New Jersey Geological Survey
Geological Survey Report 20

Temporal Variations and Sources of Pb, Cd, Cu, Ni, Fe, and Mn in Shallow Ground Water of the McDonalds Branch Basin, Lebanon State Forest, Burlington County, New Jersey

Department of Environmental Protection - Division of Water Resources

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by
Ilham Demir

New Jersey Department of Environmental Protection
Division of Water Resources
Geological Survey
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ABBREVIATIONS

A.U.	absorbance unit	Cd	cadmium
DOM	Dissolved Organic Matter	Cu	copper
meq	milli-equivalent	Fe	iron
µg	microgram	Mn	manganese
µm	micrometer	Ni	nickel
nm	nanometer	Pb	lead
PVC	polyvinyl chloride	CO_2	carbon dioxide
ZPC	zero point of charge	HNO_3	Nitric acid
		O	Oxygen

CONVERSION FACTORS

Readers who prefer to use inch-pound units instead of the SI (metric) units used in this report may use the following conversion factors.

Multiply	by	to obtain
Millimeter (mm)	0.03937	inch (in.)
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	feet (ft)
kilometer (km)	0.6214	mile (mi))
square kilometer(km^2)	0.3861	square mile (mi^2)
gram (g)	0.03527	ounce avoirdupois (oz avdp)

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CONTENTS

ILLUSTRATIONS

TABLES

APPENDIXES

Temporal Variations and Sources of Pb, Cd, Cu, Ni, Fe, and Mn in Shallow Ground Water of the McDonalds Branch Basin, Lebanon State Forest, Burlington County, New Jersey

by Ilham Demir

ABSTRACT

Concentrations of six trace metals in shallow ground water of the McDonalds Branch basin were measured for 10 months from June 1978 to March 1979. The results indicate that significant amounts of the dissolved Pb, Cu, Ni, and Fe are present in shallow ground water as metal-organic complexes. Mean summer concentrations of Pb, Cu, Fe, Mn and H were significantly higher than the mean winter concentrations, apparently due to increased production of dissolved organic matter (DOM), greater concentrations in precipitation, evapotranspiration, and, in addition, for Fe and Mn, higher rates of geochemical weathering in summer. Mean Cd concentration in ground water was also higher in summer than in winter although Cd concentration in the summer precipitation did not differ significantly from that in the winter precipitation. Apparently Cd is leached into ground water without complexing with DOM, and minor leaching of Cd bound within soil material probably occurs, especially in summer. Pb in ground water is supplied almost entirely by precipitation. Atmospheric Cu and Ni, together with evapotranspiration, also appear to be sufficient to account for Cu and Ni concentrations in ground water. The major source of Fe and Mn in shallow ground water is geochemical weathering.

INTRODUCTION

Under natural conditions trace metals enter ground-water systems through atmospheric input and decomposition of rocks, sediments, and organic matter. However, especially in industrialized countries, human activities such as construction, mining, smelting and processing of metallic ores, and combustion of fossil fuels have substantially increased the flux of trace metals into the atmosphere and into aquatic environments. Previous studies (Lazrus and others, 1970; Nriagu, 1978; Lantzy and McKenzie, 1979; Swanson and Johnson, 1980) suggested that in many places atmospherically-borne trace metals are derived primarily from human activities. Elsenreich and others (1986) demonstrated that atmospheric fluxes of Pb to both urban and rural areas in the United States correlate positively with Pb used in gasoline.

Atmospherically-borne trace metals eventually return to Earth's surface, and subsequently they are either held by soils and rocks or transported in water depending on ambient physical and chemical conditions. Streams and precipitation entering northern Lake George in the Adirondack Mountains lose part of their trace metals to the lake sediments. Elsewhere, two trace metals (Fe and Mn) transported to some northern Minnesota lakes stay in solution owing to the higher concentrations of humic and tannic acids and lower alkalinities of the lake waters (Williams and others, 1974). Increasing human activity appears to be the cause of increasing trace metal concentrations in the contemporary lake-bottom sediments of Lake Washington in Washington State (Schell and Barnes, 1974) and some California lakes (Chow, 1978).

Reliable sampling procedures and analytical techniques for studying trace metals in natural waters have been developed only within the last decade or so. The previously published data should therefore be used with extreme care. For example, a large proportion of ground-water samples were taken from steel-cased production and observation wells. Samples from such wells are vulnerable to contamination caused by reaction between steel and water.

In this study, levels of six trace metals, Pb, Cd, Cu, Ni, Fe, and Mn, in ground water collected near McDonalds Branch, a stream in Lebanon State Forest, New Jersey, were monitored during the period June 1978-March 1979 to investigate

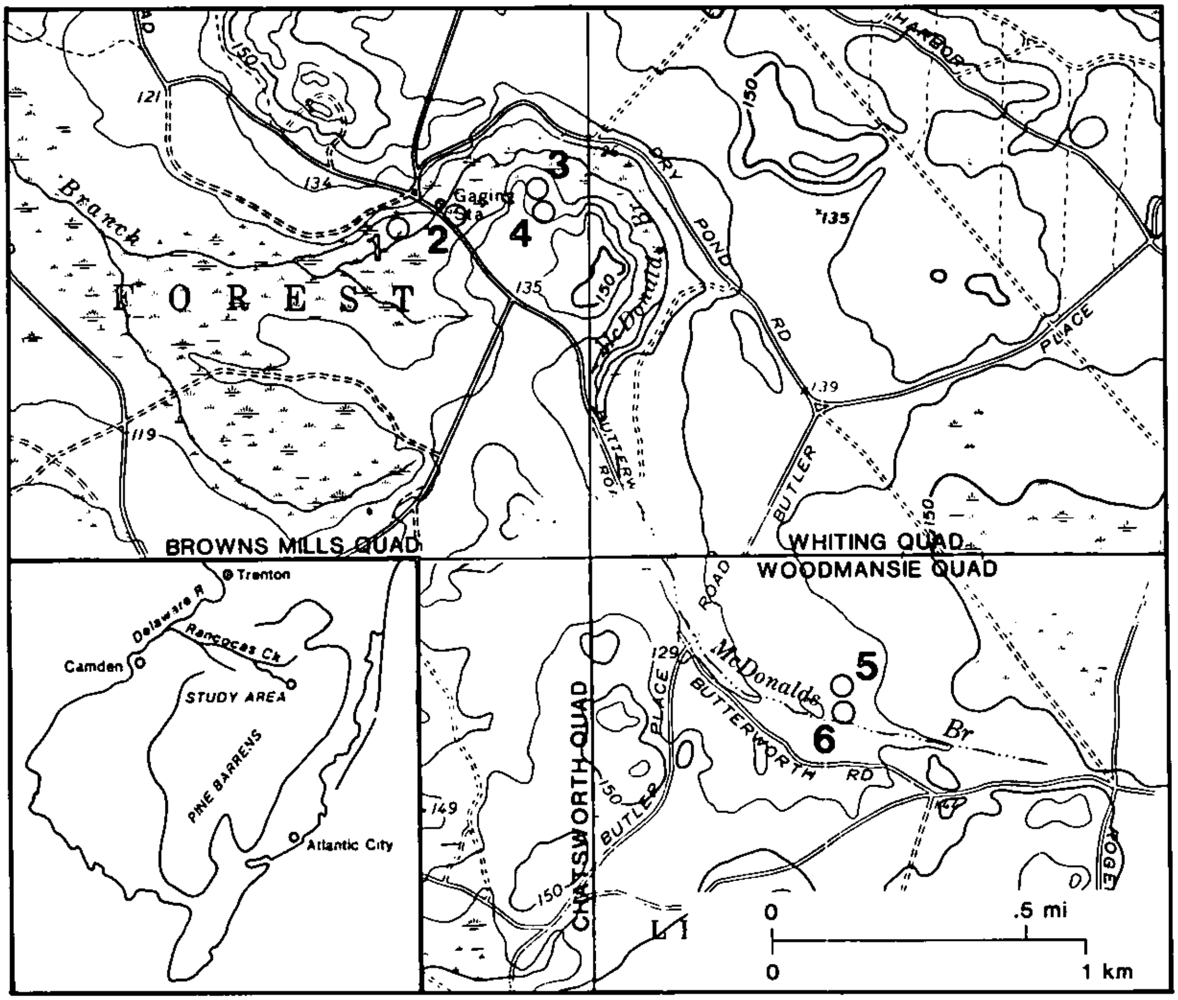

Figure 1. Location of McDonalds Branch and sampling sites.

their seasonal fluctuations. The results are interpreted in terms of atmospheric input, fluid-rock interaction, and biochemical activity.

Study Area

McDonalds Branch drains a small (6 km^2) pristine basin in the Pinelands in Lebanon State Forest in south-central New Jersey, about 56 km east of Camden. The Branch is a small headwaters brook that is tributary to Rancocas Creek, which in turn flows into the Delaware River (fig. 1). The wells were situated close to the Branch, at elevations of about 35 - 41 m (115 to 135 ft) above sea level. McDonalds Branch meanders northwestward in the study area for a distance of about 3 km.

The basin is underlain by the Cohansey Sand of Miocene (upper Tertiary) age (Zapecza, 1984). The Cohansey is unconsolidated, about 30 meters thick, and consists of gravelly sand, fine to coarse sand, and some clay lenses. In upland areas, well-drained mineral soils (Quartzipsamments and Hapludults soils (Swanson and Johnson, 1980) 50 to 100 cm thick) have developed. The soil pH ranges from 3.6 to 5.0 (Markley, 1979). Although soil particles are generally coated with iron oxides, bleaching of surface horizons under an organic matter layer, 10 cm or less in thickness, is common. Histosols (organic soils) have developed in lowlands (Swanson and Johnson, 1980) where the water table is very close to or at the land surface and thick, finely divided organic muck and peat overlie the Cohansey Sand. Top organic matter horizons are discontinuous and are burned every 2 to 5 years to reduce the hazard of forest fires and to control the forest composition. There is little mixing of the organic horizon and mineral matter of the soils owing to inhibition of soil-organism activity by low soil pH. Mineral weathering is not extensive because mineral horizons consist mostly of iron-oxide-coated silica particles. As a result these soils have a low ion exchange capacity (0-4 meq/100 g) and a low buffering capacity (Markley, 1979; Douglas and Trela, 1979). Both the ground water and stream water are very soft, ranging from 15 to 35 milligrams per liter (mg/L) in dissolved solids concentration (Swanson and Johnson, 1980). Fe might be introduced to ground water from underlying metalliferous clay of Cretaceous and Tertiary age and from glauconitic layers (Means and others, 1981).

Purpose and Scope

This study was conducted by the author, affiliated with the Illinois State Geological Survey (615 E. Peabody Drive, Champaign, IL 61820) at time of publication, in partial fulfillment of the requirements for the M.S. degree in the Department of Geology at the University of Pennsylvania in 1978-1979. Publication by the New Jersey Geological Survey is based on the fact that the study site is in New Jersey and the report contains new factual data and interpretation whose significance extends beyond the boundaries of Lebanon State Forest.

Acknowledgments

The author would like to thank Arthur Johnson and Robert Giegengack, both at the University of Pennsylvania, for their support and guidance during the course of this research; and Deborah Lord, U.S. Geological Survey, Dr. David Crerar, Princeton University, and Chen-Lin Chou, Illinois State Geological Survey, for critically reviewing the manuscript. The author would also like to thank I.G. Grossman, New Jersey Geological Survey, for carefully editing the manuscript.

Methods of Investigation

Six wells were installed in the basin (fig. 1) to collect shallow ground-water samples. The wells were cased to a depth of 1.5-2.0 m with ASTM-listed rigid PVC 3.5 cm in inside diameter. Before installation, the PVC tubes were sealed and pointed at the bottom end, perforated in their lower meter with 0.5-mm holes, and acid-washed. Three of the wells (nos. 3, 4, and 5) were in relatively well drained mineral soil and three (nos. 1, 2, and 6) were in mostly waterlogged organic soil. Wells 1 and 2 in cedar swamp, well 5 in pine lowland adjacent to a hardwood swamp, and well 6 in the hardwood swamp, were emplaced by forcing them down manually in the soft soils. Wells 3 and 4 were sunk using soil augers and a sledge hammer in pitch pine lowland mineral soil. Ground-water samples were usually, though not always, collected once every two weeks (see appendix 1) using a vacuum pump; they were stored in acid-washed polyethylene bottles. The 10-month collection period extended from June 1978 to March 1979. Before sampling, water levels in the wells were measured and the wells were pumped down to considerably below the top of the lower meter of perforated casing. After sampling the wells were emptied. The wells were capped throughout the period of study except during sampling. All sampling equipment and bottles were transported and stored in plastic bags.

The pH of the samples was determined within 2 to 4 hours after collection using glass electrodes. After the pH measurements, the samples were filtered using 1 – μm Nuclepore-membrane filters to remove suspended particles. The filtered samples were acidified with concentrated HNO_3 to prevent precipitation of dissolved substances during a storage time of 1 to 10 days. The sample-to-acid ratio was 10 to 1.

Dissolved organic matter concentrations of the samples were estimated in terms of absorbance units (A.U.) at 430 nm on a Hitachi Model 100-10 spectrophotometer using the procedure of Gjessing (1976). Trace element concentrations were determined using a double-beam Perkin-Elmer atomic absorption spectrophotometer, Model 372, with graphite-furnace atomizer. Standards were prepared using stream and precipitation waters from the study area. Blanks were prepared using triple deionized water and were periodically transported to and from the sampling sites to determine the effect of transportation, if any, on the samples. A comparison of the values of blanks and ground-water samples is shown in table 1. Immersion of a piece of PVC-cased pipe in deionized water in the laboratory for 24 hours indicated no detectable trace metal leaching from the pipe. Materials, methods, frequency of collection, and quality control for the precipitation samples are given by Swanson (1979). The basic data are in the M.S. thesis, copies of which are on file in the main library and the geology library of the University of Pennsylvania.

Presentation of data

Data obtained for ground water and precipitation from June 1978 to March 1979 are given in appendixes 1 and 2. Range, mean, and standard deviation of each measured parameter for the sampling period are given in table 2 for both ground water and precipitation. Results of t-statistics analyses (to determine differences among data sets) are given in tables 3-5, and a summary of correlation analyses of the ground water and precipitation data is given in table 6.

Trace metal and DOM concentrations in precipitation and ground water are plotted against time in figures 2-7. Each data point for ground water in the graphs is a mean value of all wells sampled. Figures 2-7 do not show March 1977 values for precipitation. These values, however, are given in appendix 2.

SEASONAL AND OTHER DIFFERENCES IN CONCENTRATIONS

Table 3 shows that concentrations in precipitation were higher during summer than during winter for Pb, Cu, Fe, and H, whereas seasonal differences for Cd, Ni and Mn were insignificant. Table 4 shows that concentrations in ground water were higher during summer than during winter for Pb, Cu, Cd, Fe, Mn, and H, whereas the seasonal difference for Ni was not significant. Table 5 shows that concentrations of dissolved Fe and Mn were substantially higher in the mineral soil than in the organic soil, whereas other elements did not differ significantly. Table 6 shows that Pb, Cu and Fe correlate positively with DOM in the ground water. Ni also correlates positively with DOM but only for the ground water within the mineral soil. For precipitation, positive correlations were observed among Pb, Fe, Cd, Ni, Mn, pH, and Cu.

Mean concentrations in the precipitation (table 2) and 50-percent evapotranspiration (Robertson, 1973) can account for mean Pb, Cd, Cu, and Ni concentrations in the ground water. However, contribution of precipitation to the concentrations of Fe and Mn in the ground water is relatively small.

The following section discusses complexation and adsorption as possible mechanisms of transport and retention of trace metals. A subsequent section deals with the temporal variation of each element in relation to atmospheric input, transport, retention, and geochemical weathering.

COMPLEXATION WITH ORGANIC MATTER

Many investigators (among them Means and others, 1981; Gjessing, 1976; Marshall, 1964; Schnitzer and Skinner, 1967; Davis, 1984) have indicated that DOM can mobilize trace metals in aquatic environments by forming soluble organo-metallic complexes. However, it is less certain whether or not a positive correlation between metals and DOM always indicates complexation. Fox (1984), for example, reported that dissolved humic acid and soluble iron appear to be chemically unassociated in estuaries despite their coincidental removal. On the other hand, complexation between organic acids and trace metals in soils and ground waters is well established (Stevenson and Ardakani, 1972; Stone and Morgan, 1984).

Using elemental analysis, functional group titrations, infrared spectrophotometry and gel filtration chromatography, Means and others (1981) characterized DOM, consisting largely of humic and fulvic acids, in the Pinelands stream waters. These organic materials are largely derived by leaching of decaying plant materials on the forest floor. Means and others found that in the Pinelands, fulvic acid has a greater total acidity and therefore metal binding capacity than humic acid. Correlation between DOM and Pb, Cu, Fe, and Ni (table 6) suggests that these metals form organo-metallic complexes with fulvic and perhaps also with humic acid, the predominant organic compounds in most soils and waters of the Pinelands. Once in the solution, these complexes may release the metals if pH decreases and ionic strength increases (Gjessing, 1976). The ionic strengths were not determined for this study. The effect of decreasing pH is detected only for the release of Pb from DOM, as indicated by a negative correlation between Pb and pH (table 6). Relatively weak DOM-metal correlations and the effect of unknown ionic strength apparently mask the relation between pH and the release of other metals from DOM. Complexation with DOM is, then, important in moving Pb, Cu, Fe, and perhaps Ni

Table 1. Mean concentrations of six trace metals in blanks and in ground water from McDonalds Branch basin, June 1978 - March 1979.

Element	Mean blank concentration (μg/L)	Number of blanks	Standard error	Mean concentration in ground water (μg/L)
Pb	2	16	0.25	12
Cd	0.4	13	0.06	1.2
Cu	2	16	0.50	7
Ni	3	16	0.50	7
Fe	7	16	1.25	440
Mn	3	17	0.70	63

Note: All samples and blanks were filtered through 1 μm Nuclepore membrane filters and acidified with concentrated, reagent-grade HNO_3. Mean concentrations in ground water were determined after subtracting the blank.

Table 2. Mean concentrations and ranges of six trace metals, DOM, and pH of precipitation and ground water in the basin, June 1978 - March 1979.

PRECIPITATION[a]

Element or constituent	Number of samples	Range	Mean	Standard deviation
pH (units)	29	3.3-4.5	3.77[b]	3.90[b]
Pb (μg/L)	29	4-118	23	23
Cd (μg/L)	29	<0.1-5.8	0.5	1.16
Cu (μg/L)	29	1-11	4	3.34
Ni (μg/L)	29	1-46	7	9.1
Fe (μg/L)	29	6-158	53	46
Mn (μg/L)	29	1-112	21	32

GROUND WATER

Element or constituent	Number of samples	Range	Mean	Standard deviation
pH (units)	80	2.8-5.4	3.97[b]	3.66[b]
DOM (absorbance unit)	75	0-2.04	0.180	0.36
Pb (μg/L)	78	<1-86	12	16.9
Cd (μg/L)	78	<0.1-13.6	1.2	2.4
Cu (μg/L)	78	<1-71	7	12.6
Ni (μg/L)	78	<1-72	7	10.4
Fe (μg/L)	78	43-2715	440	463
Mn (μg/L)	78	5-206	63	44

[a] From Swanson (1979).

[b] Calculated using H^+ concentrations.

Table 3. Differences between summer and winter concentrations in precipitation from the basin shown by T' and V values.

		SUMMER (June'78-Oct.'78)			WINTER (Nov.'78-Mar.'79)			
Element or constituent	n_1	X_1 (mean)	S_1^2 (variance)	N_2	X_2 (mean)	S_2^2 (variance)	T' (value of t-distribution)	V (degrees of freedom)
H (mole/L)	16	2.44×10^{-4}	1.6×10^{-8}	13	0.8×10^{-4}	0.8×10^{-9}	4.883[a]	17
DOM (absorbance unit)	--	--	--	--	--	--	--	--
Pb (μg/L)	16	29	724.2	13	15	234	1.760[b]	25
Cd (μg/L)	16	0.2	0.08	13	0.8	2.81	1.276	13
Cu (μg/L)	16	5.7	10.8	13	1.8	3.81	3.964[a]	25
Ni (μg/L)	16	8.5	120.9	13	4.5	30.6	1.271	23
Fe (μg/L)	16	70	1934	13	32	1658	2.391[b]	27
Mn (μg/L)	16	26	1431	13	15	534	0.963	25

Table 4. Differences between summer and winter concentrations in ground water from the basin shown by T' and V values.

		SUMMER (June'78-Oct.'78)			WINTER (Nov.'78-Mar.'79)			
Element or constituent	n_1	X_1 (mean)	S_1^2 (variance)	N_2	X_2 (mean)	S_2^2 (variance)	T' (value of t-distribution)	V (degrees of freedom)
H(mole/L)	48	1.41×10^{-4}	7.11×10^{-8}	32	0.55×10^{-4}	2.95×10^{-9}	2.168[b]	53
DOM (absorbance unit)	44	0.277	0.200	31	0.041	0.003	3.464[a]	45
Pb (μg/L)	47	18	375.78	31	2	2.58	5.629[a]	47
Cd (μg/L)	47	1.9	8.52	31	0.2	0.065	3.975[a]	47
Cu (μg/L)	47	10.8	228.19	31	1.5	3.36	4.174[a]	48
Ni (μg/L)	47	7	115.53	31	6	98.33	0.416	68
Fe (μg/L)	47	560	297651	31	259	36598	3.473[b]	61
Mn (μg/L)	47	72	2541	31	51	842	2.330[b]	75

Table 5. Differences between concentrations in ground waters from organic soil and from mineral soil in the basin shown by T' and V values.

		ORGANIC SOIL			MINERAL SOIL			
Element or constituent	n_1	X_1 (mean)	S_1^2 (variance)	N_2	X_2 (mean)	S_2^2 (variance)	T' (value of t-distribution)	V (degrees of freedom)
H(mole/L)	42	9.63×10^{-5}	2.4×10^{-8}	38	11.96×10^{-5}	6.76×10^{-8}	0.853	64
DOM (absorbance unit)	41	0.165	0.114	34	0.198	0.148	0.391	66
Pb (μg/L)	42	13	377.23	36	10	166.58	0.813	72
Cd (μg/L)	42	1.4	6.41	36	1.0	4.93	0.743	76
Cu (μg/L)	42	6	130.86	36	9	182.47	1.049	69
Ni (μg/L)	42	8	176.04	36	6	21.69	0.913	52
Fe (μg/L)	42	289	145340	36	616	230601	3.294[a]	66
Mn (μg/L)	42	48	841.9	36	83	2453	3.727[a]	55

[a] significant at $p = 0.01$.

[b] significant at $p = 0.05$.

Note: For equal variance,

$$T' = \frac{|X_1 - X_2|}{S_p \left(\frac{1}{n_1} + \frac{1}{N_2}\right)^{1/2}} \; ; \quad V = n_1 + N_2 - 2 \; ; \; S_p = \left(\frac{(n_1-1)S_1^2 + (N_2-1)S_2^2}{V}\right)^{1/2}$$

For unequal variance:

$$T' = \frac{|X_1 - X_2|}{\left(\frac{S_1^2}{n_1} + \frac{S_2^2}{N_2}\right)^{1/2}} \; ; \qquad V = \frac{\left(\frac{S_1^2}{n_1} + \frac{S_2^2}{N_2}\right)^2}{\frac{\left(\frac{S_1^2}{n_1}\right)^2}{n_1 - 1} + \frac{\left(\frac{S_2^2}{N_2}\right)^2}{N_2 - 1}}$$

Equality of variance was tested using F-distribution.

Table 6. Correlation coefficients between various constituents in precipitation and ground water.

PRECIPITATION			GROUND WATER		
	n	r		n	r
Pb-pH[a]	29	-0.556[b]	Pb-pH[a]	78	-0.258[c]
Ni-pH[a]	29	-0.487[b]	Pb-DOM	75	0.682[b]
Fe-pH[a]	29	-0.476[b]	Cu-DOM	75	0.427[b]
Cu-pH[a]	29	-0.434[b]	Fe-DOM	75	0.410[b]
Pb-Fe	29	0.687[b]	Pb-Cu	78	0.354[b]
Pb-Ni	29	0.386[c]	Pb-Fe	78	0.344[b]
Cu-Fe	29	0.491[b]	Pb-Cd	78	0.495[b]
Ni-Fe	29	0.464[b]	Cu-Fe	78	0.368[b]
Mn-Fe	29	0.411[c]	Ni-DOM[d]	34	0.553[b]

[a] calculated using H^+ concentrations.
[b] significant at p = 0.01.
[c] significant at p = 0.05.
[d] only for the ground water of the mineral soil.

in the study area. However, not all of the variations in metal concentrations are accounted for by variations in DOM because the DOM-metal correlation coefficients are smaller than unity. Other factors, such as temperature, respiring microorganisms, changing CO_2 and O_2 levels, growing roots, and fluctuation of the water table are also involved in the mobilization of trace metals monitored.

ADSORPTION AND pH

Iron oxides are known to be an efficient sink for trace elements (Gadde and Laitinen, 1974; Schwertmann and Taylor, 1977). The mechanism of this retention is moot. Adsorption or desorption of H^+ on the surface of metal oxides results in net surface charge. Adsorption of metal ions is probably accompanied by release of H^+ from the surface (Davis, 1984). The zero point of charge (ZPC) ranges from pH 6.5 to pH 10.4 for different oxides of the type $(Metal)_2O_3$ which includes all Fe^{3+}-oxides (Parks, 1965). The pH of ground water in the study area ranges from 2.8 to 5.4, suggesting that the exchange sites on Fe-oxides are loaded mostly by H^+ ions. Therefore, trace element adsorption on Fe-oxide coatings should be insignificant at these low pH values. The very small proportions of the trace elements that may be adsorbed on Fe-oxide coatings may subsequently be mobilized and transported by humic substances within the aquifer. Vuceta and Morgan (1978) reported that oxide surface hydroxyls and organic matter compete for the adsorption of metals if organic matter is not itself absorbed on oxide surfaces.

Mean pH value in ground water higher than that in the precipitation (table 2) indicates that there is still a geochemical control on the pH of the ground water. Means and others (1981) found that H^+ in the precipitation of the Pinelands ecosystem is balanced by SO_4^{2-}. They also found that the maximum atmospheric SO_4^{2-} inputs to the basin occurred in summer whereas the maximum SO_4^{2-} output through the streams occurred in winter. Generally lower pH values but higher H^+ in summer precipitation than in winter precipitation (table 3) also indicate higher H^+ input in summer during the study period. Apparently, flushing of the atmospherically introduced H^+ from upper soil horizons increases in wet months of winter. However, in summer, internally generated H^+ in the ground water increases due to increased organic acid production, resulting in a lower mean pH (but higher mean H^+) value of ground water in summer than in winter (table 4).

Trace metals may also be adsorbed on silica surfaces (Wilding and others, 1977). A small amount of surface charge on silica minerals arises from Si-O broken bonds and Si-OH bonding around particle edges. This type of charge is also pH-dependent and increases with decreasing particle size. Leckie and James (1974) indicated that the ZPC may be as low as pH 2-3 for quartz. However, because the silica surface charge is very small compared to the Fe-oxide surface charge, and because most silica grains in shallow aquifers of the Pinelands are coated with Fe-oxides, metal adsorption by silica surfaces is also negligible for this study.

TRACE METALS

Lead

Dissolved Pb in common geological environments exists as Pb^{2+} in acid solutions if it is not complexed with organic matter (Vuceta and Morgan, 1978). Atmospherically-borne Pb accumulates chiefly in the soil due to its complexation with organic matter (Reiners and others, 1975; Benninger and others, 1975; Van Hook and others, 1977; Heinrichs and Mayer, 1977; Siccama and Smith, 1978). This appears to be true also for the study area because Pb levels in the precipitation are significantly higher than those in the ground water (table 2), and Pb positively correlates with DOM in the ground water (table 6, fig. 2). Pb-organic-matter complexes apparently become more soluble and/or Pb is released from organic matter, thus raising the concentrations of Pb in ground water during summer because of decreased pH (increased H^+, table 4), increased microbiological activity and higher temperature. Because Fe- and Mn-oxides and quartz do not adsorb Pb under low pH conditions (Gadde and Laitinen, 1974; Leckie and James, 1974), Pb adsorption on inorganic phases in the study area, where pH is low (table 2), is unlikely or minimal.

Because atmospheric Pb is the source of Pb in ground water, change in the atmospheric input can cause observable changes in Pb levels in ground water. A sharp decrease in the mean Pb content of regular-grade gasoline after 1979 (Elsenreich and others, 1986) and accordingly decreasing Pb input to the atmosphere may have reduced the seasonal averages of Pb concentration in the ground water following the completion of this study.

Cadmium

Low Cd concentrations, which are about at the detection limit of the method used, make the precise determination of its sources difficult, but Cd concentrations in the ground water can be accounted for by precipitation and evapotranspiration. There is no correlation between Cd and DOM in the ground water (fig. 3), a finding consistent with previous investigations (Davis, 1984; Norvell, 1972) showing that Cd does not complex with organic matter in aqueous systems. It thus appears that atmospherically-borne Cd and perhaps also a very small amount of Cd weathered from the soil minerals move into the ground water as Cd^{2+}. Mean Cd concentration in the ground water (1.2 μg/L) is higher than that in the precipitation (0.5 μg/L). The greater-than-twofold difference may be caused in part by evapotranspiration of about 50 percent. Because the concentrating effect of evaporation in summer is likely to be close to that in winter in the study area (Swanson and Johnson, 1980) and because mean Cd concentration in summer precipitation is not significantly different from that in winter precipitation (table 3), higher Cd levels of the ground water in summer probably result from leaching of a small amount of Cd bound within soil material due to lower pH, warmer temperature and, accordingly, higher rate of chemical weathering.

Copper

Cu and DOM in the ground water are positively correlated (table 6), suggesting that organic layers of soil adsorb and subsequently release Cu in the form of dissolved Cu-organic-matter complexes. In a study of adsorption of Cu^{2+} and Cd^{2+} on alumina and organic matter in aqueous systems, Davis (1984) found that Cu^{2+} was partitioned primarily between the surface-bound organic matter and dissolved organic matter, and that complexation with the surface-bound organic matter was stronger than that with uncovered alumina surface hydroxyls. Trace element adsorption on inorganic surfaces is insignificant in the study area so that mobility of Cu is apparently controlled by the dissolution-precipitation reactions and by the mobility of organic matter. The Cu in the ground water appears to be accounted for by atmospheric input and the evapotranspiration of 50 percent. Mean Cu concentration in the ground water is higher in summer (table 4, fig. 4) because of increased mean atmospheric input (table 3, fig. 4) and increased mobility of Cu^{2+} due to lower pH (higher H^+, table 4).

Nickel

Table 6 shows a correlation between Ni and DOM for the ground water of mineral soil but not for that of organic soil. At first, this suggests that either Ni-organic-matter complexes are unstable in reduced environments, or Ni probably precipitates as an insoluble Ni-sulfide in swamps, because their waterlogged organic soils generate significant amounts of H_2S, especially in summer. However, mean Ni concentrations of ground water for summer and for winter are similar (table 4, fig. 5), and there is no significant difference between Ni concentration in the ground water of the mineral soil and the organic soil (table 5). It seems that other chemical processes mobilize Ni in the study area, and the Ni-DOM correlation may or may not be coincidental. The mean Ni concentration in summer precipitation is not significantly different from that in winter precipitation (table 3), and the mean concentrations in the ground water and precipitation are similar for the 10-month period of study (table 2). It appears then that Ni in the ground water is basically supplied by atmos-

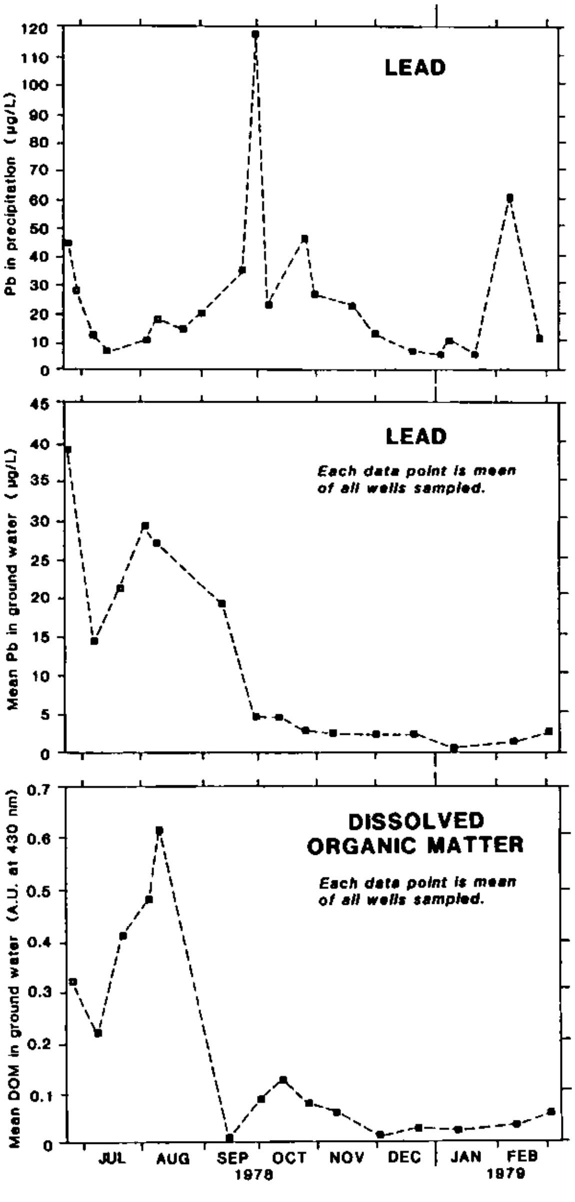

Figure 2. Seasonal variations of lead in precipitation, and of lead and dissolved organic matter in ground water, McDonalds Branch basin.

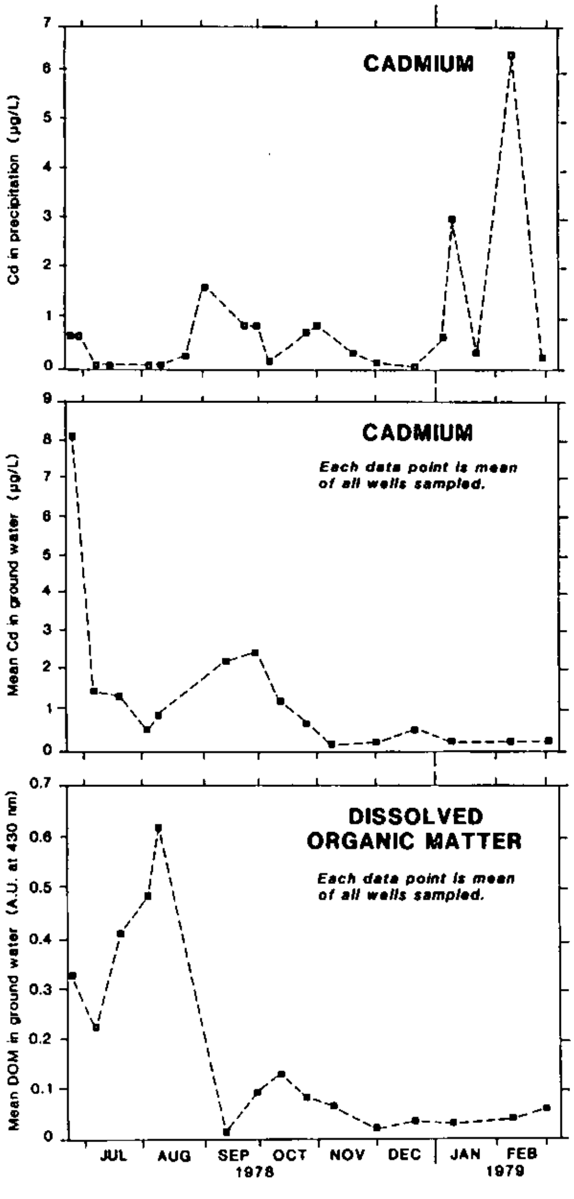

Figure 3. Seasonal variations of cadmium in precipitation, and of cadmium and dissolved organic matter in ground water, McDonalds Branch basin.

pheric input. The chemical factors that control the mobility of this atmosphericaly-borne Ni in the soil of the study area cannot be determined with the present data.

Iron

Fe concentrations in the ground water are much higher than can be accounted for by evapotranspiration of precipitation (fig. 6). The especially high Fe concentration within the mineral soil (table 5), which contains more Fe oxides, indicates the importance of geochemical weathering. Thus, Fe in the ground water is mainly geochemical, not atmospheric, in origin. One of the sources of Fe might be the underlying metalliferous clay and glauconitic beds (Means and others, 1981). A positive correlation between Fe and the DOM in the ground water (table 6) indicates that another source of Fe is the reduction and removal of ferric Fe from Fe compounds in the soil by acidic organic-matter-rich waters seeping down from the organic layers. This may be the cause of bleached surface horizons below organic-matter layers within the

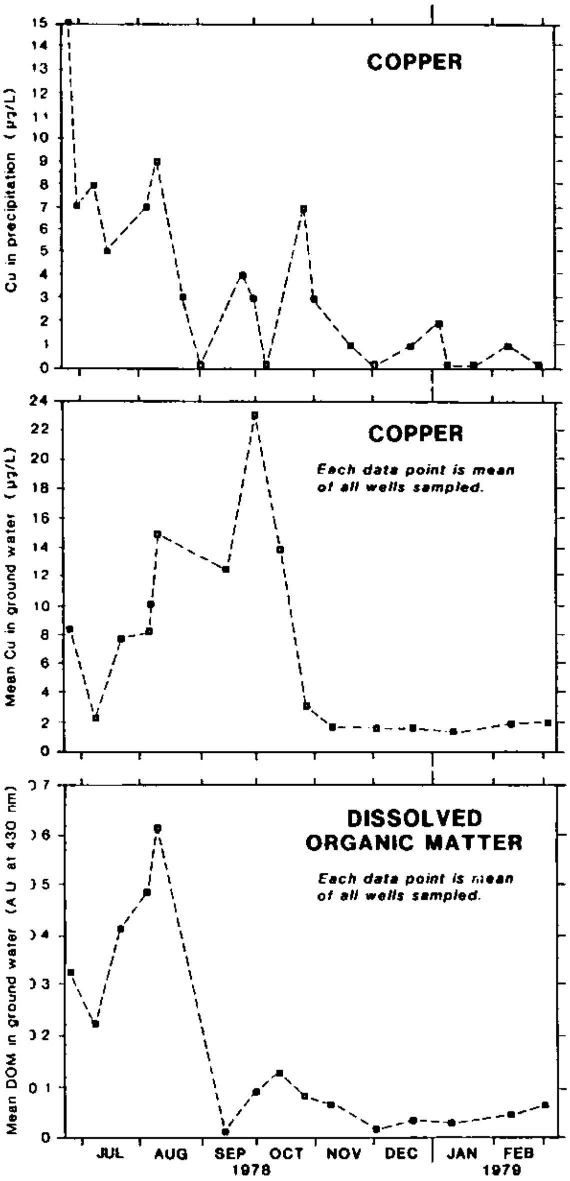

Figure 4. Seasonal variations of copper in precipitation, and of copper and dissolved organic matter in ground water, McDonalds Branch basin.

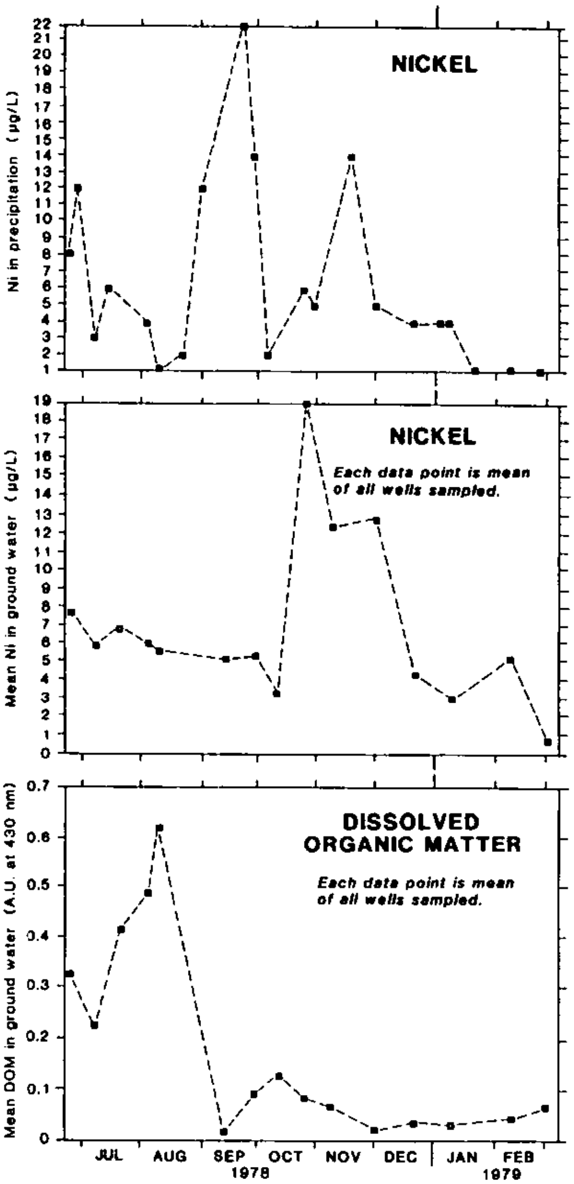

Figure 5. Seasonal variations of nickel in precipitation, and of nickel and dissolved organic matter in ground water, McDonalds Branch basin.

mineral soil, although at least some of this Fe is redeposited in the B horizon.

Manganese

There is no correlation between Mn and DOM in the ground water, and the mean ground-water concentration exceeds the mean precipitation concentration by threefold (table 2). Mean Mn concentration in ground water is higher in summer than in winter (table 4, fig. 7), but seasonal difference for precipitation is insignificant for this element (table 3, fig. 7). Furthermore, mean Mn concentration for the mineral soil is significantly higher than that for the organic soil (table 5). These relationships indicate that geochemical weathering is the major source of Mn in the ground water, and that atmospheric input contributes somewhat less. Dissolution of Mn-oxides by fulvic acid and other organics has been demonstrated in the laboratory (Stone and Morgan, 1984). This might also be occurring in the Pinelands to some extent. However, simple dissolution-precipitation reactions that do not involve organic matter apparently are dominant mechanisms controlling the mobility of Mn in the study area. In summer, increased chemical activity due to warmer temperature accelerates weathering and mobilization of Mn.

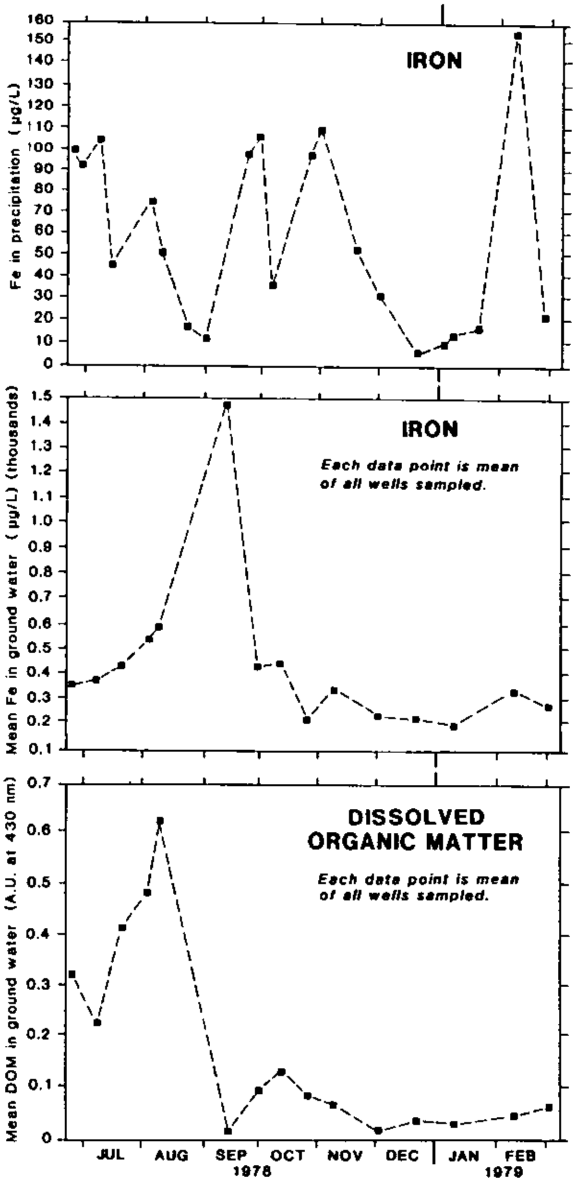

Figure 6. Seasonal variations of iron in precipitation, and of iron and dissolved organic matter in ground water, McDonalds Branch basin.

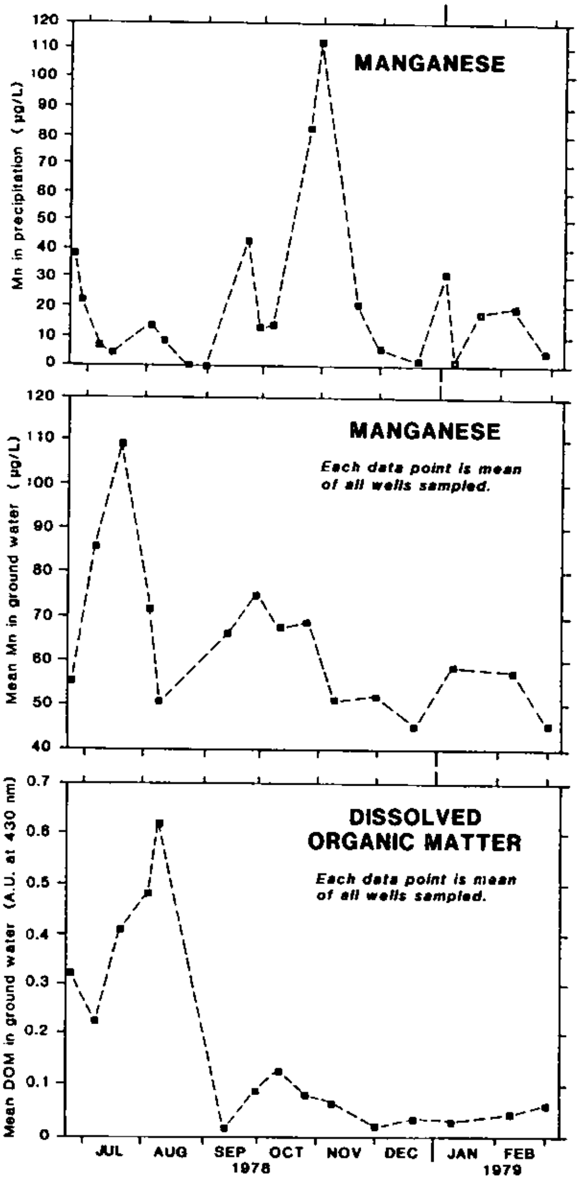

Figure 7. Seasonal variations of manganese in precipitation, and of manganese and dissolved organic matter in ground water, McDonalds Branch basin.

CONCLUSIONS

Pb, Cu, Ni, and Fe are leached from soils and/or sedimentary rocks into the ground water both as organo-metallic complexes and as dissolved ions in the McDonalds Branch Basin, Pinelands, New Jersey. The leaching of Pb, Cu, Fe, and Mn increases in summer owing to increased microbiological activity and chemical weathering. Atmospherically-borne Pb, almost the only Pb source in the ground water, is largely accumulated by the forest floor, owing to complexation with organic matter. Precipitation and an evapotranspiration rate of 50 percent account for Cu concentrations in the ground water. Fe in the ground water originates mainly from geochemical weathering of soil and sedimentary minerals. Atmospherically-borne Ni supplies most of Ni in the ground water. Cd, primarily atmospheric, does not complex with organic matter, but is leached into the ground water as Cd^{2+}. Geochemical weathering probably contributes a very small amount of Cd to ground water, especially in summer. Like Cd, Mn does not appear to complex with organic matter; Mn in the ground water is supplied by geochemical weathering of the soil material and, to a lesser extent, by atmospheric input.

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APPENDIX 1

Trace metal levels in ground water

Trace metal levels in ground water, June 1978-March 1979 (after subtraction of mean values of blanks)*

Date of collection	Well no.	pH (units)	Organic matter (A.U.)	µg/L						Depth to water table (cm)
				Pb	Cu	Ni	Cd	Fe	Mn	
6/22/78	1	4.7	0.01	86	23	10	13.6	132	124	20
	2	5.4	0.311	23	4	12	0.6	117	50	0
	3	3.3	0.395	21	4	4	13.6	447	33	9
	6	3.2	0.57	28	2	5	4.6	699	13	0
	mean	4.2	0.322	39.5	8.3	7.8	8.1	349	55	7.3
7/6/78	1	4.7	0.02	6	1	4	2.6	63	89	20
	2	4.2	0.04	8	1	1	0.6	168	123	0
	3	3.7	0.21	11	4	15	1.6	601	112	9
	6	3.7	0.625	32	2	4	0.6	638	17	0
	mean	4.1	0.224	14.3	2	6	1.4	367	88	7.3
7/19/78	1	3.9	0.025	55	2	5	2.6	72	96	32
	2	4.3	0.02	12	3	2	0.6	62	79	2.5
	3	3.7	0.34	19	2	4	<0.1	646	146	14
	4	4.2	0.65	6	21	16	1.6	696	206	53
	5	4.7	-	-	-	-	-	-	-	47
	6	4.3	1.03	15	11	8	1.6	656	19	0
	mean	4.2	0.413	21.4	7.8	7	1.3	426	109	25
8/3/78	1	4.2	0.02	18	3	2	2	98	51	12.5
	2	3.1	0.035	20	2	<1	<0.1	164	56	5
	3	2.8	0.17	34	6	<1	<0.1	617	87	15
	4	4.9	0.165	8	4	9	0.2	745	143	53
	5	4.6	1.1	59	25	19	0.1	808	73	52
	6	3.6	1.4	39	9	6	0.2	782	19	0
	mean	3.9	0.482	29.7	8.2	6	0.4	536	72	23
8/8/78	1	4.5	0.02	11	3	1	<0.1	522	52	7.5
	2	4.5	0.04	13	5	2	<0.1	227	42	3.8
	3	4.0	0.2	33	17	6	1.2	690	54	18
	4	4.8	0.14	8	8	6	0.6	516	116	49
	5	4.6	2.04	39	38	17	0.7	774	30	55
	6	4.0	1.28	60	19	2	2.2	743	11	0
	mean	4.4	0.62	27.3	15	5.7	0.8	579	51	22
9/13/78	1	4.2	0.01	5	8	2	3.3	162	53	2.5
	2	4.4	0.01	8	5	2	0.7	452	42	2.5
	3	3.7	0.01	14	24	6	0.6	1675	90	18
	4	4.3	0.01	8	4	10	0.7	1649	187	50
	5	4.9	-	23	19	7	0.1	2715	10	45
	6	3.7	-	59	14	4	7.5	2185	12	0
	mean	4.2	0.01	19.5	12.3	5.2	2.2	1473	66	20

* Values < 1.0 were arbitrarily set to 0.1 and those < 0.1 were set to 0.01 in statistical calculations and in plots.

Appendix 1. Trace metal levels in ground water* (cont.)

Date of collection	Well no.	pH (units)	Organic matter (A.U.)	μg/L						Depth to water table (cm)
				Pb	Cu	Ni	Cd	Fe	Mn	
9/29/78	1	4.7	0.01	3	10	1	5.3	60	73	10
	2	4.5	0.02	1	2	7	2.1	50	44	5
	3	3.8	0.17	12	53	4	1.3	619	111	20
	4	4.9	0.06	3	1	7	2.0	689	141	53
	5	3.7	0.19	4	49	8	1.9	728	6	88
	mean	4.3	0.09	4.6	23	5.4	2.5	429	75	35.2
10/11/78	1	4.7	0.01	2	3	<1	<0.1	110	73	7.5
	2	4.7	0.04	2	1	6	0.6	68	41	5
	3	4.1	0.09	1	1	6	1.8	588	131	26
	4	4.9	0.07	6	<1	2	0.5	577	141	55
	5	3.95	-	2	7	5	2.3	627	10	66
	6	4.0	0.43	16	71	2	1.8	655	8	10
	mean	4.4	0.128	4.8	13.9	3.5	1.2	436	67	28
10/25/78	1	4.7	0.01	3	1	72	0.2	79	76	12.5
	2	4.5	0.02	2	1	13	<0.1	47	46	6.4
	3	4.0	0.025	3	<1	1	0.3	302	92	24
	4	4.6	0.025	3	<1	<1	0.3	200	113	58
	6	3.9	0.32	4	12	9	2.4	388	17	15
	mean	4.3	0.08	3.0	2.8	19	0.6	203	69	23
11/8/78	1	4.8	0.01	2	<1	8	<0.1	45	58	13
	2	4.65	0.01	2	<1	2	<0.1	43	27	37
	3	4.15	0.01	2	<1	5	<0.1	488	76	23
	4	5.0	0.05	3	1	4	0.2	508	87	58
	6	4.1	0.24	3	6	43	0.3	596	7	33
	mean	4.5	0.064	2.4	1.5	12.4	0.1	336	51	33
12/1/78	1	4.8	0	2	1	10	0.2	59	64	0
	2	4.6	0	2	2	39	<0.1	93	32	8
	3	3.9	0	2	1	3	0.1	422	67	20
	4	4.7	0.025	3	2	6	0.2	134	76	60
	6	3.7	0.05	3	2	6	0.1	421	19	0
	mean	4.3	0.015	2.4	1.6	12.8	0.12	226	52	18
12/21/78	1	4.7	0.015	1	<1	12	<0.1	55	48	0
	2	4.6	0.03	2	2	1	0.3	48	26	5
	3	4.1	0.015	4	2	3	0.5	340	72	23
	4	4.7	0.03	2	2	4	0.8	117	80	58
	5	4.5	0.045	2	1	5	1.2	309	5	76
	6	3.65	0.05	5	1	1	0.1	393	39	0
	mean	4.4	0.031	2.7	1.4	4.3	0.5	210	45	27

* Values < 1.0 were arbitrarily set to 0.1 and those < 0.1 were set to 0.01 in statistical calculations and in plots.

Appendix 1. Trace metal levels in ground water* (cont.)

Date of collection	Well no.	pH (units)	Organic matter (A.U.)	µg/L						Depth to water table (cm)
				Pb	Cu	Ni	Cd	Fe	Mn	
1/10/79	1	4.7	0.01	<1	<1	5	0.1	53	46	0
	2	4.5	0.035	1	<1	1	0.1	44	92	0
	3	4.1	0.045	1	1	3	0.3	395	93	18
	4	4.5	-	-	-	-	-	-	-	53
	5	4.2	0.02	1	1	3	0.2	243	5	-
	mean	4.4	0.028	0.8	1.0	3	0.18	184	59	18
2/10/79	1	4.7	0	<1	<1	15	<0.1	130	60	0
	2	4.6	0.02	<1	1	2	<0.1	93	47	0
	3	4.3	0.07	6	3	2	0.4	550	80	13
	4	4.2	0.1	1	5	3	0.4	345	93	45
	5	4.3	0.03	<1	<1	4	0.2	508	8	48
	mean	4.4	0.044	1.5	1.8	5.2	0.2	325	58	21
3/1/79	1	4.9	0	<1	<1	<1	<0.1	47	59	0
	2	4.7	0.02	1	<1	<1	0.3	47	55	0
	3	4.6	0.02	5	<1	1	0.3	283	77	8
	4	4.1	0.18	2	2	<1	0.3	283	59	35
	5	4.2	0.02	3	1	1	<0.1	354	5	18
	6	3.8	0.13	5	8	2	0.1	579	18	0
	mean	4.4	0.062	2.7	1.9	0.7	0.2	266	46	10

* Values < 1.0 were arbitrarily set to 0.1 and those < 0.1 were set to 0.01 in statistical calculations and in plots.

APPENDIX 2

Trace metal levels in precipitation

Trace metal levels in precipitation (dry fallout plus rain or snow) from May 1978 to March 1979*

Date of	Sample	pH			µg/L			
collection	number	(units)	Pb	Cu	Ni	Cd	Fe	Mn
6/22/78	6	3.75	28	8	12	0.1	93	22
6/22	7	3.7	13	9	3	<0.1	105	7
7/6	8	4.5	7	6	6	<0.1	46	5
7/19	9	3.4	11	8	4	<0.1	76	14
8/3	10	3.6	26	11	1	<0.1	82	12
8/9	11	3.6	9	8	1	<0.1	21	5
8/9	12	3.6	10	7	2	<0.1	17	1
8/22	13	3.8	20	1	2	<0.1	19	1
8/22	14	3.7	20	1	12	1.1	13	1
9/1	15	3.7	19	2	14	<0.1	28	1
9/22	16	3.6	38	4	6	0.3	111	106
9/22	17	3.3	49	9	46	0.5	158	23
9/29	18	3.3	118	4	14	0.3	107	13
10/6	19	3.5	23	1	2	0.1	37	14
10/25	20	4.0	47	8	6	0.2	99	83
10/30	21	3.9	27	4	5	0.3	101	112
11/19	22	4.1	16	1	5	<0.1	37	20
11/19	23	4.05	29	3	22	<0.1	70	21
12/1	24	4.1	13	1	5	<0.1	33	6
12/21	25	4.1	7	1	4	<0.1	8	3
12/21	26	4.45	7	2	4	<0.1	6	1
1/5/79	27	4.1	4	8	6	<0.1	12	1
1/5	28	4.3	7	1	2	<0.1	8	4
1/5	29	4.2	7	1	3	0.8	12	87
1/9	30	4.0	11	1	4	2.5	15	1
1/23	31	4.0	6	1	1	<0.1	18	18
2/10	32	4.1	61	2	1	5.8	155	20
2/26	33	3.8	12	1	1	<0.1	23	5
3/19	34	4.2	12	1	1	1.3	22	5

* Data adapted from Swanson, 1979; values after subtraction of mean values of blanks

Values <0.1 were arbitrarily set to 0.01 in statistical calculations and in plots.

For those dates with more than one sample, mean concentrations were used in the plots.

Temporal variation and sources of Pb, Cd, Cu, Ni, Fe, and Mn in shallow ground water from the McDonalds Branch basin, Lebanon State Forest, Burlington County, New Jersey (New Jersey Geological Survey, Geological Survey Report 20)

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