thames River, Oxford County), AG10 (North Creek, tributary of Twenty Mile Creek, Lincoln County), and AG13 (west branch of Hillman Creek, Essex County). Watershed areas range from 1890 to 5410 ha with the main agricultural activities being cash crops, pasture and mixed grains. Detailed descriptions of the agricultural areas and the watersheds, including climatic zones, soil types and potential for pollutant transfer to water systems, agricultural land use inventory, and fertilizer use are available in other reports.[4,5] Maps of locations and watershed boundaries are in Frank and Ripley[5] and Ihnat;[1] sampling locations are detailed in the latter.

Stream water sampling sites, one in each watershed (with an additional field erosion site in AG5) were selected near the outlet sites of the streams from the watersheds and were usually at gauging stations on the upstream side of the bridges transversing the streams. Sampling sites for this project are identical to the sites from which water and bottom sediment samples were taken for another project[6] within the IJC program.

FIGURE 1 Locations of agricultural watershed sites in southern Ontario selected for detailed studies.

Figure 1. Locations of Agricultural watershed sites in southern Ontario, selected for detailed phase II studies.

AGRICULTURAL AREAS AND
REPRESENTATIVE WATERSHEDS ★

SCALE (KM)

0 10 20 30 40 50   100

LAKE ONTARIO

LAKE ERIE

LAKE HURON

Sample collection and chemical analysis

Sample collection, preparation and chemical analysis procedures are detailed elsewhere.[1,3] Typically 11 samples of water were collected and preserved with 2 ml/l of $(1+1)HNO_3$ or $(1+1)$ HCl; final pH was <2.5. One half of the samples were vacuum-filtered in the field through 0.45 μm cellulose acetate membrane filters prior to the addition of perserving acid. Typically each watershed site was sampled four times during the study (1976 and spring of 1977); each sampling provided 2–4 unfiltered and 2 filtered natural water samples, duplicate samples of suspended sediment, and also unfiltered and filtered distilled water control samples to monitor field processing.

From one to six months after receipt from the field, water samples were subsampled by the author and distributed to cooperating laboratories for analysis using methods centering on atomic absorption spectrometry and electrochemistry. Suspended sediment samples and solid material remaining after evaporation of acidified water samples (denoted residue) were analyzed by atomic absorption spectrometry and optical emission spectrography. Analyses of unfiltered waters yielded dissolved + extractable concentrations of the trace metals, whereas analyses of water samples passing through 0.45 μm filters, corrected for filtration contamination, gave measures of dissolved levels. Summations of trace metal concentrations obtained by (1) analysis of unfiltered samples and contributions by residues and (2) dissolved concentrations in filtered water samples and contributions of suspended sediments, gave total concentrations.

A good deal of effort went into assuring that analytical data resulting from this investigation were reliable as far as possible under the control of the author. Central to the attainment of accurate data was the implementation of a data quality assurance program involving controls and tests on sample collection, filtration and analytical method performances.[1,2] The participation of several laboratories using four and two independently different analytical approaches to water and solid analyses, respectively was an important facet of quality control.[1,3]

Analytical data were averaged over field and laboratory subsamples and analytical methods. The typical datum was the average over two field samples. Typically, for dissolved, suspended sediment-contributed and total concentrations of the trace metals, the data were means over (2, 4), (2, 2) and (4, 8) (analytical methods and total number of analyses) respectively. Every datum has associated with it an uncertainty in the form of a standard error, which indicates the precision of the datum; since independent methodology was brought to bear on the work, the standard error can also be taken to give an estimate of accuracy.

RESULTS AND DISCUSSION
Suspended sediment

Over all six watersheds (total of 27 samplings) suspended sediment concentrations ranged from 2 ± 12 mg/l (mean $\pm$ standard error)† to 740 $\pm$ 10 mg/l, or 19000 mg/l including data for the field erosion site in AG5, with a median of ca 20 mg/l. Although a few "event" samples were collected during periods of rapid flow, after rainfall and during spring run-off, the bulk of samples were collected during slower flow periods and have rather low suspended sediment levels; one half of samples had concentrations below 20 mg/l.

Masses of residues remaining after acid-treatment of unfiltered water samples were converted to concentrations in the original water samples. Residue concentrations were lower than the corresponding suspended sediment levels (Figure 2). Whereas at the two intermediate and two high sediment levels, the ratio of residue to suspended sediment concentration, is constant at 0.70, it seems to drop with decreasing sediment concentration, to a value of 0.4 in the vicinity of 50 mg/l. Data uncertainty at lower suspended sediment loads precludes definitive extrapolation to this region. This relationship suggests increasing acid-solubility of the suspended sediments with decreasing sediment level and suggests different physical and/or chemical properties for suspended sediments at low and high concentrations, with a gradation of character in-between. It is logical to expect suspended sediments from low level streams to consist of smaller, lighter particles capable of being supported by the low energy stream. The scarcity of data from this study precluded comparison of suspended sediment levels and thus a comparison of soil erosion rates among the six watersheds.

Ranges of concentrations (μg/g on a 70° dry basis) of the four trace elements in suspended sediments from the six watersheds were found to be 23–119 for Cu, 50–290 for Zn, 0.1–7.9 for Cd, and 21–280 for Pb, with median concentrations $\pm$ standard error of 52 ± 5, 165 ± 39, 1.1 ± 0.8, and 70 ± 36 μg/g for Cu, Zn, Cd and Pb respectively. These data are listed in Table I which summarizes all pertinent trace element concentration data obtained in this study. Plots of trace element concentrations in suspended sediments as a function of suspended sediment concentration in Figure 3 show suggestions of interesting enrichment relationships. The clearest relationship exists for Cu due to the good analytical precision. In this case, the level of Cu in the sediments drops from ca 70 μg/g at sediment levels in the vicinity of 50 mg/l, to a constant value of ca 30 μg/g for

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†Throughout this paper, standard error is derived from analytical precision and does not relate to distribution of data over watersheds.
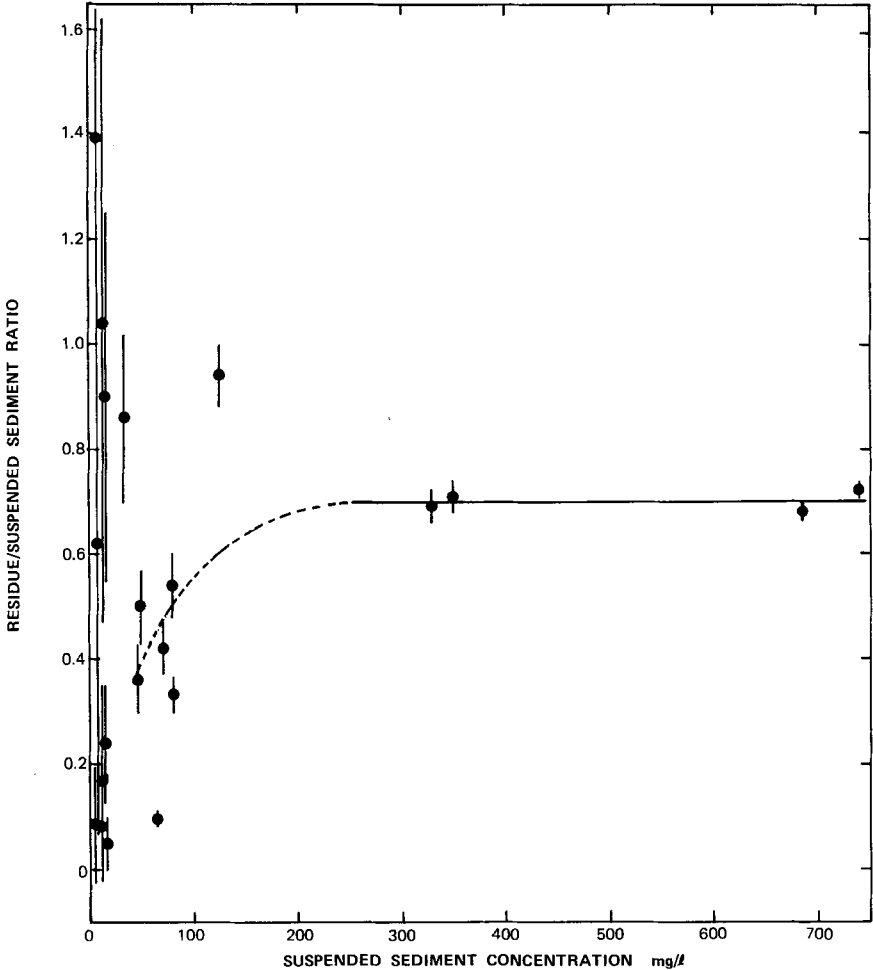
FIGURE 2   Residue concentration/suspended sediment concentration ratio as a function of suspended sediment concentration. Error bars here and in all subsequent figures represent standard errors, $s/\sqrt{n}$, where s is the standard deviation and n is the number of observations.

waters with high suspended sediment levels. Similar trends seem to occur for Cd and Pb, but the greater uncertainties in the data make these relations less clearly evident. Curiously, such a trend is not evident for Zn, an element closely related to Cd, which shows a rather constant level of $170\,\mu g/g$ over all samples. In all instances, the points for the extremely high sediment level of $19,000\,mg/l$ for the field erosion event sample fall into the patterns suggested by the remaining lower sediment level (10–$740\,mg/l$) data.
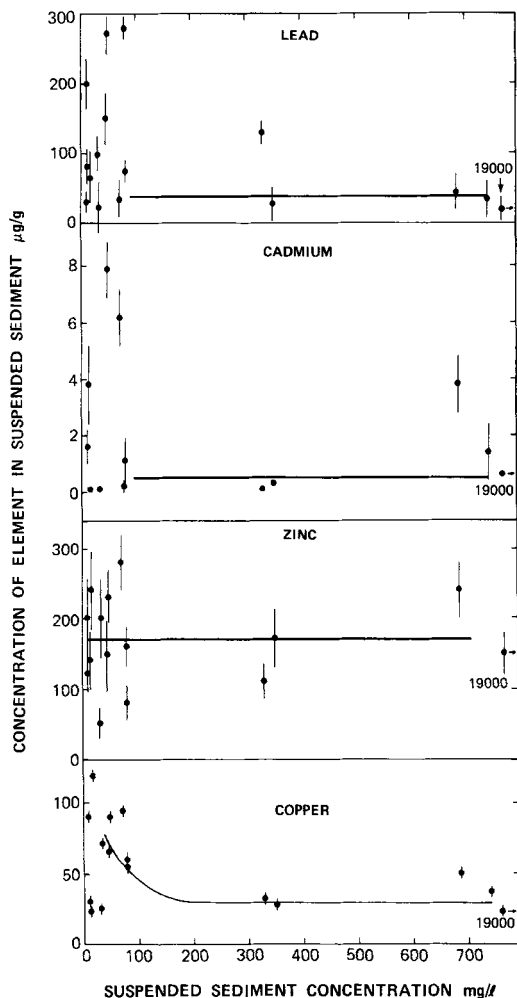
FIGURE 3   Concentration of trace element in suspended sediment as a function of suspended sediment concentration.

It would be interesting to relate these relationships to mineralogical and chemical characterizations of these suspended sediments. The most relevant available data are those on correlations of trace element levels with properties of soils taken from these six watersheds reported by Whitby *et al.*.[7] These authors reported significant (($p < 0.05$) positive Cu-organic matter, Cu-clay and Zn-clay correlations. As presumably the sediments are derived mainly from soils of the area, and high clay content

is indicative of smaller particle size, our sediment Cu enrichment findings agree with the soil Cu-clay correlation. Other investigators[8-10] studying suspended and bottom sediments also observed a correlation of increasing trace element concentration with decreasing particle size. Turekian and Scott,[11] however, reported no significant differences in trace element contents of different size fractions of bottom sediment from one river, and Angino[12] reported the composition of stream water and sediment to be discharge-independent.

Invariably, levels of Cu, Zn, Cd and Pb in residues were substantially lower than in the corresponding suspended sediments (Table I) with medians only 0–23% as large. These relationships are graphically explored in Figure 4 in which the ratio, concentration of element in residue/concentration of element in suspended sediment, is plotted against suspended sediment concentration. For Cu and Zn, ratios of *ca* 0.3 and 0.4 respectively, at suspended concentration levels in the range 300–740 mg/l, seem to fall as the sediment level decreases. This behavior shows that an increasing proportion of the trace element in the suspended sediment is leached-out by acid as the suspended sediment level decreases, and again suggests a gradual change in the physical and/or chemical character of the particulate material with its concentration in the stream. The point for the extremely high sediment level of 19,000 mg/l in the Cu graph, at a ratio of *ca* 0.7 indicates an even smaller fraction of Cu susceptible to acid leaching at this high sediment level. For Pb, a constant ratio of *ca* 0.25 is evident over the entire *ca* 10–740 mg/l range of sediment concentration. For bottom sediments from the Saguenay fjord, Loring[10] observed a clear increase in non-detrital (acetic acid-soluble) contribution to total Zn content going from sands to muds (decreasing particle size); similar but less conclusive trends were evident for Cu and Pb. If we assume low suspended sediment concentrations to be synonymous with smaller particle size, then the trace element-extractability phenomenon observed in this study is akin to that reported by Loring.

Garrett and Hornbrook[13] found a strong relationship between Zn and organic content in lake-bottom sediments, with the concentration of the element increasing with increasing organic content, estimated from loss on ignition, over the range 0–12% loss on ignition. With this information and the positive Cu-organic matter correlation reported by Whitby *et al.*[7] for soils from these Ontario watersheds, we may speculate increasing organic content of suspended sediments occurring at decreasing sediment levels in stream waters. It is interesting to observe the similarity of the three suspended sediment parameters, acid-solubility, trace element extractability and trace element concentration depicted in Figures 2, 4 and 3, respectively. In all three cases where transitions between behaviour at
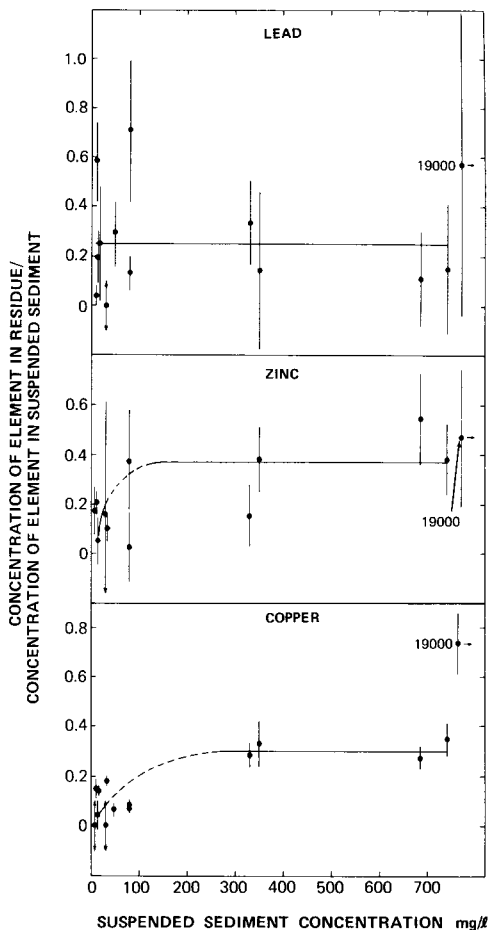
FIGURE 4   Ratio of concentration of element in residue to its concentration in suspended sediment, as a function of suspended sediment concentration. Arrows on both ends of standard error bars indicate that the the error is unknown and greater than indicated.

low and high suspended sediment levels are indicated, these transitions occur in the region of *ca* 10–300 mg/l.

Water

Concentrations of dissolved trace elements, defined as levels in natural water filtrates passing through 0.4–0.45 μm filters, are compiled in Table I. Dissolved, as defined here, thus encompasses the sum of the trace elements distributed over a range of all possible species present in solution ranging

TABLE I
Summary of Cu, Zn, Cd and Pb concentrations in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13

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

[a]Range of mean concentrations, one per sampling date, in 1976 and spring 1977, found in samples from the six watersheds.
[b]Total number of associated sampling dates.
[c]Standard error is the analytical error associated with the median value; it does not relate to the distribution of the population from which the median was extracted.

from true solutions of hydrated and complexed forms through elements associated with larger organic species to colloidal dispersions and particles up to *ca* 450 nm in diameter. The term is not restricted to true molecular solutions but does have a practical significance. Levels listed in the table have rather large associated relative errors resulting primarily from the necessity to apply some rather large corrections for filtration procedure contamination. For samples from all watersheds, median concentrations ± standard error of elements in dissolved form were found to be ($\mu g/l$): 2.0 ± 1.8, 3.1 ± 2.7, 0.07 ± 0.06, and 0.1 ± 0.2 for Cu, Zn, Cd and Pb respectively.

Contributions of suspended sediments to trace element levels in the stream waters were computed from concentrations of suspended sediments in the water samples and concentrations of trace elements in the sediments (Table I). Over all the samples, suspended sediments contributed median concentrations $\pm$ standard error of 4.3 ± 0.6, 9.1 ± 2.8, 0.09 ± 0.06, and $3.1 \pm 1.1 \mu g/l$ of Cu, Zn, Cd and Pb respectively

Total concentrations of trace elements in stream waters (Table I) may be defined as the sums of contributions from suspended sediment and dissolved forms discussed above. They were in fact determined in two independent ways, as discussed above, based on concentrations measured in unfiltered and filtered water samples plus the appropriate contributions of suspended sediments and residues, and the best selected values have been listed here. Total median concentrations $\pm$ standard error were 3.9 ± 2.6, 17.2 ± 4.9, 0.08 ± 0.02 and $3.7 \pm 1.0 \mu g/l$ for Cu, Zn, Cd and Pb respectively.

Total, dissolved and suspended sediment-contributed levels of Cu, Zn, Cd and Pb are plotted, as functions of suspended sediment concentration, in Figures 5, 6, 7 and 8 Respectively. Reasonably firm relations could be established for Cu, Zn and Pb, particularly for the first two elements, but not for Cd due to the scarcity and imprecision of data. The most striking observation is the invariability with suspended sediment concentration of concentrations of dissolved trace element, over the range ca 10–740 mg of suspended sediment/l, and even extending to the one field erosion site sample with 19,000 mg sediment/l. The high values for dissolved Cu and Pb, of $18.5 \mu g$ Cu/l and $13.1 \mu g$ Pb/l are ca $9 \times$ and $40–130 \times$ as large as the respective median values. Curiously, both are for one sampling on March 26, 1976 of AG4. Unfortunately, both also result from one analysis by one method, and consequently no significance can be attached to them on the basis of existing information. They may be true anomalies of AG4 but may also be artifacts of sampling and analysis. Levels of dissolved Zn and Cd for the same sample look "normal".

Concentrations of suspended sediment-contributed, and total trace elements, on the other hand, are related to suspended sediment concentration in a ca linear fashion over the 10–740 mg/l range. Three outlying points may be noted, a suspended Pb, and a total Cu and Pb concentration, all of which are associated with the AG4-Mar. 26, 1976 sampling, suggesting that no significance should be attached to these outliers.

Due to scarcity of data, concentrations of dissolved and total trace elements and suspended sediments cannot be firmly related to watershed and sampling time. Much more representative information for each watershed gathered from a more detailed sampling program covering
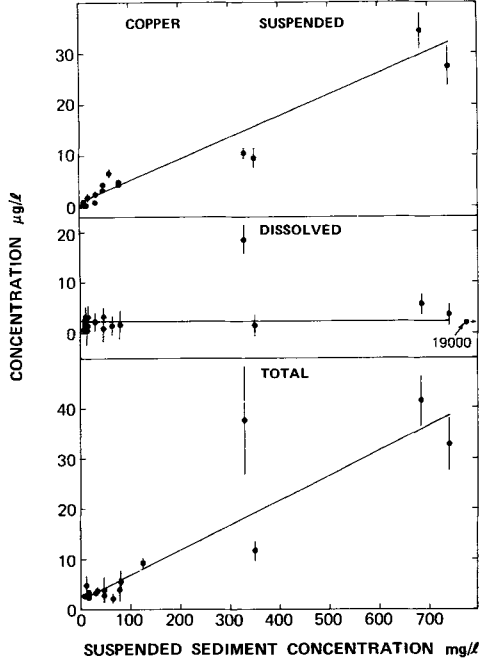
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FIGURE 5 Total, dissolved, and suspended sediment-contributed levels of copper as functions of suspended sediment concentration in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13.

normal and event flows is needed to characterize the different streams. Similar observations of the independence of dissolved trace element levels on concentration and composition of suspended solids have been reported by others[11,12,14,15] and determined by the author from data reported by Silker.[16] In both this work and literature reports, dissolved trace element levels exhibit scatter about median values. It would be of interest to seek out the parameter correlated with this and ascertain whether unattainment of equilibrium,[15] among the dissolved and particulate fractions of stream waters is a factor responsible for extreme values.

Comparison of data with literature reports

It was of interest to compare the data for stream water components obtained in this work with results for natural waters reported by other workers. In particular, it was of interest to compare these data with other PLUARG work on the same watersheds, encompassing identical sampling dates, and in fact, identical samples. Detailed comparisons of suspended
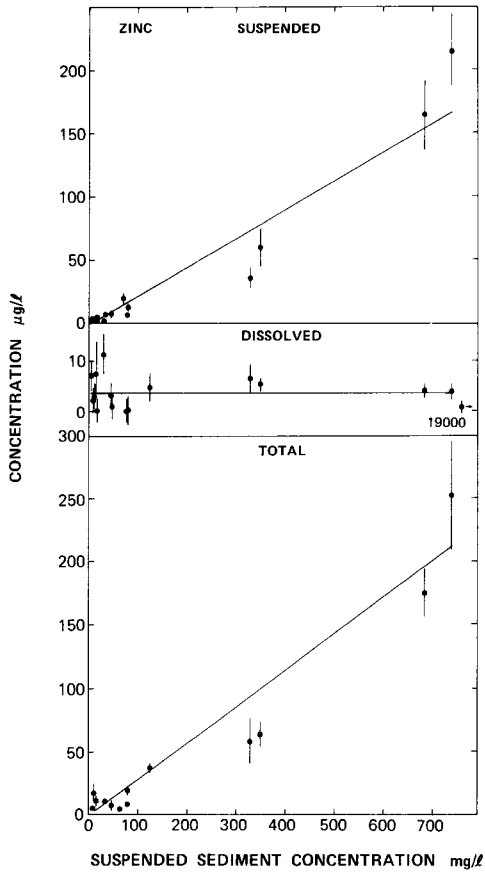
FIGURE 6 Zinc; refer to Figure 5 for details.

sediment concentrations, and suspended sediment-contributed, dissolved and total trace element levels determined in this study, were made with values reported by Whitby et al.,[6] Gaynor[17] and by the Ontario Ministry of the Environment (OME), the latter data obtained as NAQUADAT (National Water Quality Data, Fisheries and Environment Canada) printouts. The samples used by Whitby et al. were essentially identical to the ones studies here, those of Gaynor were from watershed AG13, whereas data obtained by OME during their extensive monitoring program of all watersheds were chosen to correspond in respect of watershed and sampling date.
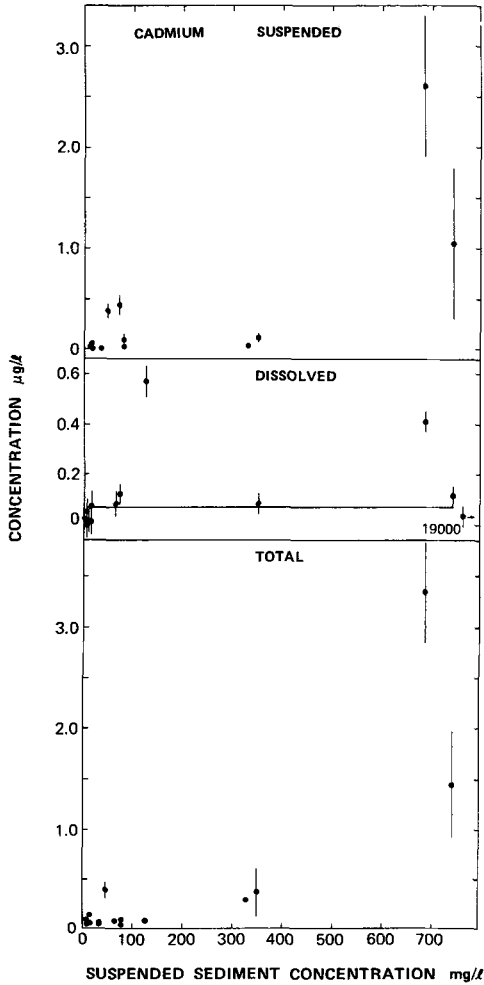
Figure 7   Cadmium; refer to Figure 5 for details.

Although values for the contributions of suspended sediments to
concentrations of Cu, Zn, Cd and Pb in waters of four of the watersheds
agreed reasonably well with the corresponding data reported by Whitby *et
al.*,[6] many dissolved and total concentrations determined by the latter
workers were extremely high, seemingly due to a contamination problem.
Comparative summaries between our data and those of OME and
Gaynor[17] for the four trace elements are presented in Table II. Values for
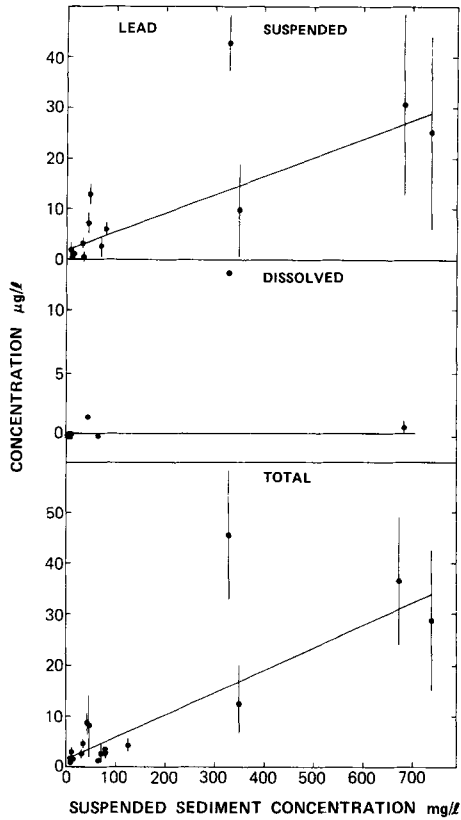
FIGURE 8   Lead; refer to Figure 5 for details.

total levels reported by OME and Gaynor are conceptually not total concentrations as they were based on acid- (NAQUADAT code 48006, Fisheries and Environment Canada[18]) or solvent-extraction[3,17] methods respectively, but would be expected to be fairly close (especially in the case of low sediment waters) to total levels to permit comparison. Ranges and median values for Cu and Zn found in this study agree well with corresponding data reported by OME and Gaynor. For Cd and Pb, analytical methodologies used by these two laboratories appeared insufficiently detective to measure the low natural levels of these elements and no comparisons could be made.

A final comparison was made of concentration data from this study with literature information for other "unpolluted" surface natural waters.

TABLE II

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

| Element | This work[a] | | Literature[b] | | Water[c] |
	Range	Median	Range	Medians or means	
Cu	2.2–445	3.9 ± 2.6	<1–230	5[d], 8[e]	A
			0.4–150	1.16[f], 1.2[g], 2.0 ± 1.8[h],	
				3[i], 4.7[j], 6.9[k], 15[l]	O
Zn	4.3–2500	17.2 ± 4.9	<1–820	5.5[d], 12[e]	A
			0.3–620	1.5[g], 7.8[j], 8[l], <10[i]	O
Cd	0.03–13.4	0.08 ± 0.02		<0.6[e], <1[d]	A
			0.02–6	0.045[m], <0.5[k], <1[i], 1.0[j]	O
Pb	0.9–433	3.7 ± 1.0	<1–76	<2[d], <11[e]	A
			0.3–200	0.015[n], 0.26[f], 0.5[g],	
				0.7 ± 0.8[h], 0.8[j], <1[i],	
				4[l], 5.4[k]	O

[a]Date from Table I for a total of 15–19 samples from the 6 watersheds.

[b]All levels reported in the literature may not, strictly speaking, be total concentrations; ranges and medians were either reported or estimated by the author from data reported; means were reported. Agricultural watershed data based on $ca > 123$ to 1028 samples from 6 watersheds; data for other waters based on $ca > 52$ to >647 samples from >28 to >203 waters throughout the world.

[c]A-PLUARG agricultural watersheds; O-other natural waters. All waters may not be truly unpolluted.

[d]Ontario Ministry of the Environment; sampling of the 6 watersheds.

[e]Gaynor[17] watershed AG13.

[f]Turekian and Kleinkopf;[24] streams and lakes in Maine, USA.

[g]Bradford et al.;[25] High Sierra Lakes, California, USA

[h]Poldoski et al.;[26] Lakes Huron and Superior and incoming streams.

[i]Fisheries and Environment Canada;[27] Canadian rivers.

[j]Chan;[20] Niagara river; Ontario, Canada.

[k]Phillips et al.;[28] two rivers through Melbourne, Australia.

[l]Chawla and Chau;[29] Lake Erie.

[m]Doolan and Smythe;[19] three rivers in Australia.

[n]Hirao and Patterson;[30] stream run-off from Thompson Canyon, California, USA

Information for total element levels is included in Table II; a comparison of dissolved levels is presented in Table III. With respect to total Cu, the median level observed in this study is in excellent agreement with the typical median reported in the literature. Our median total Zn and Pb concentrations are somewhat higher than the corresponding literature data, whereas total Cd data cannot be compared with most of the reported data because of the generally poor detectivities of literature methods. However, the median value of 0.045 μg/l reported by Doolan and Smythe[19] for total Cd concentrations in three Australian rivers agrees excellently with our median of 0.08 μg/l for the Ontario watersheds. For concentrations of elements in dissolved form, our median values for Cu, Zn, Cd and Pb are in excellent agreement with the respective means

TABLE III

Comparison of concentration of dissolved Cu, Zn, Cd and Pb in waters of agricultural watersheds 1, 3, 4, 5, 10 and 13 with literature data for other "unpolluted" fresh natural waters

	Concentration μg/l			
	This work[a]		Literature[b]	
Element	Range	Median	Range	Medians or means
Cu	0.5–18.5	2.0±1.8	0.20–280	1.6[e], 2.24[d], 5.3[e], 15[f]
Zn	0.1–11.4	3.1±2.7	0–1183	0[e], 3.5[e], 14.4[d], 64[f]
Cd	0.00–0.57	0.07±0.06	0.004–120	0.2[e], 9.5[f]
Pb	0.0–13.1	0.1±0.2	0.058–140	0.2[e], 4.0[e], 23[f]

[a]Data from Table I for a total 11–21 samples from the 6 watersheds.
[b]Analyses of typically 0.45 μm-filtered water samples. Medians or means reported in literature; medians estimated by this author from data reported. Data based on $ca > 1690$ samples from > 131 waters; all waters may not be truly unpolluted.
[e]Chan;[20] Niagara river, Ontario, Canada.
[d]Silker;[16] Columbia river, Washington, USA.
[e]Durum and Haffty;[31, 32] rivers in USA and Canada.
[f]Kopp;[33] US surface waters.

reported by Chan[20] for his survey of the Niagara River (Ontario). Our Cu median of 2.0 μg/l also agrees excellently with the 2.24 μg/l extracted from the work of Silker[16] on water from the Columbia River (Washington, USA). Other literature data for the four elements are higher than those from this study.

The ranges of dissolved and total concentrations and medians/means for these four trace elements reported in the literature are large. Trace element concentrations in natural waters are dependent on many variables including sampling time in relation to run-off and thus equilibrium considerations and soil conditions that it is surprising the agreements are so good. Values could also depend on pollution, and could also reflect insufficiencies in analytical methodologies and contamination during sampling and analysis. It is concluded that, with perhaps the exception of Cd and Pb, and within the stated confidence limits, the concentrations of Cu and Zn, reported here are reasonably reliable estimates of the levels of these elements in streams draining the six agricultural watersheds.

Mechanisms of transport

The proportion of the element carried by the suspended sediment, expressed as a percentage of the total concentration in the stream water, is plotted as a function of the suspended sediment level in Figure 9. Some conclusions in respect of the mechanisms of transport of Cu and Zn can be drawn from information in this Figure. The proportion of the total
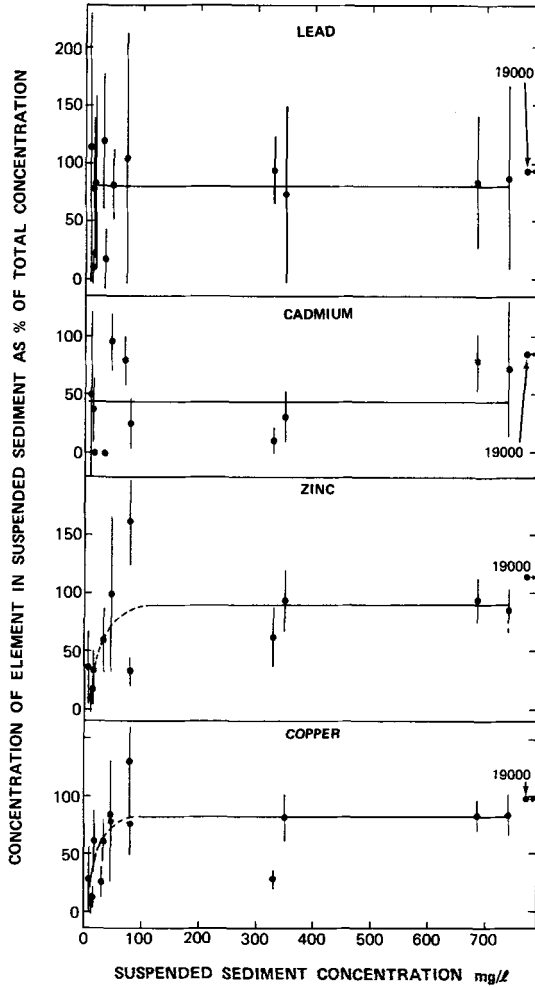
FIGURE 9   Percentage of total element concentration contributed by suspended sediment as a function of suspended sediment concentration in agricultural watersheds.

element level associated with particulate stream material, was observed to increase with suspended sediment concentration over the range *ca* 10–100 mg/l, and thereafter remained constant at 80–90% up to 740 mg/l. These proportions would be expected to increase slowly with sediment load to approach 100% at high sediment levels as suggested by the 19,000 mg/l point. The Cu and Zn curves cross 50% at a suspended sediment concentration of *ca* 20 mg/l.

It thus appears that the dominant mechanism of transport, at least for Cu and Zn, depends on the suspended sediment level in the stream. In waters with low suspended sediment levels, below ca 20 mg/l, the majority of the Cu and Zn is transported in dissolved form, whereas the suspended sediment accounts for most of the transport of these trace elements at higher particulate levels. Fully one half of the water samples collected had suspended sediment concentrations below ca 20 mg/l. Thus both dissolved and suspended transport mechanisms are of importance in these watershed streams, and in general, suspended sediment levels should be quoted when discussing transport mechanisms. Sediment transport during rainstorms and spring runoff, however, seems like the most important mechanism for removing large amounts of elements from these watersheds over the course of a year. Rather large errors arising from experimental uncertainties and propagation of error for the quotients, however, suggest that these conclusions be accepted with reservation. No such trends were noticed for Cd and Pb; the very low levels of Cd and Pb in natural waters, coupled with the experimental difficulties associated with their measurement, precluded firm conclusions regarding these elements.

Only scant reference to details concerning transport mechanisms of Cu, Zn, Cd and Pb have been found in the literature although the behaviour of other trace elemtns has been reported. Relations of transport mechanisms to sediment loads have not generally been mentioned. Kopp and Kroner[21] reported on a comparison of dissolved and suspended Cu, Zn and Pb based on analytical data from a water quality surveillance program. Over a number of different locations, mean levels of dissolved Cu and Zn were higher than the corresponding suspended levels; data for Pb was said to be in error due to sampling problems. It is difficult to read more information into their findings as comparisons for the individual waters were not made, and no sediment levels were reported. Gibbs[22] investigated the distribution of Cu and several other trace elements among five mechanisms of transport and observed a similar distribution for the widely separated Amazon and Yukon rivers. The majority of the Cu (93.1–96.7%) was transported with the particulate load, and incorporation into the crystal structures of the sediments was the most important mechanism. Lead was found by Angino[12] to be approximately equally divided between dissolved and suspended phases in waters from Kansas rivers in contrast to the occurrence of the bulk of the load of Fe and Mn in the suspended phase. In an interesting study of stream supply of dissolved trace elements to the oceans, Kharkar et al.[14] discussed relations between dissolved and desorbable (from suspended sediment) concentrations from several elements but not for those of interest here. Turekian[15] concluded that more cationic but not anionic species of trace

metals are absorbed effectively on particles carried by streams and have very little chance of leaving an estuary in solution. Analyses by Davey and Soper[23] of ocean water, for dissolved and particulate forms of Cu, Zn, Cd and Pb, indicated 66, 85, 100 and 44% respectively, to be in dissolved form. In none of these studies, however, was an attempt made to relate distributions of trace elements between dissolved and particulate forms to suspended sediment concentrations.

CONCLUDING REMARKS

Appropriate analytical methodology with detection limits equal to or generally better than the 1 $\mu g/l$ requested by PLUARG was developed and adapted to the measurement of trace levels of the elements of interest in water and sediments. Application of laboratory data quality control procedures and cooperation of other experienced analytical laboratories gave fairly reliable results for dissolved, suspended sediment-contributed, and total concentrations of the elements.

The concordance of results for dissolved and total concentrations of these elements with literature data for other natural waters suggests no gross effects of agricultural practices on trace element levels in streams. Conclusions regarding partition between dissolved and suspended phases and mechanisms of transport were formulated. For Cu and Zn, the dominant mechanism of transport within the stream depends on the suspended sediment level. Some conclusions regarding the physical and/or chemical characteristics of the suspended sediment as a function of its concentration in the stream were also presented.

Although considerable effort and diligence were directed to the generation of analytical information regarding trace element concentrations in stream waters, and reasonably reliable data were realized for Cu and Zn, somewhat large imprecision is associated with some data, and their accuracy cannot be firmly defined. Specifically, the very low levels of Cd and Pb in natural waters, coupled with experimental difficulties associated with their measurement, gave rise to uncertain data and precluded firm conclusions regarding these two elements. Reliable, detailed, and representative information in respect of important trace elements in natural water system is needed to interrelate conclusively trace element levels among the various stream components, to get a good understanding of the sources and mechanisms of element transport and to provide a reliable data base for current and future comparisons.

Acknowledgements

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