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**ATMOSPHERIC INPUT and GEOCHEMICAL CYCLING
of SELECTED TRACE ELEMENTS in
WALKER BRANCH WATERSHED**

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ATMOSPHERIC INPUT AND GEOCHEMICAL CYCLING OF SELECTED
TRACE ELEMENTS IN WALKER BRANCH WATERSHED*

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ABSTRACT

Integrated studies of atmospheric and aquatic chemistry have been used to quantify the cycling of selected trace elements in Walker Branch Watershed, Oak Ridge, Tenn. The relative elemental contribution of wet deposition and aerosol impaction have been evaluated. Data for the concentrations of Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn in rain and their input (in g/ha) for the period June, 1973-July, 1974 are presented. The total amounts of metals (expressed as g/ha) for the time period were as follows: Cd, 158; Cr, 41; Cu, 248; Hg, 3.3; Mn, 291; Ni, 108; Pb, 252; and Zn, 512. Comparison of elemental ratios in rain to those of soil indicate that Cd, Cu, Hg, and Pb in rain are enriched with respect to soil by 1 to 3 orders of magnitude and must thus have a non-soil source. Elemental ratios from fly ash are comparable to rain ratios for Cu, Zn, and Cd. Chromium and Mn seem to be soil derived whereas Pb can be attributed to automotive emissions. The concentration of 34 elements has also been measured in air particulate matter. Using enrichment factor calculations, the data indicate that 16 elements have a natural geochemical origin whereas Ag, As, Au, Br, Cd, Cl, Co, Cu, Hg, I, Na, Pb, S, Se, V, and Zn are enriched. Arsenic, Co, Cu, Hg, Se, V, and Zn possess enrichment factors very close to those of fly ash and can thus tentatively be attributed to three coal-fired steam plants in the vicinity of Oak Ridge. Lead is attributed to automotive emissions. Using previously measured deposition velocities, we estimate that, of the elements measured in rain, only Cr and Mn have a significant input through dry deposition (impaction) and amount to 21 and 16% of the total input, respectively. Data on stream water trace

element transport and speciation in dissolved and particulate forms for a 6-month period and a summary mass balance calculation are also reported. Concentrations of trace elements in the dissolved fraction were relatively constant; thus, export of dissolved forms is a simple function of discharge. Considerable variation in stream particulate metal concentration illustrates the complexity of suspended sediment source mechanisms. The particulate fraction represents a significant transport mechanism for Cr, Hg, and Mn. Calculations used to identify sources of trace elements lead to speculation that dissolved and particulate Pb and Cd entering the watershed may be of anthropogenic origin while dissolved and particulate Pb and particulate Cd species transported from the watershed may be as products of natural soil or geochemical weathering. Budget calculations indicate that the watershed efficiently retains Pb (97-98% of the input), Cd (94-95%), and Cu (82-84%), while it less readily accumulates Cr (59%), Mn (57%), Zn (73-75%), and Hg (69-75%).

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INTRODUCTION

The combined combustion of fossil fuels (i.e., fuel oils, lignite coal, and natural gas) may introduce some elements into the atmosphere and subsequently into the aquatic and terrestrial environment at rates comparable to those of natural processes (Bertine and Goldberg, 1971). Current literature indicates that sulfur is introduced to the atmosphere by fossil fuel burning at rates which are comparable to the combined emissions from volcanoes and from the anaerobic areas of the world (Kellog et al., 1972). The annual amount of CO_2 introduced into the atmosphere has been calculated at 13×10^{15} g which is close to the amount of CO_2 produced by photosynthesis on land and in the sea - 50×10^{15} g (Hitchcock and Wechsler, 1972). More lead has been transferred from land to the oceans by the use of tetraethyl lead as an antiknock additive in gasolines than has been added to the marine environment through rivers by natural weathering processes (Tatsumoto and Patterson, 1963). Likewise, Andren et al. (1974) have shown that 1.5 to 2.5 times as much Se is mobilized by man through coal burning as by natural weathering.

Although recent literature contains information on the atmospheric concentration of many elements (Davis et al., 1972; John et al., 1973; Tanner et al., 1974), data for their removal are not readily available. Such considerations have prompted us to investigate the atmospheric input of several elements into the environment as well as their geochemical cycling and transport through a terrestrial-aquatic ecosystem. Specifically, this research has the following objectives: (1) To derive relationships between levels of trace

elements in air, rain, and dry deposition and, by this data and the known atmospheric pollutant input, differentiate between natural and anthropogenic origins (Andren and Lindberg, 1975); (2) to study the transport processes and actual input-output budgets for several trace elements by utilizing the hydrologically well-calibrated Walker Branch Watershed in Oak Ridge, Tennessee (Lindberg and Andren, 1975)

METHODS OF SAMPLING AND ANALYSIS

The Walker Branch Watershed (WBW) has been described in detail elsewhere (Nelson, 1970; Peters et al., 1970; Henderson and Harris, 1975; and Elwood and Henderson, 1973). The study site (Fig. 1) is a 97.5 hectare (ha) catchment located on the Oak Ridge Reservation in Oak Ridge, Tenn. It consists of two gaged subcatchments, the east and the west branches, which contain 59.1 and 38.4 ha, respectively. Elevation ranges from 285 to 375 m, and the slope averages 30%. Both basins are underlain by Knox dolomite of Cambrian and Ordovician age. Soils of the Fullerton and Bodine series occupy over 90% of the catchment area. The predominant clay mineral in the soils is kaolinite.

Both catchments are drained by small, perennial spring-fed streams. Discharge is maximum during the winter months and lowest in late summer and early fall. Average width of the streams in summer during base flow conditions is about 2 m. Chert and weathered dolomite constitute the dominant materials of the stream bottom substrata. Stream bed slope of the east and west fork below the limits of perennial

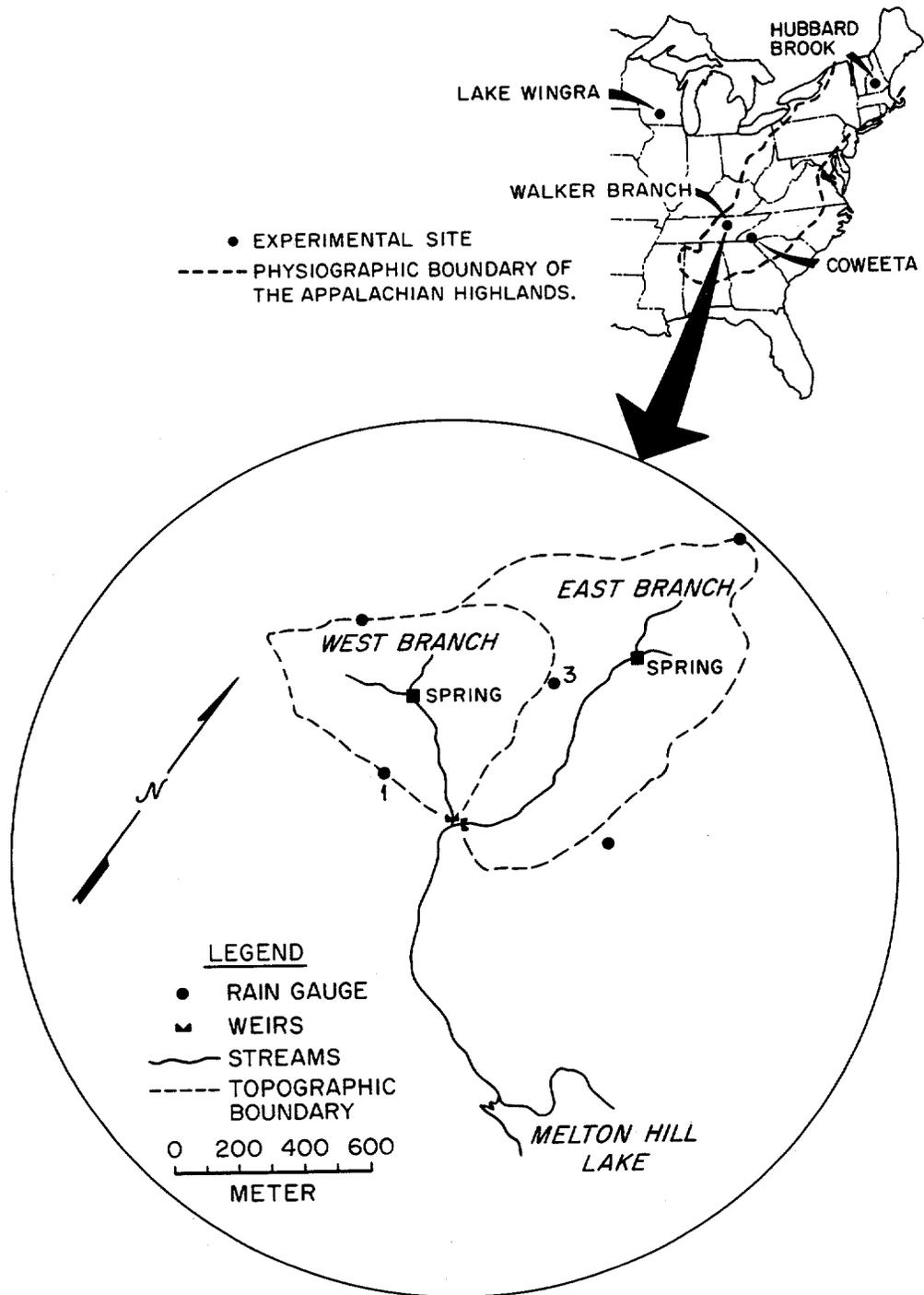


Fig. 1. Walker Branch Watershed Study Area - indicating stream and precipitation sample sites.

flow averages 3.4 and 4.3%, respectively. Although there is channel expansion during storms, there is very little, if any, overland flow on this catchment. The 23-year mean precipitation in this area is approximately 130 cm/yr (McMaster, 1967). Meteorological and hydrological parameters such as precipitation and stream discharge are measured by techniques already described in detail by Nelson et al. (1970) and Elwood and Henderson (1974).

Two of five permanent gauging stations (1 and 3) were used to collect monthly rain samples for elemental analysis. Previous data (Henderson, personal communication) indicate that there is less than a 5-cm/yr difference in precipitation between stations at the watershed.

At each of the gauging stations an automated precipitation collector (Wong Industries) remains open during periods of precipitation only, thus excluding dry fallout. The moisture sensing grid that activates the lid is thermostatically controlled so that snow and sleet as well as rain are collected. The sensing grid is maintained at a temperature sufficient to evaporate moisture from the grid shortly after precipitation ceases, causing the lid to close.

The rain collection bottles are preacidified with a combination of HCl and HClO_4 to pH 1 to prevent adsorption and biological activity in the container. The metal concentration reported in rain is thus total acid leachable. The solvent extraction - atomic absorption procedure of Brewer et al. (1969) modified by the addition of high molecular weight quaternary amines (Andren, 1973) was used for the determination of dissolved metals in stream water and precipitation.

Solid samples were analyzed by non-destructive neutron activation analysis (NAA), while Cd and Pb in solid samples were analyzed by radioisotope dilution spark source mass spectrometry (IDSSMS).

Stream water samples, collected at each of the spring and weir (basin) sites indicated in Fig. 1, were filtered through 0.4 μ Nucleopore filters immediately upon collection and then acidified as above. Elements in water ($< .40 \mu$) and suspended sediments ($> .40 \mu$) were then analyzed as above.

Aerosol samples were collected at the weir sites (see Fig. 1) using Hi-vol air samplers with Whatman 41 filter paper for the collection surface. Since Hi-vol samplers have been shown to cause Cu contamination (Hoffman and Duce, 1971) 5 l/min vacuum pumps with nucleopore filters were also used.

Filter impurity levels have been shown to be very important (Davis et al., 1972) and have been reported for Whatman 41. Using neutron activation analyses, we have determined filter impurities for Nucleopore filters. The data are presented in Table 1. By comparing published impurity levels for other filter materials, we conclude that Nucleopore filters contain the least amount of impurities.

Analytical precision for the three analytical procedures were as follows: AAS, 5-18%; IDSSMS, $< 5\%$; NAA, 1-12%.

THEORETICAL CONSIDERATIONS

Although the watershed approach to trace element cycling is not unique, few workers have integrated the various element cycling pathways that are now theorized as having significant influences on

Table 1. Impurity Levels in Nucleopore Filters^{a,b} (ng/filter)

Element	ng	St. Dev.	Element	ng	St. Dev.
Al	810	±27.0	K	<300	—
As	<0.1	—	La	<0.79	—
Au	0.12	±0.06	Mg	<2000	—
Ba	<110	—	Mn	14	±6
Br	12	±1.0	Mo	<12	—
Ca	<400	—	Na	1150	±50
Cd	<1.0	—	Ni	<300	—
Ce	<3	—	Pb	<2.0	—
Co	61	±28	Rb	<25	—
Cr	340	±40	Sb	<0.8	—
Cs	<1.0	—	Sc	<0.1	—
Cu	<69	—	Se	<4.4	—
Eu	<0.1	—	Sr	<240	—
Fe	1580	±400	Th	<0.7	—
Hf	<0.68	—	Ti	<170	—
Hg	4.3	±1.1	V	6.0	±0.8
I	<3.2	—	Zn	610	±20

^a0.4 μ pore size, 47 mm diameter, and an average weight of 17.2 mg.

^bMeasurements represent an average of 4 different filters.

trace element budgets in natural watersheds. It is becoming apparent that integrated studies of atmospheric chemistry with soil, biological, and aquatic chemistry are needed to fully characterize trace metal cycling. Such studies require a well-defined, easily monitored, yet dynamic system such as the Walker Branch Watershed study area. Before presenting our data, it is worthwhile to review some practical and theoretical aspects of the mechanisms responsible for elemental input and output in a forested watershed.

Input Mechanisms

Aerosols in the atmosphere range in size from 10^{-3} to 10μ radius (Israel and Israel, 1973), being limited by coalescence under Brownian motion at the lower end and by fallout under gravity at the upper end. Lee et al. (1972) have measured aerosol size distributions in six U.S. cities. Their results indicate that an average of 74% of the particle mass exists in the less than 2μ fraction. Aerosols are produced from five major sources: (1) continental dust, (2) sea spray, (3) anthropogenic effluent, (4) chemical reactions between trace gases, and (5) volcanism. Of the major components it is believed that Al, Si, and Fe arise largely from continental sources and Cl and Na are derived from maritime sources, i.e., cyclic sea salt (Junge, 1963).

The major anthropogenic atmospheric emissions in the vicinity of Oak Ridge are primarily derived from three coal-fired steam plants with a combined coal consumption of about 7×10^6 tons per year. (Although there are a foundry and a ferro-alloy plant approximately 40 km to the west, these plants are located behind a ridge and in a valley with a

north-south orientation and are assumed to have a minor impact on the Walker Branch landscape.) Using atmospheric emission data from the Allen Steam Plant in Memphis, Tenn. (Klein et al., 1974a; Bolton et al., 1973; and Andren et al., 1974), the minimum annual atmospheric discharge into the Oak Ridge area for individual elements has been estimated assuming comparable stack precipitator efficiencies (actually the Allen plant runs at $\sim 99\%$, while the steam plants in our area run close to 85-90% efficiency for total particulate removal; thus, we get a minimum estimate) and correcting for relative coal combustion rates (Table 2).

Aerosols are removed from the atmosphere by (1) wet deposition, (2) sedimentation, and (3) impaction on obstacles.

1. Wet desposition - Aerosols with radii from 0.1 to 0.2 μ are essential for raindrop formation which occurs during condensation on these particles (Junge, 1963). Droplets also collect particles under 0.1 μ by Brownian motion and by the water vapor gradient. These processes have been referred to as "rain out". A second process influencing wet deposition is called "washout". This occurs when falling raindrops collect particles by impaction on their way to the ground. Thus the two mechanisms together are known as wet deposition. The formation of rain has been observed to rapidly remove major constituents from the atmosphere (Junge, 1963).

2. Sedimentation - Falling particles accelerate until a constant velocity is reached - the terminal velocity. This velocity depends on the density, gravitational acceleration, and aerosol diameter as well as the viscosity of the air. Calculated terminal velocities for rigid spheres of unit density in air are presented in Table 3. From

Table 2. Estimated Minimum Annual Atmospheric Discharge
of Elements from Coal-Fired Steam Plants Around
the Oak Ridge Area

Element	Atmospheric Discharge (tons/year)	Element	Atmospheric Discharge (tons/year)
Al	142	Mn	0.95
As	0.95	Mo	0.35
Ba	1.4	Na	18.9
Br	23.6	Ni	0.028
Ca	47.3	Pb	0.95
Cd	0.09	Rb	0.33
Ce	0.19	Sb	0.95
Co	0.09	Sc	0.047
Cr	1.4	Se	1.89
Cs	0.05	Si	25.34
Cu	0.70	Sm	0.014
Eu	0.0024	Sr	0.032
Fe	284	Ta	0.0033
Ga	0.24	Th	0.047
Hf	0.0095	Ti	18.9
Hg	0.47	U	0.095
K	43	V	1.89
La	0.095	Zn	9.46
Mg	236		

Table 3. Settling Velocities (cm/sec) of Spherical Particles of 1 g/cm³ Density at Ground Level^a

Particle Radius (μ)	Terminal Velocity (cm/sec)
0.01	1.43×10^{-5}
0.1	2.32×10^{-4}
1	1.32×10^{-2}
10	1.23×10^0

^aIsrael and Israel (1973).

these calculations and the observed particle diameter of aerosols (Lee et al., 1972), it is evident that sedimentation is unimportant as a removal mechanism.

3. Impaction - Because of wind advection and turbulence, particles suspended in air, are able to strike the surface of vegetation, soil, or water. This process is thus strongly dependent on meteorological conditions as well as the configuration of the depositional surface. Chamberlain (1953), Chamberlain and Chadwick (1966), and Cawse and Peirson (1972) have used an expression for depositional flux, $D = Vg \cdot C$, where D = rate of deposition ($\text{ng}/\text{cm}^2/\text{sec}$), C = concentration in air above the depositional surface (ng/m^3), and Vg = depositional velocity (cm/sec). Chamberlain estimated that the maximum deposition velocity due to impaction in a forest could be as high as 5 cm/sec . Cawse and Peirson (1972), however, measured Vg values for 29 elements that averaged less than 0.38 cm/sec .

An evaluation of the relative importance of the two input mechanisms will be treated in more detail later in this report.

Output Mechanisms

The dissolved elemental transport from the watershed is due to the combined effect of four physical processes that ultimately determine the chemical composition of the two streams. These processes are (1) direct trace element incorporation into the streams from rain, (2) surface runoff and associated leaching from vegetation and litter, (3) soil water input, and (4) spring water input. Although existing data do not permit a complete evaluation of all sources, a preliminary discussion of their relative importance will follow in a later section.

Chemical factors that control the elemental composition of natural waters are mineral-water equilibria, and such kinetically controlled processes as sorption, crystal substitutions, coprecipitation, biological uptake and transformations, and colloid formations (Jenne, 1968; Stumm and Morgan, 1970; and Hem, 1972). The usefulness of thermodynamic equilibria calculations in explaining the occurrence and behavior of trace elements in water has, in general, not been vindicated. Berner (1974), however, stated that "equilibrium models predict in what direction reactions are proceeding, but what is needed, in addition, are kinetic models actually describing reactions." It is beyond the scope of this report to further detail the possible chemical reaction mechanisms involved in the watershed; however, we hope to investigate these mechanisms to some extent in our future research.

Previous studies (Biggs et al., 1973; Beck et al., 1974) have in some cases neglected what may be for certain elements an important cycling process, suspended stream sediment trace metal transport. Lindberg et al. (1974) have shown that in river-estuarine systems the particulate fraction may account for 60-80% of the Hg in the water column. Similar results have been reported in fresh water systems (de Groot et al., 1971; Cranston and Buckley, 1972; Bothner and Carpenter, 1972). Jenne (1968) reviewed the status of the chemistry of trace metals in soils and freshwater, pointing out the need for studies of the affinity of organic matter as well as Fe and Mn oxides for trace elements in stream environments. In addition, Turekian and Scott (1967) and Kharkar et al. (1968) have studied dissolved Ag, Cr, Co, Cs, Mn, Mo, Ni, Rb, Sb, and Se in

several streams and following laboratory adsorption experiments have suggested the possible importance of particulate transport for these elements. Gibbs (1973) determined that in two major river systems from 82-99% of the Fe, Ni, Co, Cr, Cu and Mn was associated with various particulate fractions. Therefore, our analyses have included trace metal concentrations on suspended sediments in order to assess the role of stream particulates in the transport of trace elements from the watershed.

RESULTS AND DISCUSSION

Wet Deposition - The concentrations of Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn in rain for the period June 1973 - July 1974 are presented in Table 4 together with the amount of precipitation. The average concentrations for the 14-month period for Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn are 10.5, 1.9, 14.4, 0.18, 14.8, 5.7, 15.6, and 34.9 $\mu\text{g}/\ell$, respectively. The metal concentration in rain should depend on amount of rain, frequency of rain, wind speed, and wind direction prior to rainfall as well as the strength of any anthropogenic emissions. No correlation has been found with any of the meteorological parameters and the metal concentrations found in rain. It is possible, however, that a finer sampling time resolution would provide a better explanation for the observed metal concentrations in rain. The anthropogenic source terms will be discussed in more detail in a later section.

Metal input by rain (in g/ha) to the WBW is presented in Table 5. During the 14-month period the metal input varies by an order of magnitude between months for Cd, Cr, Cu, Hg, and Mn, whereas

Table 4. Metal Concentration in Rain at Walker Branch Watershed ($\mu\text{g}/\text{l}$)

Month	Rainfall (cm)	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
1973									
June	13.96	4.3	0.8	23.8	—	16.8	3.7	13.8	40.6
July	15.24	13.2	1.2	18.6	—	17.0	6.4	16.1	47.0
August	4.21	22.0	1.4	13.4	0.10	17.1	9.1	18.4	53.4
September	7.36	16.7	1.5	10.8	0.09	17.1	6.7	13.9	35.8
October	8.79	14.0	1.5	9.5	0.14	15.9	5.5	11.7	27.0
November	27.33	11.4	3.9	8.2	0.12	14.6	4.9	9.5	18.2
December	24.14	5.0	3.4	3.6	0.54	26.2	4.3	22.4	17.6
1974									
January	24.47	9.6	3.4	21.0	0.13	19.3	8.1	13.8	18.9
February	13.47	9.6	3.0	17.4	0.35	12.3	7.9	5.0	31.2
March	19.74	4.3	1.1	10.3	0.08	14.8	7.6	11.0	18.1
April	9.01	3.6	0.7	16.2	0.16	6.0	6.3	16.9	38.8
May	17.66	4.5	0.7	13.9	0.21	6.7	2.8	15.4	36.4
June	5.10	12.4	1.9	12.0	0.10	7.4	3.9	21.7	44.4
July	2.74	6.3	1.7	23.6	0.13	16.1	3.2	28.9	61.2

Table 5. Metal Input in Rain to Walker Branch Watershed (g/ha)

Month	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
1973								
June	6.0	1.2	33.2	—	23.4	5.2	19.3	56.7
July	20.1	1.8	28.4	—	25.9	9.8	24.5	71.6
August	9.3	0.6	5.6	0.04	7.2	3.8	7.8	22.5
September	12.3	1.1	8.0	0.07	12.6	4.9	10.2	26.4
October	12.3	1.3	8.4	0.12	14.0	4.8	10.3	23.7
November	31.2	10.7	22.4	0.33	39.9	13.4	26.0	49.7
December	11.1	7.5	8.0	1.20	58.0	9.5	49.6	39.0
1974								
January	23.7	8.4	51.8	0.32	47.6	20.0	34.1	46.6
February	12.9	4.1	23.4	0.47	16.5	10.6	6.7	42.0
March	8.4	2.2	20.2	0.16	29.0	14.9	21.6	35.5
April	3.3	0.6	14.8	0.15	5.5	5.8	15.4	35.4
May	7.8	1.2	23.9	0.36	11.5	4.8	26.5	62.7
June	6.3	1.0	6.1	0.05	3.8	2.0	11.1	22.6
July	4.5	0.5	6.5	0.04	4.4	0.9	7.9	16.8

Ni, Pb, and Zn show a lesser variation. The average metal input by rain during the period investigated is shown in Table 6 together with other investigators' data (Cawse and Peirson, 1972; Lazrus et al., 1970; and Biggs et al., 1973). One can only make an approximate comparison between the data since the rain collection vessels were not acidified in the other investigations (ours were). It is clear, however, that some variation exists between different areas and that a measurable amount of trace elements is brought to the terrestrial and aquatic environment via wet deposition. The total metal input by rain for a one-year period (June, 1973 - June, 1974) into WBW (in kg) has also been calculated as follows: Cd, 15.4; Cr, 4.0; Cu, 24.2; Hg, 0.32; Mn, 28.4; Ni, 10.5; Pb, 24.6; and Zn, 49.9.

In an effort to better understand possible sources for the elements measured in rain, the ratios of Cd, Cr, Cu, Hg, Pb, and Zn to Mn have been computed for rain, soils from the Tennessee area (Bolton et al., 1974), and flyash collected at the Allen Steam Plant in Memphis, Tenn. (Klein et al., 1974a). (Although these soil and flyash samples were collected in the Memphis, Tenn. area, they presently represent the best available trace metal data. Since we consider only very large differences in ratios, i.e., 2-3 orders of magnitude, to be significant, we feel confident in extrapolating these data in our work.) Manganese was chosen as it exhibits the least sample-to-sample variation of the dissolved elements studied. Relative elemental enrichments in the finest particle size fractions from the flyash in Memphis should be comparable to the ones produced in the Oak Ridge area which are most readily transported to the Watershed landscape (Klein et al., 1974b). These ratios are summarized in Table 7 for comparative purposes.

Table 6. Comparison of Trace Element Input by Rain between Four Different Areas (g/ha/month)

	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Avg. for 32 stations in the U.S. ^a	—	—	16.3	—	—	3.2	25.0	74.4
Avg. for 8 stations in Delaware Watersheds ^b	6.9	—	3.0	0.1	—	—	5.2	—
Northwest England ^c	<21.0	3.4	27.3	<0.25	9.7	<7.2	<16.3	101.0
This Study	12.8	3.0	19.3	0.27	21.1	7.6	20.5	41.6

^aLazrus et al. (1970).

^bBiggs et al. (1973).

^cCawse and Peirson (1972).

Table 7. Elemental Ratios in Walker Branch Watershed
Rain, Soil,^a and Fly Ash^b

	Cd/Mn	Cr/Mn	Cu/Mn	Hg/Mn	Pb/Mn	Zn/Mn
Rain	0.39	0.11	1.47	0.01	1.8	3.8
Soil	0.002	0.13	0.043	6×10^{-5}	0.04	0.7
Fly Ash	0.12	2.1	1.1 ^c	0.0001	0.27	13.7

^aSoil elemental data taken from Bolton et al. (1974).

^bFly ash data taken from Klein et al. (1974).

^cJuel Emory (personal communication).

From these computations it is clear that Cd, Cu, Hg, and Pb in rain are enriched with respect to soil by 1 to 3 orders of magnitude and must thus have another source. The flyash ratios are comparable to rain ratios for Cu and Cd and possibly for Zn. Chromium seems to be derived from soil, whereas Pb must have another source which most probably results from automotive emissions (further discussion follows).

Dry Deposition - The elemental concentration for 34 elements in air for the month of July 1974 are presented in Table 8. Rancitelli et al. (1973) have stated that most elements contained in aerosols seem to have a natural geochemical origin. However, many recent investigations have clearly shown that some of the most toxic elements in air have a man-induced origin. The elements of anthropogenic origin can be identified and their relative enrichment over a natural geochemical origin estimated by means of a relative enrichment factor (E.F.). The E.F. computation is based on an accurate measurement of a reference element in each sample known or suspected to be of natural origin and believed to be relatively inert chemically in the atmosphere (Rahn, 1971; Zoller et al., 1974; Johansson et al., 1974). In our calculations we have chosen Ce because it seems to vary only slightly between soil samples and is not enriched in flyash (Klein et al., 1974a). In addition, of the five possible reference elements suggested by previous workers which we investigated (Al, Ce, Eu, Lu, and Hf), Ce exhibited the least overall sample-to-sample and temporal variation (see also the discussion in a later section). Once again, as the E.F. method is a useful means of handling atmospheric trace element data for comparative purposes, and since only very large

Table 8. Walker Branch Watershed
Elemental Concentration in Air
at Ground Level (ng/m³),
July, 1974

Ag	0.17	I	0.45
Al	823	K	223
As	1.35	La	0.55
Au	0.001	Lu	0.008
Br	23	Mn	14
Ca	472	Na	201
Cd	4.1	Pb	90
Ce	0.6	Rb	1.0
Cl	345		
Co	0.34	Sc	0.12
Cr	1.7	Se	1.05
Cs	0.07	Ta	0.07
Cu	8.2	Tb	0.008
Eu	0.009	Th	0.10
Fe	313	Ti	66
Hf	0.05	V	3.6
Hg	0.13	Zn	23.4

differences are taken as significant, we feel confident in our use of the Memphis data. Thus, if Ce is chosen as the reference element, then the E.F. for any other element, X, in the aerosol sample can be determined by:

$$E.F. = \frac{[X] \text{ aerosol} / [Ce] \text{ aerosol}}{[X] \text{ soil} / [Ce] \text{ soil}}$$

The result of this normalization process is that elements which are soil derived will have enrichment factors near unity (0.3-1.7, due to the measured variations in Ce concentration) while contaminant elements will have factors ranging up to several orders of magnitude.

Enrichment factors calculated from data in Table 8 are shown in Table 9 together with E.F.'s calculated for flyash (Klein et al., 1974a). From these calculations it is apparent that Al, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Mn, Rb, Sc, Ta, Tb, Th, and Ti in aerosols have a natural geochemical origin. Likewise, Ag, As, Au, Br, Cd, Cl, Co, Cu, Hg, I, Na, Pb, S, Se, V, and Zn are enriched. The Cl, I, Na, and Ca probably are enriched because of the sea salt component (Junge, 1963) which can readily be seen from the Cl/Na ratio (1.72 in WBW aerosols; 1.8 in sea water). However, the remaining 13 elements can probably be attributed to anthropogenic sources. From these calculations it is evident that As, Au, Co, Cu, Se, V, and Zn are close to the aerosol E.F.'s for each element. Thus their enrichment appears to be influenced by the three coal-fired steam plants in the vicinity of Oak Ridge. The high enrichment of Cd cannot be explained at the present time. Lead also has a much higher enrichment in the aerosols and thus must have another source. The most obvious source is, of course,

Table 9. Comparison of Enrichment Factors^a between Aerosols from Walker Branch Watershed and Fly Ash Collected at Allen Steam Plant

Element	Aerosol	Fly Ash	Element	Aerosol	Fly Ash
Ag	236	—	K	1.6	0.7
Al	1.9	0.9	La	1.6	0.6
As	35.2	57	Lu	1.0	—
Au	35.4	35	Mn	1.8	0.4
Br	982	—	Na	3.7	0.3
Ca	4.2	1.4	Pb	485	17.5
Cd	402	30	Rb	1.0	1.1
Cl	295	—	S	4.8	—
Co	4.1	5.2	Sc	1.1	1.8
Cr	2.0	4.5	Se ^b	380	2174
Cs	0.3	1.0	Ta	0.5	1.3
Cu	13.7	35	Tb	1.0	—
Eu	1.1	1.0	Th	1.1	1.4
Fe	1.2	2.9	Ti	2.7	1.6
Hf	0.6	0.4	V	8.1	13.3
Hg ^b	504	5800	Zn	7.2	9.2
I	100	—			

$${}^a\text{E.F.} = (\text{Element/Ce})_{\text{fly ash or aerosol}} / (\text{Element/Ce})_{\text{soil}}$$

^bE.F. here is the sum of particulate plus gaseous effluent. E.F. for Hg when just the particulate phase is taken into account is ~0.5; for Se it is 160.

automotive emissions. The ratio of Br/Pb in this study is 0.26. The ratio of Br/Pb in the ethyl fluid of gasoline is 0.39. Various authors, however, have shown that the leaded aerosol from automotive emissions loses from 40-50% of the Br by an unknown mechanism (Ter Haar and Bayard, 1971; and Martens et al., 1973). The average Br/Pb ratio for 9 stations close to traffic in the San Francisco Bay area (Martens et al., 1973) was thus 0.25. It is quite evident that the observed E.F. for Pb (485) and Br (982) are almost totally derived from automotive emissions. A considerable amount of Br is also produced by the coal-fired steam plants. However, this is almost all in the gaseous form and would not be collected by the aerosol sampler (Klein et al., 1974a).

An estimation of the dry deposition can now be made using the relationship, $V_g = D/C$ (Chamberlain, 1953; and Cawse and Peirson, 1972) for the month of July 1974. Deposition velocities, V_g , due to impaction have been measured by Cawse and Peirson (1972) for selected trace elements according to their particle size distribution. Utilizing these data is an improvement over the usual method of applying a fixed V_g to all elements as it takes into account the obvious influence of particle size on deposition. The deposition velocities calculated by Cawse and Peirson are presented in Table 10 together with the quantity of element brought into WBW by wet deposition. Table 10 also includes the dry deposition component expressed as a percentage of the total deposition. Such an extrapolation of the Cawse and Peirson data requires the assumption that the aerosol trace metal size distribution in air masses studied by those authors approximates that in Walker Branch ambient air. The

Table 10. Comparison of Wet and Dry Deposition
for Selected Elements (July, 1974)

Element	Wet Deposition	Dry Deposition		
	(g/ha)	Vg ^a	g/ha	% of Total Deposition
Cd	4.5	<0.1	<0.21	<4.5
Cr	0.5	0.29	0.13	20.6
Cu	6.5	0.07	0.15	2.3
Hg	0.04	<0.1	<0.01	<20.0
Mn	4.4	0.24	0.87	16.5
Ni	0.9	<1.1	—	—
Pb	7.9	<0.18	<3.9	<33.1
Zn	16.8	0.20	1.7	9.2

^aVg = Deposition velocity due to impaction (cm/sec)
Cawse and Peirson (1972).

recent work of Lee suggests the validity of this assumption, although we have no actual data at this time for comparison. The deposition velocities were determined in a non-forested area and thus probably represent a lower limit when applied to Walker Branch Watershed. The calculations indicate that Cr and Mn have a significant dry deposition component constituting 20.6 and 16.5%, respectively, of the total deposition. A longer sampling period, will, however, be necessary to further evaluate the relative contribution of impaction to total deposition.

Stream output mechanisms - During the past year we have initiated an intensive study of the transport and cycling of several elements on the particulate matter in WBW streams as well as selected elements in dissolved form. Data spanning 14 months for dissolved metals (June 1973 - August 1974) and 6 months for particulate matter (January 1974 - June 1974) have been collected. Appendix A presents the complete suspended sediment and dissolved trace metal data collected from the various sample locations. Table 11 summarizes this data as mean values and standard deviations at each station for the entire period studied. Of particular interest are the relatively minor monthly variations in dissolved trace metal concentrations. Four elements in the dissolved form exhibit mean concentrations with standard deviations of less than 50% for all sample sites and the standard deviations of all but one element are less than 85%. There are also only slight variations in concentrations between the East and West forks and from spring to basin for the dissolved species. Thus, although our sampling covered a period

Table 11. Variations in Dissolved and Suspended Mean Trace Metal Concentrations in Walker Branch Streams

Element	Dissolved ^a (µg/l)		Suspended ^b (µg/g)	
	Spring ^d	Basin ^e	Spring ^d	Basin ^e
	East Fork			
Cd	0.44 ± 23% ^f (n = 29)	0.46 ± 30% (30)	0.38 ± 71% (2)	0.61 ± 21% (2)
Cr	0.44 ± 29% (29)	0.46 ± 20% (30)	117 ± 12% (9)	246 ± 91% (9)
Cu	2.14 ± 21% (29)	2.50 ± 23% (30)	<186 ± 180% (8)	<657 ± 190% (8)
Hg		0.05 ± 170% (7)	16.5 ± 160% (9)	8.1 ± 62% (9)
Mn	2.09 ± 25% (27)	2.05 ± 14% (28)	3,320 ± 170% (9)	2,490 ± 120% (8)
Ni	0.39 ± 28% (28)	0.44 ± 25% (29)	<17,000 ± 140% (9)	<16,300 ± 98% (7)
Pb	0.28 ± 61% (29)	0.31 ± 50% (30)	6.62 ± 67% (2)	8.36 ± 6% (2)
Zn	6.29 ± 34% (29)	7.74 ± 40% (30)	8.36 ± 8% (2)	<493 ± 67% (8)
ΣS.S.C (mg/l)			5.3 ± 62% (12)	3.6 ± 82% (12)
	West Fork			
Cd	0.55 ± 40% (n = 29)	0.55 ± 33% (30)	0.34 ± 120% (2)	0.54 ± 30% (2)
Cr	0.39 ± 26% (31)	0.44 ± 45% (30)	248 ± 74% (9)	229 ± 77% (9)
Cu	2.55 ± 54% (30)	3.65 ± 34% (30)	<821 ± 190% (8)	237 ± 118% (8)
Hg		0.03 ± 85% (7)	17.7 ± 89% (9)	11.7 ± 81% (9)
Mn	4.87 ± 45% (30)	3.87 ± 43% (30)	1,320 ± 71% (9)	1,850 ± 93% (9)
Ni	0.46 ± 39% (30)	0.48 ± 23% (30)	8,250 ± 68% (6)	9,440 ± 76% (7)
Pb	0.27 ± 85% (29)	0.36 ± 61% (30)	13.0 ± 25% (2)	7.43 ± 26% (2)
Zn	7.60 ± 45% (29)	10.47 ± 85% (30)	693 ± 134% (7)	762 ± 33% (8)
ΣS.S.C (mg/l)			2.8 ± 46% (12)	2.8 ± 89% (12)

^aSamples collected from 6-73 to 8-74.

^bSamples collected from 1-74 to 6-74.

^cTotal stream suspended sediment load.

^dAt the baseflow origin of each fork.

^eAt the point of discharge of each fork from the watershed.

^fRelative standard deviation.

of varying meteorological and hydrological conditions (see Table 12) as well as canopy evapotranspiration and soil moisture, the dissolved trace element values remained relatively stable. The suspended sediment trace metal concentrations, on the other hand, exhibit mean values with standard deviations ranging to well over 100% (Table 11).

On the time scale studied, no significant correlations exist between stream discharge and dissolved element concentrations in either branch, indicating that a simple dilution function often observed on a finer time scale for dissolved nutrient element transport from WBW (Elwood and Henderson, 1974) may not apply to the trace elements. Future studies on the role of individual storm sequences in trace metal transport will provide the in-depth data necessary to evaluate this process. However, the maximum discharge of any dissolved constituent very closely corresponds with the maximum stream discharge in the watershed (see Table 13). Similar observations have been reported for other watersheds (Turner et al., 1974; Taylor et al., 1971; Ryden et al., 1972).

The relative contribution of the dissolved versus suspended species to the net trace metal transport by the streams on a monthly and semi-annual time scale is presented in Table 14. Although the measured stream suspended loads are quite low throughout the study period (Table 12), this fraction represents a significant trace element transport for Cr, Hg, Mn, and possibly for Cu, Ni, and Zn on a 6-month basis. It is of interest that there is a relatively large variation in the proportion of the transport due to particulate matter from month to month as this indicates the possible importance of hydrological, climatological, and vegetative variations on trace element cycling and speciation.

Table 12. Walker Branch Watershed Total Discharge and Suspended Sediment Transport

Month	Period	Discharge		Total Suspended Sediment Transport		Precipitation (cm)
		m ³	m ³ /ha	kg	kg/ha	
January	1-31	252,019	2,584	2,328	23.87	24.5
February A ^a	1-14	60,411	619	247	2.53	7.2
February B ^a	15-28	76,245	782	312	3.20	6.3
Total	1-28	136,656	1,401	559	5.74	13.5
March A	1-15	47,965	492	140	1.43	4.6
March B	16-31	124,102	1,272	199	2.04	15.2
Total	1-31	172,067	1,764	338	3.47	19.8
April A	1-14	71,346	732	269	2.76	7.9
April B	15-30	30,775	316	81	0.83	1.2
Total	1-30	102,121	1,047	350	3.59	9.1
May A	1-15	34,799	357	133	1.36	10.4
May B	16-31	34,752	356	126	1.29	7.3
Total	1-31	69,551	713	259	2.66	17.7
June	1-30	28,399	291	68	0.70	5.1

^aA and B refer to the first and second halves (sampling periods) of each month.

Table 13. Correlation Coefficients (r) for Monthly Total Stream Discharge (m³/ha) vs Dissolved Trace Element Transport (g/ha) from Walker Branch Watershed (January-June, 1974)

Element	n	r	Significance
Cd	6	0.99	p _{>} 0.01
Cr	6	0.96	p _{>} 0.01
Cu	6	0.91	p _{>} 0.05
Hg	6	0.82	p _{>} 0.05
Mn	6	0.90	p _{>} 0.05
Ni	6	0.95	p _{>} 0.01
Pb	6	0.82	p _{>} 0.05
Zn	6	0.94	p _{>} 0.01

Table 14. Proportion of Trace Metals Transported as Dissolved and Particulate Species in the Walker Branch Stream

Period	Cd		Cr		Cu		Hg	
	% Dis.	% Part.						
January	99.4	0.6	22.5	77.5			73.3	26.7
February			26.0	74.0	>87	<13	45.5	54.5
March			55.7	44.3	>93	<7	33.3	66.7
April			30.9	69.1	>88	<12	50.0	50.0
May	99.6	0.4	56.5	43.5	>63	<37	71.4	28.6
June			52.2	47.8	40.6	59.4	2.0	98.0
6 Months	99.4	0.6	32.4	67.6	>83	<17	55.3	44.7

Period	Mn		Ni		Pb		Zn	
	% Dis.	% Part.						
January	84.4	15.6						
February	21.8	78.2	>2	<98	89.6	10.4	>87	<13
March	86.3	13.7					>94	<6
April	50.8	49.2	>3	<97			74.7	25.3
May	23.8	76.3	>1	<99	97.1	2.9	78.2	21.8
June	20.9	79.1	>1	<99			71.5	28.5
6 Months	41.4	58.6	>2	<98	92.7	7.3	>85	<15

The complete input-output data (in total grams of element per hectare of watershed) collected during the period January to June 1974 are described on an individual monthly and total semiannual basis in Table 15. Dry deposition input has been estimated based on the July aerosol data from Tables 8 and 10 being proportioned over the 6-month period (this assumes that the relative contribution of dry deposition to total atmospheric deposition is time independent over the 6-month period). Hydrologic and meteorological data used in the calculations are summarized in Table 12. Table 16 summarizes all metal cycling data in the form of a monthly and semiannual elemental mass balance in the watershed including the efficiency of the Walker Branch Watershed system to retain trace metals entering through atmospheric processes. Though individual element retentions are variable from month to month, it is apparent that over the 6-month period the watershed is efficient in retaining Cd (94-95% of the input), Cu (82-84%), and Pb (97-98%) while Cr (59%), Mn (57%), Zn (73-75%), and Hg (69-75%) are more readily released, leading to the following order of retention efficiencies: $Pb > Cd > Cu > Zn > Hg > Cr > Mn$. During this same period only 13% of the total hydrologic input was retained which suggests that for all these trace metals, most of which enter in the dissolved form, soils and vegetation exert a strong influence on retention. Processes such as adsorption into both the inorganic and organic soil and litter fractions as well as biological uptake are important in this cycling and are under further study.

It is interesting to speculate on the relative order of retention provided by the previous calculations. With the exception of Cd, Hg,

Table 15. Trace Element Cycling Budget for Selected Heavy Metals
in Walker Branch Watershed - 1974

Period	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
<u>Wetfall Input (g/ha)</u>								
January	23.7	8.4	51.8	0.32	47.6	20.0	34.1	46.6
February	12.9	4.1	23.4	0.47	16.5	10.6	6.7	42.0
March	8.4	2.2	20.2	0.16	29.0	14.9	21.6	35.5
April	3.3	0.6	14.8	0.15	5.5	5.8	15.4	35.4
May	7.8	1.2	23.9	0.36	11.5	4.8	26.5	62.7
June	6.3	1.0	6.1	0.05	3.8	2.0	11.1	22.6
6 months	62.4	17.5	140.2	1.51	113.9	58.1	115.4	244.8
<u>Dry Deposition Input (g/ha)</u>								
January	<1.11	2.18	1.19	<0.08	9.5		<16.7	4.7
February	<0.61	1.07	0.54	<0.12	3.3		< 3.3	4.2
March	<0.40	0.57	0.46	<0.04	5.8		<10.6	3.6
April	<0.16	0.16	0.34	<0.04	1.1		< 7.5	3.5
May	<0.37	0.31	0.55	<0.09	2.3		<13.0	6.3
June	<0.30	0.26	0.14	<0.01	0.8		< 5.4	2.3
6 months	<2.95	4.55	3.22	<0.38	22.8		<56.5	24.6
<u>Stream Output Dissolved (g/ha)</u>								
January	1.21	0.86	6.78	0.11	6.23	0.88	0.98	20.85
February	0.64	0.51	3.74	0.05	3.24	0.60	0.43	13.90
March	0.69	0.78	3.60	0.03	5.43	0.88	0.35	9.95
April	0.53	0.34	4.43	0.02	4.69	0.43	0.67	8.97
May	0.27	0.35	1.73	0.05	3.61	0.26	0.15	5.28
June	0.14	0.12	1.14	<2E-4	1.26	0.11	0.08	3.18
6 months	3.48	2.96	21.42	0.26	24.46	3.16	2.66	62.13
<u>Stream Output Suspended (g/ha)</u>								
January		2.96		0.04	1.15			
February	0.004	1.45	<0.58	0.06	11.65	<23.3	0.05	<2.14
March		0.62	<0.26	0.06	0.86			<0.62
April		0.76	<0.58	0.02	4.55	<15.7		<3.04
May	0.001	0.27	<1.02	0.02	11.59	<46.0	0.02	<1.47
June		0.11	<1.67	0.01	4.77	<20.6		<1.27
6 months	0.02	6.17	<4.95	0.21	34.57	<19.2	0.21	<10.86

Table 16. Trace Element Mass Balance for Walker Branch, January - June, 1974

Period	Cd	Cr	Cu	Hg	Mn	Pb	Zn
Total atmospheric input ^a - g/ha							
January	23.7-24.8	10.6	53.0	0.32-0.40	57.1	34.1-50.8	51.3
February	12.9-13.5	5.2	23.9	0.47-0.59	19.8	6.7-10.0	46.2
March	8.4-8.8	2.8	20.7	0.16-0.20	34.8	21.6-32.2	39.1
April	3.3-3.5	0.7	15.1	0.15-0.19	6.6	15.4-22.9	38.9
May	7.8-8.2	1.5	24.4	0.36-0.45	13.8	26.5-39.5	69.0
June	6.3-6.6	1.3	6.2	0.05-0.06	4.6	11.1-16.5	24.9
6 months	62.4-65.4	22.1	143.4	1.51-1.89	136.7	115.4-171.9	269.4
Total stream output ^b - g/ha							
January	1.21	3.82	6.78-7.62	0.15	7.38	0.98	20.85-23.17
February	0.64	1.96	3.74-4.32	0.11	14.89	0.48	13.90-16.04
March	0.69	1.40	3.60-3.86	0.09	6.29	0.35	9.95-10.57
April	0.53	1.10	4.43-5.01	0.04	9.24	0.67	12.01
May	0.27	0.62	1.73-2.75	0.07	15.20	0.17	6.75
June	0.14	0.23	2.81	0.01	6.03	0.08	4.45
6 months	3.5	9.1	23.09-26.37	0.47	59.0	2.9	67.9-73.0
Watershed retention ^c - percent							
January	95	64.0	86-87	53-63	87.1	97-98	55-59
February	95	62.3	82-84	77-81	24.8	93-95	65-70
March	92	50.0	81-83	44-55	81.9	98-99	73-75
April	84-85	-57.1	67-71	73-79	-40.0	96-97	69
May	97	58.7	89-93	81-84	-10.1	99-100	82.6
June	98	82.3	54.7	80-83	-31.1	99-100	82.1
6 months	94-95	58.8	82-84	69-75	56.8	97-98	73-75

^aWet fall + impaction.

^bDissolved + suspended.

^cPercent of total atmospheric input.

and possibly Pb, it resembles the Irving-Williams series (Irving and Williams, 1948) for organometallic complex stabilities ($\text{Hg} > \text{Cu} > \text{Pb} > \text{Zn} > \text{Cd} > \text{Mn}$). According to some investigators (Beckwith, 1959; Khanna and Stevenson, 1962) this series is also followed by metals in metal-soil organic matter complexes. This suggests that, on a simplified scale, it may be possible to view watershed cycling of trace metals in terms of soil reaction control mechanisms. Mercury is known to exist in or be transformed into volatile species (Johnson and Braman, 1974), and this may account for the fact that the watershed is less efficient in accumulating Hg than the series would predict. Conversely, accelerated plant uptake of Cd relative to the other elements could explain its position in the watershed retention scale. Finally the transposition of Pb and Cu may be due to the fact that Pb has a much greater relative dryfall input than does Cu. An element entering in a stable particulate phase is likely to be less reactive and hence less readily transported from the watershed as an aqueous species.

Since the initial Irving-Williams work was presented (Irving and Williams, 1948), a number of investigators (Ahrens, 1966; Albert, 1950; Martell, 1971; and Rashid, 1972) have presented data which have refuted the original series to some extent. Many of these recent series are based on laboratory determinations of conditional stability constants for actual soil humic and fulvic acid metallic complexes (Schnitzer, 1971; Schnitzer and Skinner, 1967; Randhawa and Broadbent, 1965; and Malcolm et al., 1968) and have shown that soil type, moisture content, and acidity, as well as species of the trace metal initially present, will influence the relative stabilities to the extent that no one

series should be extrapolated to various soil types. The technique most often used to determine natural organic matter-metal stability constants has recently received some criticism (Clark and Turner, 1969; and Schnitzer and Hansen, 1970). Although our metal retention analogy to the Irving-Williams series is quite speculative, it provides an interesting hypothesis for a possible controlling mechanism operating on trace element cycling in WBW.

In an attempt to determine other possible cycling and transport mechanisms for dissolved elements in the WBW, a technique often used in marine and interstitial water chemistry (Riley and Chester, 1971; Nissenbaum et al., 1972; Presley et al., 1972; and Lindberg and Harris, 1974) has been applied to our data. This involved the normalization of all elements to one parameter that seems to be relatively stable (conservative) in the system under study. We have chosen Cr as it exhibits a mean concentration over a 6-month period, and at four sampling sites with a standard deviation of $\pm 30\%$ of the mean ($n = 47$). Appendix B illustrates individual [element]/[Cr] ratios for the dissolved species studied at each station and sampling time. On a monthly basis, for individual stations, only Hg shows consistently significant variations (factor of 10) at the east spring and west spring and basin, while Mn, Ni, and Cu show such variations at only one station each. Overall, Cu, Hg, Mn, Ni, and Zn exhibit significant variations while Cd and Pb do not. This may be an indication of a relatively constant source for the latter two metals. All of these values are summarized for ease of comparison in Table 17. In comparing various sites it is apparent that there are no significant

Table 17. Mean Dissolved Element to Cr Ratios (X/Cr) and Standard Deviations for Selected Sampling Sites in Walker Branch Watershed (January-June, 1974)

Sample	Cd/Cr	Cu/Cr	Hg/Cr	Mn/Cr	Ni/Cr	Pb/Cr	Zn/Cr	Cr ^a
East Spring	1.1	4.8	0.12	5.3	0.94	0.78	18	0.44
$\sigma(n)$	0.3 (11)	1.6 (11)	0.11 (6)	1.4 (11)	0.49 (11)	0.58 (11)	9 (11)	0.18 (11)
East Basin	1.1	6.2	0.13	4.8	0.92	0.97	19	0.43
$\sigma(n)$	0.3 (12)	1.7 (12)	0.15 (5)	1.4 (11)	0.27 (11)	0.46 (12)	10 (12)	0.11 (12)
East Fork	1.1	5.5	0.13	5.0	0.93	0.88	19	0.43
$\sigma(n)$	0.3 (23)	1.7 (23)	0.12 (11)	1.4 (22)	0.39 (22)	0.52 (23)	9 (23)	0.15 (23)
West Spring	1.3	5.3	0.07	15	1.1	0.70	16	0.36
$\sigma(n)$	0.8 (12)	1.8 (12)	0.06 (6)	8 (12)	0.6 (12)	0.43 (12)	8 (12)	0.08 (12)
West Basin	1.4	9.4	0.06	13	1.1	0.65	25	0.39
$\sigma(n)$	0.4 (12)	5.7 (12)	0.05 (8)	7 (12)	0.3 (12)	0.37 (11)	11 (12)	0.11 (12)
West Fork	1.4	7.3	0.06	14	1.1	0.67	21	0.38
$\sigma(n)$	0.6 (24)	4.6 (24)	0.05 (14)	8 (24)	0.4 (24)	0.39 (23)	11 (24)	0.09 (24)
East and West Springs	1.2	5.0	0.09	10	1.0	0.73	17	0.41
$\sigma(n)$	0.6 (23)	1.7 (23)	0.09 (12)	8 (23)	0.5 (23)	0.50 (23)	9 (23)	0.13 (23)
East and West Basins	1.3	7.8	0.09	8.8	1.0	0.82	22	0.41
$\sigma(n)$	0.4 (24)	4.4 (24)	0.10 (13)	6.6 (23)	0.3 (23)	0.44 (23)	11 (24)	0.11 (24)
WBW ^b	1.2	6.4	0.09	9.6	1.0	0.78	20	0.40
$\sigma(n)$	0.5 (47)	3.6 (47)	0.10 (25)	7.1 (46)	0.4 (46)	0.47 (46)	10 (47)	0.12 (47)

^aRepresents mean values and standard deviations for Cr concentrations ($\mu\text{g/l}$) for each station.

^bWalker Branch Watershed as a whole.

differences in individual element/Cr ratios throughout the study area on a 6-month average basis. On this basis the dissolved element chemistry of the four sample sites seems to be quite similar.

Table 18 presents mean elemental ratios for WBW stream water, rain, and soils from the Memphis area (as discussed previously). The elements Cd, Cu, Hg, and Zn as dissolved species appear to be primarily precipitation derived; Mn reflects either a soil or a rain source; and Pb seems to be primarily of a soil origin. Dissolved Pb shows an order of magnitude depletion from the precipitation. This is in line with the view that this element is effectively retained in the watershed.

Possible sources of metals associated with the stream suspended sediment can be assessed through the use of relative enrichment factors (E.F.) presented earlier for aerosols, again using Ce as the reference element. Cerium appears to be a particularly good reference element for the suspended matter since it exhibits a mean concentration of $80.4 \mu\text{g/g} \pm 4.9 (\sigma_X)$ compared to a mean soil concentration of $84 \mu\text{g/g}$. Appendix C presents individual E.F.'s for the particulate species studied at each station and sampling time. As opposed to the dissolved species element/Cr ratios (Table 17), all trace elements exhibit factor of 10 variations in E.F.'s for each sample station and collection time, indicating a greater influence of meteorological, hydrological, and landscape conditions on suspended sediment chemistry and again pointing out the need for individual storm sequence studies. Mean E.F.'s for individual stations over the six-month period are summarized in Table 19. Due to the large monthly variations in E.F.'s for each element, however, no significant conclusions can be drawn concerning possible differences

Table 18. Mean Dissolved Element to Cr Ratios for Walker Branch Watershed Stream Water, Rain, and Soils (January-June, 1974)

Sample	Cd	Cu	Hg	Mn	Ni	Pb	Zn
Rain (6 month mean)	4.6 ± 1.6	12 ± 8	0.14 ± 0.11	7.5 ± 3.6	4.5 ± 2.8	12 ± 9	27 ± 21
Soils ^a	0.02	0.33	0.0004	7.7	—	0.31	5.4
Stream Water ^b	1.2 ± 0.5	6.4 ± 3.6	0.09 ± 0.1	9.6 ± 7.1	1.0 ± 0.4	0.78 ± 0.50	20 ± 10

^aFrom Bolton et al. (1974).

^bFrom Table 19, MBW as a whole.

Table 19. Mean Suspended Sediment Trace Element Enrichment Factors^a and Standard Deviations for Selected Sampling Sites in Walker Branch Watershed (January-June, 1974)

Sample	Cd	Cr	Cu	Hg	Mn	Pb	Zn
East Spring $\sigma(n)$	0.25 0.21 (2)	0.95 0.55 (8)	6.3 10 (8)	504 645 (8)	8.0 13 (8)	0.30 0.28 (2)	0.60 0.50 (7)
East Basin $\sigma(n)$	0.25 0.07 (2)	2.3 2.2 (8)	29 56 (8)	252 202 (8)	6.3 8.0 (8)	0.20 0 (2)	1.1 0.77 (7)
East Fork $\sigma(n)$	0.25 0.13 (4)	1.6 1.7 (16)	18 41 (16)	378 480 (16)	7.2 10 (16)	0.25 0.17 (4)	0.85 0.67 (14)
West Spring $\sigma(n)$	0.17 0.18 (2)	2.4 2.0 (8)	39 77 (8)	533 553 (8)	2.4 1.6 (8)	0.50 0.28 (2)	1.8 1.7 (7)
West Basin $\sigma(n)$	0.31 0.02 (2)	3.3 2.8 (8)	17 27 (8)	500 402 (8)	5.5 6.0 (8)	0.30 0 (2)	2.4 1.2 (8)
West Fork $\sigma(n)$	0.24 0.13 (4)	2.9 2.4 (16)	28 57 (16)	517 468 (16)	3.9 4.6 (16)	0.40 0.20 (4)	2.1 1.4 (15)
East and West Springs $\sigma(n)$	0.21 0.17 (4)	1.7 1.6 (16)	22 56 (16)	519 580 (16)	5.2 9.2 (16)	0.40 0.26 (4)	1.2 1.4 (14)
East and West Basins $\sigma(n)$	0.28 0.05 (4)	2.8 2.5 (16)	23 43 (16)	376 333 (16)	5.9 6.8 (16)	0.25 0.06 (4)	1.8 1.2 (15)
WBW ^b $\sigma(n)$	0.24 0.12 (8)	2.2 2.2 (32)	23 49 (32)	447 471 (32)	5.5 8.0 (32)	0.33 0.19 (8)	1.5 1.3 (29)

^aE.F. = $(T.E./Ce)_{sample} / (T.E./Ce)_{soil}$.

^bWalker Branch Watershed as a whole.

in stream particulate matter chemistry between the four sampling points. Within the individual standard deviations for each element the chemical source of the stream suspended sediment appears to be similar from site to site.

Table 20 presents mean E.F.'s for stream suspended sediments, fly-ash (Klein et al., 1974a) and aerosols (from Table 8). The stream particulate-associated elements with E.F. near unity (1 ± 0.7 , where 0.7 is 2σ of the mean Ce concentration in the suspended matter) are Cd, Cr, Pb, Zn, and possibly Mn. Enrichment factors of unity indicate soil derivation. However, in comparing these factors to those of the aerosols collected in the watershed, it is apparent that Cr and Mn (which have comparable E.F. for suspended sediments and aerosols) could also be of secondary atmospheric derivation, while Pb and Cd (which show significant depletion from the aerosols) and Zn can only be assumed to be soil derived. The E.F. for Cu suggests a combination of soil and aerosol derivation, while the E.F. for Hg closely approximates that of the actual aerosols.

Earlier results presented in this report indicate that automotive emissions may be the cause of considerable Pb enrichment in both aerosol and rain at WBW. The low E.F. for Pb in stream particulate matter and the relative depletion of dissolved stream water Pb (compared to rain) indicate, however, that Pb leaving the system may be of soil or natural geochemical origin. This significant depletion of Pb (by a factor of 1500) and Cd on stream suspended sediments (factor of 1400) from the aerosol input further supports the conclusion that these elements must be actively removed from the atmospheric input and adsorbed or taken up biologically by some segment of the watershed.

Table 20. Trace Element Enrichment Factors^a for Walker Branch
Suspended Sediments, Fly Ash, and Aerosols
(January-June, 1974)

Sample	Cd	Cr	Cu	Hg	Mn	Pb	Zn
East Basin (6 month mean)	0.25 ± 0.13	1.6 ± 1.7	18 ± 41	380 ± 480	7.2 ± 10	0.25 ± 0.17	0.85 ± 0.67
West Basin (6 month mean)	0.24 ± 0.13	2.9 ± 2.4	28 ± 57	517 ± 468	3.9 ± 4.6	0.40 ± 0.20	2.1 ± 1.4
Fly Ash ^b	12.5	7.5	27	5800	2.6	16.7	9.2
Aerosol ^c	340	2.8	46	512	3.0	500	7.2

$$a_{EF} = \left(\frac{\text{trace element concentration}}{\text{Ce concentration}} \right)_{\text{sample}} / \left(\frac{\text{trace element concentration}}{\text{Ce concentration}} \right)_{\text{soil}}$$

^bFrom Klein et al. 1974.

^cFrom Table 8 (July, 1974, collection only).

The possible consequences of net annual gains of certain trace elements by WBW can be estimated through calculations of enrichment factors and doubling times for various components of the watershed. Using biomass data for three sizable ecosystems compartments, total living vegetation, litter, and soil along with data on the initial standing pool of Cd, Pb, and Zn in each compartment (Van Hook et al., 1973), we have constructed Table 21. Soil pools have been estimated using an active soil depth of 75 cm (approximate root zone depth, W. F. Harris, personal communication), an average soil bulk density of 1.2 g/cc (Peters et al., 1972) and WBW soil elemental concentrations from Van Hook et al. (1973) and Fortescue et al. (1973) (Cd = 0.12 $\mu\text{g/g}$; Pb = 8.6 $\mu\text{g/g}$; Zn = 12.8 $\mu\text{g/g}$). The enrichment ratio is defined as the relative increase in the trace metal pool in any one compartment assuming the entire watershed 6-month net gain of that trace metal is absorbed by one compartment (calculated as: concentration after 6 months' enrichment/concentration before enrichment). Doubling time is defined as the number of years it would take for any compartment to double its initial trace element concentration, making the same above assumptions (calculated as: initial standing pool/annual net gain). Although it is unlikely that any element is entirely accumulated by an individual compartment, it is nevertheless interesting to compare the results of these calculations for Cd, Pb, and Zn.

If we assume that an enrichment ratio of > 1.5 is detectable, then only Cd would significantly show an accumulation, having the greatest influence on the litter pool. However, recent data (EATC-11, 1974) suggest that for certain soils Cd is more soluble in the organic

Table 21. Effect of Net Gain of Cd, Pb, and Zn by Walker Branch Watershed on Various Compartments of the Ecosystem

Component	Bigmass (10^3 kg/ha)	Initial Standing Pool - g/ha						Six Month Net Watershed Gain (g/ha) ^b						Enrichment Ratio ^c						Doubling Time-Years ^d					
		Cd		Pb		Zn		Cd		Pb		Zn		Cd		Pb		Zn		Cd		Pb		Zn	
Total living vegetation ^a	155.7	25	341	1102	—	—	—	—	—	—	—	3.4	1.4	1.2	0.2	1.2	2.8								
Litter ^a (O ₁ and O ₂)	23.2	13	853	1972	—	—	—	—	—	—	—	5.6	1.2	1.1	0.1	3.0	5.0								
Total vegetation ^a	178.9	38	1194	3074	—	—	—	—	—	—	—	2.6	1.1	1.1	0.3	4.2	7.7								
Soil profile to 75 cm ^e	9×10^6	1.1×10^3	7.8×10^4	1.2×10^5	—	—	—	—	—	—	—	1.1	1.0	1.0	9	277	302								
Walker Branch Watershed	—	—	—	—	60	141	199	—	—	—	—	—	—	—	—	—	—								

^aVan Hook et al. (1973).

^bMean value from ranges given in Table 17 (Cd 58.9-61.9; Pb 112.5-169; Zn 196.4-201.5).

^c(Concentration after 6 months' enrichment/concentration before enrichment).

^d(Initial standing pool/annual net gain).

^eFortescue et al. (1973), and Van Hook et al. (1973).

litter layer than Pb and thus moves more rapidly into the soil. If this assumption is made for WBW soils it is obvious that over the 6-month time scale no trace element enrichments would be detectable. The doubling times, also calculated in Table 21, are relatively short for Cd in the living vegetation and litter compartment, and are also quite small for Pb and Zn in the living vegetation. However, since uptake for these elements is likely divided among all these compartments, with the bulk eventually entering the soil compartment, it is apparent that a net gain of trace elements by the watershed probably would not manifest itself in the soil profile for a number of years, although enrichments in the upper soil horizons may show up more rapidly.

SUMMARY

We have integrated studies of atmospheric and aquatic chemistry in an attempt to quantify the cycling of selected trace elements through the Walker Branch Watershed. Comprehensive data have been collected for rain and dry fallout as well as for stream dissolved and particulate output for a 6-month period. The conclusions drawn from this study to date are as follows:

1. Based on monthly sampling intervals the wet deposition input of Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn shows no correlation with such meteorological parameters as wind speed and rain frequency. Shorter collection intervals are recommended for future studies.
2. Ratios of Cd, Cu, Hg, and Pb to Mn in rain are enriched with respect to similar ratios for soil by 2 to 3 orders

of magnitude. Fly ash ratios from a coal fired steam plant for Cu and Hg and possibly Zn and Cd are comparable to rain ratios. Chromium seems to be soil derived, whereas lead appears to be derived from automotive emissions.

3. Based on elemental concentrations in air and previously measured deposition velocities, we have estimated the dry input (by impaction) as a percentage of total input for Cd, Cr, Cu, Hg, Mn, Pb, and Zn. These calculations indicate that only Cr and Mn have a significant dry deposition component constituting approximately 21 and 16%, respectively, of the total deposition. We emphasize, however, that these conclusions are based on a one-month sampling period of elemental air concentrations and estimates of minimum deposition velocities to the watershed landscape.
4. Individual sample concentrations of Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn in the dissolved form from Walker Branch Watershed vary only slightly from monthly means while concentrations of the same elements on particulate material vary considerably from month to month, indicating the complexity of suspended sediment source mechanisms. This emphasizes the need for future studies to concentrate on individual storm sequence sampling.
5. Although the stream suspended loads were relatively low during this period, this fraction represents a significant (> 40% of the total) transport mechanism for Cr, Hg, and Mn.

6. A six-month elemental mass balance shows that the watershed efficiently retains Pb (97-98% of the atmospheric input), Cd (94-95%), Cu (82-84%), while it less readily accumulates Cr (59%), Mn (57%), Zn (73-75%), and Hg (69-75%).
7. Calculations of elemental ratios of the dissolved species to Cr (which shows the least overall variations) and calculations of enrichment factors of various elements over possible source concentrations lead to the speculation that dissolved and particulate Pb and Cd entering the watershed are of anthropogenic origin while dissolved and particulate Pb and particulate Cd species being transported from the area are of a natural geochemical origin. Similar calculations suggest that dissolved Cd in stream water may be precipitation derived.
8. Possible net annual gains of Pb, Cd, and Zn by Walker Branch Watershed have been estimated through enrichment factors and doubling times for various components of the watershed. Doubling times for certain organic compartments are relatively short (0.1-5 years) but, assuming the final sink for these metals to be the soil profile, doubling times are tens to hundreds of years.

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APPENDIX A

Appendix A-1. Individual Dissolved Trace Element Concentrations
($\mu\text{g}/\text{l}$) at East Spring in Walker Branch Watershed

Period	Cd	Cu	Cr	Mn	Ni	Pb	Zn	Hg
1973								
June	0.32	1.48	0.48	1.04	0.38	0.18	6.14	—
	0.54	3.12	0.45	1.66	0.36	0.20	4.63	—
July	0.43	2.23	0.51	1.68	0.43	0.28	4.18	—
	0.39	1.93	0.62	2.14	—	0.42	4.99	—
August	0.36	2.09	0.43	1.93	0.40	0.33	4.59	—
	0.47	2.34	0.53	2.39	0.51	0.48	5.67	—
September	0.51	2.74	0.48	2.83	0.34	0.42	7.18	—
	0.53	2.28	0.41	—	0.44	0.53	7.44	—
October	0.47	2.57	0.37	2.14	0.63	0.23	8.14	—
	0.39	2.61	0.44	—	0.52	0.36	9.11	—
November	0.34	1.93	0.39	2.63	0.30	0.09	5.19	—
	0.41	2.12	0.48	2.13	0.38	0.12	5.08	—
December	0.36	1.84	0.43	1.92	0.34	0.09	6.44	—
	0.63	2.41	0.33	1.74	0.52	0.09	9.18	—
1974								
January A	0.32	1.69	0.30	1.64	0.64	0.46	11.52	0.023
January B ^a	—	—	—	—	—	—	—	—
February A ^a	0.42	2.30	0.32	1.89	0.44	0.18	7.63	—
February B	0.44	2.36	0.36	2.84	0.36	0.31	8.14	0.054
March A	0.25	1.33	0.24	1.14	0.23	0.12	6.91	0.071
March B	0.43	2.18	0.47	2.72	0.34	0.19	7.33	—
April A	0.51	1.59	0.93	1.88	0.17	0.22	8.82	0.006
April B	0.48	1.92	0.51	2.33	0.30	0.31	6.18	—
May A	0.34	1.39	0.43	2.17	0.29	0.27	4.89	0.003
May B	0.53	1.83	0.48	3.14	0.42	0.14	4.73	0.084
June A	0.41	1.79	0.36	2.01	0.34	0.18	5.16	—
June B	0.68	2.04	0.39	1.79	0.37	0.29	6.03	—
July A	0.33	2.11	0.49	1.67	0.31	0.23	4.73	—
July B	0.48	2.48	0.33	2.18	0.44	0.31	4.15	—
August A	0.43	1.93	0.27	1.84	0.36	0.29	6.23	—
August B	0.56	2.61	0.61	2.91	0.41	0.24	6.94	—

^aA and B refer to the first half and second half, respectively, of each month.

Appendix A-2. Individual Dissolved Trace Element Concentrations
($\mu\text{g/l}$) at East Basin in Walker Branch Watershed

Period	Cd	Cu	Cr	Mn	Ni	Pb	Zn	Hg
1973								
June	0.37	1.79	0.52	2.14	0.32	0.15	7.64	—
	0.43	4.14	0.44	1.87	0.44	0.24	5.77	—
July	0.48	2.33	0.50	1.91	0.51	0.36	4.04	—
	0.51	2.18	0.55	2.01	0.46	0.44	6.19	—
August	0.39	3.04	0.55	—	0.39	0.30	7.33	—
	0.48	3.67	0.48	1.86	0.71	0.50	7.14	—
September	0.67	2.33	0.44	2.34	0.83	0.44	9.88	—
	0.61	2.61	0.41	2.41	0.43	0.55	12.13	—
October	0.63	2.33	0.48	1.83	0.39	0.36	8.19	—
	0.42	2.44	0.52	2.14	0.42	0.43	7.48	—
November	0.43	2.67	0.41	1.93	0.44	0.28	6.34	—
	0.42	1.91	0.63	2.13	0.46	0.26	6.66	—
December	0.40	1.95	0.54	2.66	0.34	0.18	7.56	—
	0.51	2.15	0.33	1.88	0.55	0.26	8.95	—
1974								
January A	0.35	2.41	0.33	1.93	0.34	0.64	14.10	0.044
January B ^a	0.44	1.88	0.24	—	—	0.37	5.68	—
February A ^a	0.44	2.07	0.32	2.19	0.48	0.32	8.31	—
February B	0.52	2.52	0.52	1.88	0.40	0.44	8.44	0.054
March A	0.25	2.23	0.57	1.76	0.33	0.14	6.33	—
March B	0.33	2.18	0.41	2.28	0.47	0.33	5.18	—
April A	0.52	3.44	0.38	2.63	0.38	0.49	9.81	0.003
April B	0.44	3.12	0.41	1.54	0.42	0.36	8.14	—
May A	0.43	2.67	0.37	2.17	0.36	0.32	6.77	0.013
May B	0.67	3.41	0.62	2.49	0.28	0.18	4.78	0.240
June A	0.44	2.17	0.48	1.88	0.42	0.44	5.19	—
June B	0.72	2.31	0.54	1.91	0.47	0.61	6.01	—
July A	0.41	2.08	0.55	2.21	0.38	0.54	10.28	—
July B	0.43	2.23	0.47	2.04	0.44	0.47	8.41	—
August A	0.38	2.01	0.38	1.63	0.41	0.31	9.13	—
August B	0.64	2.66	0.55	1.85	0.44	0.57	10.33	—

^aA and B refer to the first half and second half, respectively, of each month.

Appendix A-3. Individual Dissolved Trace Element Concentrations
($\mu\text{g/l}$) at West Spring in Walker Branch Watershed

Period	Cd	Cu	Cr	Mn	Ni	Pb	Zn	Hg
1973								
June	0.83	4.2	0.22	2.9	0.19	0.41	17.6	—
	0.75	2.61	0.27	3.05	0.22	0.30	15.0	—
July	0.71	2.43	0.32	4.98	0.62	0.49	8.18	—
	0.76	2.01	0.28	3.88	0.52	0.40	6.36	—
August	0.67	2.28	0.36	5.84	0.71	0.41	6.31	—
	0.59	3.01	0.41	3.71	0.59	0.30	8.04	—
September	0.78	2.22	0.54	3.18	0.68	0.51	10.11	—
	0.71	3.14	0.47	4.05	0.53	0.61	9.81	—
October	0.84	3.52	0.51	3.81	0.58	0.47	12.13	—
	0.81	2.43	0.55	4.28	0.47	0.27	8.41	—
November	0.64	2.49	0.54	6.73	0.67	0.34	7.12	—
	0.48	1.77	0.50	3.27	0.44	0.13	5.07	—
December	0.29	1.47	0.30	4.12	0.33	0.08	3.74	—
	0.23	1.55	0.34	4.84	0.28	0.10	4.52	—
1974								
January A	0.32	1.34	0.24	3.84	0.24	0.08	3.64	0.014
January B ^a	0.19	1.38	0.42	3.12	0.27	0.13	4.16	—
February A ^a	0.40	1.90	0.33	3.99	0.84	0.19	12.1	—
February B	0.34	2.12	0.38	6.14	0.28	0.14	7.08	0.070
March A	0.53	0.88	0.53	10.7	0.73	0.97	5.6	0.070
March B	0.44	1.74	0.41	6.21	0.32	0.16	7.2	—
April A	0.54	1.75	0.43	4.98	0.25	0.23	3.8	0.011
April B	0.42	2.33	0.36	3.12	0.37	0.18	6.12	—
May A	1.05	1.64	0.29	6.03	0.51	0.28	10.5	0.010
May B	0.38	2.42	0.32	4.70	0.29	0.23	8.01	0.006
June A	0.41	2.10	0.36	12.6	0.36	0.27	4.54	<0.001
June B	0.48	2.30	0.29	5.60	0.38	0.32	6.19	<0.001
July A	0.52	2.21	0.54	3.26	0.69	0.38	4.47	—
July B	0.47	4.87	0.44	6.71	0.44	0.50	6.44	—
August A	0.43	8.13	0.41	2.69	0.61	0.54	8.51	—
August B	0.49	4.17	0.38	3.89	0.50	0.43	5.77	—

^aA and B refer to the first half and second half, respectively, of each month.

Appendix A-4. Individual Dissolved Trace Element Concentrations ($\mu\text{g/l}$) at West Basin in Walker Branch Watershed

Period	Cd	Cu	Cr	Mn	Ni	Pb	Zn	Hg
1973								
June	0.65	4.0	0.56	2.02	0.43	0.38	12.4	—
	0.59	3.64	0.40	4.12	0.39	0.41	10.21	—
July	0.81	3.92	0.36	3.12	0.54	0.53	14.16	—
	0.82	3.69	0.37	4.02	0.39	0.54	10.71	—
August	0.62	3.41	0.44	2.87	0.62	0.72	13.41	—
	0.88	4.92	0.37	2.89	0.73	0.91	19.42	—
September	0.77	4.84	0.62	3.91	0.60	0.64	14.43	—
	0.64	3.91	0.43	3.14	0.53	0.60	10.87	—
October	0.95	4.03	1.07	2.48	0.32	0.27	16.11	—
	0.71	3.83	0.57	3.22	0.51	0.34	8.44	—
November	0.65	4.11	0.47	4.31	0.62	0.41	12.33	—
	0.44	3.11	0.38	2.81	0.41	0.19	7.31	—
December	0.27	1.70	0.29	3.82	0.36	0.27	7.14	—
	0.37	2.22	0.34	2.90	0.47	0.18	4.80	—
1974								
January A	0.47	2.19	0.36	2.74	0.28	0.12	3.91	0.044
January B ^a	0.64	4.13	0.42	3.14	0.40	0.39	8.21	—
February A ^a	0.38	2.04	0.27	3.14	0.34	0.16	13.00	—
February B	0.48	3.80	0.33	2.14	0.50	0.29	10.04	0.007
March A	0.44	1.32	0.55	3.87	0.62	0.14	7.8	0.065
March B	0.50	2.14	0.38	4.14	0.54	0.24	4.93	—
April A	0.55	5.56	0.23	7.58	0.42	0.33	6.21	0.022
April B	0.42	3.84	0.38	3.73	0.42	0.09	11.12	—
May A	1.10	1.98	0.62	10.6	0.49	0.21	10.17	0.026
May B	0.37	2.89	0.38	3.84	0.34	0.21	7.18	0.015
June A	0.40	5.29	0.42	4.89	0.33	0.41	14.64	0.001
June B	0.51	3.87	0.34	5.74	0.38	0	11.44	0.001
July A	0.56	3.12	0.99	3.63	0.54	0.40	14.91	—
July B	0.69	5.60	0.45	5.43	0.64	0.59	13.12	—
August A	0.48	6.14	0.39	3.14	0.55	0.44	3.32	—
August B	0.52	4.22	0.36	3.60	0.51	0.66	12.38	—

^aA and B refer to the first half and second half, respectively, of each month.

Appendix A-5. Individual Stream Particulate Trace Element Concentrations ($\mu\text{g/g}$) at Two Spring Sites in Walker Branch Watershed

Period	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
<u>East Spring</u>								
1974								
January ^a	—	486	—	12.1	190	—	—	330
February A ^b	—	<11.4	<58	14.5	192	<2420	—	<32
February B ^b	0.19	103	<51	0.9	1095	<3142	3.52	—
March A ^c	—	127	<53	10.9	211	—	—	<37
April A	—	88	<108	2.2	578	<1960	—	564
April B	—	126	<103	85.3	3029	<10600	—	590
May A	0.57	77	<69	3.1	18300	<68000	9.71	311
May B	—	29	<15	7.5	3680	<13950	—	123
June ^a	—	<6	1030	12.3	2580	<20100	—	<16
<u>West Spring</u>								
1974								
January	—	671	—	19.0	217	—	—	—
February A	—	364	<128	34	210	<3790	—	1693
February B	0.62	519	<66	5.0	859	<2560	10.62	—
March A	—	100	<89	33	1050	—	—	<46
April A	—	58	<288	2.5	908	<3920	—	583
April B	—	211	<289	44.4	1350	—	—	756
May A	<0.06	141	<1060	8.2	2940	<14120	15.29	765
May B	—	103	<50	3.6	2200	<9720	—	306
June	—	68	4600	9.5	2170	<15380	—	705

^aWhole month (first and second halves combined for sufficient sample).

^bA and B refer to the first half and second half (first and second sampling periods), respectively, of each month.

^cSecond half missed.

Appendix A-6. Individual Stream Particulate Trace Element Concentrations ($\mu\text{g/g}$) at Two Basin Sites in Walker Branch Watershed

Period	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
<u>East Basin</u>								
1974								
January ^a	—	566	—	6.4	210	—	—	—
February A ^b	—	124	<52	13.8	192	3060	—	31
February B ^b	0.52	227	<104	5.0	3090	7730	8.81	—
March A ^c	—	259	<67	17.8	278	—	—	37
April A	—	125	<143	3.8	661	1970	—	674
April B	—	673	<140	6.3	5270	17700	—	712
May A	0.70	81	<67	2.2	1710	6900	7.91	514
May B	—	82	1086	9.8	8510	34900	—	635
June	—	74	3600	7.4	12040	41800	—	848
<u>West Basin</u>								
1974								
January	—	430	—	8.4	175	—	—	—
February A	—	600	<173	32	182	<4270	—	554
February B	0.65	268	<124	7.1	3920	<9470	8.82	1136
March A	—	113	<167	23	353	—	—	673
April A	—	131	<109	3.4	591	<2590	—	828
April B	—	204	<200	11.7	1000	<3750	—	829
May A	0.42	145	<100	4.8	3150	<10500	6.04	578
May B	—	92	<96	6.4	2730	<12000	—	424
June	—	82	924	8.6	4510	<23470	—	1070

^aWhole month (first and second halves combined for sufficient sample).

^bA and B refer to the first half and second half (first and second sampling periods), respectively, of each month.

^cSecond half missed.

APPENDIX B



Appendix B-1. Individual Dissolved Element to Cr Ratios (X/Cr)
for Two East Fork Stations in Walker Branch Watershed
(January-June, 1974)

Period	Cd/Cr	Cr/Cr	Cu/Cr	Hg/Cr	Mn/Cr	Ni/Cr	Pb/Cr	Zn/Cr
<u>Spring</u>								
1974								
January A ^a	1.1	1.0	5.6	0.08	5.5	2.1	1.5	38
January B ^a	—	1.0	—	—	—	—	—	—
February A	1.3	1.0	7.2	—	5.9	1.4	0.56	23
February B	1.2	1.0	6.6	0.15	7.9	1.0	0.86	23
March A	1.0	1.0	5.5	0.30	4.8	0.96	0.50	29
March B	0.91	1.0	4.6	—	5.8	0.72	0.40	16
April A	0.55	1.0	1.7	0.01	2.0	0.18	0.24	9.5
April B	0.94	1.0	3.8	—	4.6	0.59	0.61	12
May A	0.79	1.0	3.2	0.01	5.0	0.67	0.63	11
May B	1.1	1.0	3.8	0.18	6.5	0.88	0.29	9.8
June A	1.1	1.0	5.0	—	5.6	0.94	2.2	14
June B	1.7	1.0	5.2	—	4.6	0.95	0.74	15
<u>Basin</u>								
1974								
January A ^a	1.1	1.0	7.3	0.13	5.8	1.0	1.9	43
January B ^a	1.8	1.0	7.8	—	—	—	1.5	24
February A	1.4	1.0	6.5	—	6.8	1.5	1.0	26
February B	1.0	1.0	4.8	0.10	3.6	0.77	0.85	16
March A	0.44	1.0	3.9	—	3.1	0.58	0.25	11
March B	0.80	1.0	5.3	—	5.6	1.1	0.80	13
April A	1.4	1.0	9.1	0.01	6.9	1.0	1.3	26
April B	1.1	1.0	7.6	—	3.8	1.0	0.88	20
May A	1.2	1.0	7.2	0.04	5.9	0.97	0.86	18
May B	1.1	1.0	5.5	0.39	4.0	0.45	0.29	7.7
June A	0.92	1.0	4.5	—	3.9	0.88	0.92	11
June B	1.3	1.0	4.3	—	3.5	0.87	1.1	11

^aA and B refer to the first and second half (sampling periods) of each month.

Appendix B-2. Individual Dissolved Element to Cr Ratios (X/Cr)
for Two West Fork Stations in Walker Branch Watershed
(January-June, 1974)

Period	Cd/Cr	Cr/Cr	Cu/Cr	Hg/Cr	Mn/Cr	Ni/Cr	Pb/Cr	Zn/Cr
<u>Spring</u>								
1974								
January A ^a	1.3	1.0	5.6	0.06	16	1.0	0.33	15
January B ^a	0.45	1.0	3.3	—	7.4	0.64	0.31	10
February A	1.2	1.0	5.8	—	12	2.5	0.58	3.7
February B	0.89	1.0	5.6	0.18	16	0.74	0.37	19
March A	1.0	1.0	1.7	0.08	2.0	1.4	1.8	11
March B	1.1	1.0	4.2	—	15	0.78	0.39	18
April A	1.3	1.0	4.1	0.03	12	0.58	0.53	8.8
April B	1.2	1.0	6.5	—	8.7	1.0	0.50	17
May A	3.6	1.0	5.7	0.03	21	1.8	0.97	36
May B	1.2	1.0	7.6	0.02	15	0.91	0.72	25
June A	1.1	1.0	5.8	—	35	1.0	0.75	13
June B	1.7	1.0	7.9	—	19	1.3	1.1	21
<u>Basin</u>								
1974								
January A ^a	1.3	1.0	6.1	0.12	7.6	0.78	0.33	11
January B ^a	1.5	1.0	9.8	—	7.5	0.95	0.93	20
February A	1.4	1.0	7.6	—	12	1.3	0.59	48
February B	1.5	1.0	12	0.02	6.5	1.5	0.88	30
March A	0.80	1.0	2.4	0.12	7.0	1.1	0.25	14
March B	1.3	1.0	5.6	—	11	1.4	0.63	13
April A	2.4	1.0	24	0.10	33	1.8	1.4	27
April B	1.2	1.0	10	—	9.8	1.2	0.24	29
May A	1.8	1.0	3.2	0.04	17	0.79	0.34	16
May B	0.97	1.0	7.6	0.04	10	0.89	0.55	19
June A	0.95	1.0	13	0.002	12	0.79	0.98	35
June B	1.5	1.0	11	0.003	17	1.1	—	34

^aA and B refer to the first and second half (sampling periods) of each month.

APPENDIX C



Appendix C-1. Individual Suspended Sediment Trace Element
Enrichment Factors (E.F.)^a for Two Spring Stations
in Walker Branch Watershed
(January-June, 1974)

Period	Cd	Cr	Cu	Hg	Mn	Pb	Zn
<u>East Spring</u>							
1974							
January	—	—	—	—	—	—	—
February A ^a	—	<0.2	<3.1	597	0.4	—	<0.1
February B ^b	0.1	1.1	<1.8	22	1.5	0.1	—
March A	—	1.7	<2.3	336	0.4	—	<0.1
April A	—	0.9	<3.7	52	0.8	—	1.1
April B	—	1.3	<3.4	1984	3.9	—	1.1
May A	0.4	1.2	<3.5	110	36	0.5	0.9
May B	—	1.1	<1.9	676	18	—	0.9
June	—	<0.1	31	256	3.0	—	<0.03
<u>West Spring</u>							
1974							
January	—	—	—	—	—	—	—
February A	—	6.2	<7.3	1349	0.5	—	5.3
February B	0.3	4.7	<2.0	106	1.0	0.3	—
March A	—	0.9	<2.7	693	1.2	—	<0.1
April A	—	0.6	<10	63	1.3	—	1.2
April B	—	2.8	<13	1387	2.4	—	1.9
May A	<0.04	1.8	<46	249	5.0	0.7	1.8
May B	—	1.2	<1.9	94	3.2	—	0.6
June	—	1.0	226	326	4.2	—	1.9

$${}^a\text{E.F.} = \left(\frac{\text{trace element concentration}}{\text{Ce concentration}} \right)_{\text{sample}} / \left(\frac{\text{trace element concentration}}{\text{Ce concentration}} \right)_{\text{soil}};$$

soil ratios from Bolton et al. (1974).

^bA and B refer to the first and second halves (sampling periods) of each month.

Appendix C-2. Individual Suspended Sediment Trace Element Enrichment Factors (E.F.)^a for Two Basin Stations in Walker Branch Watershed (January-June, 1974)

Period	Cd	Cr	Cu	Hg	Mn	Pb	Zn
<u>East Basin</u>							
1974							
January	—	—	—	—	—	—	—
February A ^a	—	2.2	<3.1	568	0.4	—	<0.1
February B ^b	0.2	1.4	<2.1	72	2.5	0.2	—
March A	—	3.2	<2.8	515	0.4	—	<0.1
April A	—	1.2	<4.7	87	0.8	—	1.2
April B	—	7.5	<5.2	163	7.6	—	1.5
May A	0.3	0.7	<2.1	47	2.0	0.2	0.9
May B	—	1.2	53	332	16	—	1.7
June	—	1.0	162	233	21	—	2.1
<u>West Basin</u>							
1974							
January	—	—	—	—	—	—	—
February A	—	10.2	<9.8	1259	0.4	—	1.7
February B	0.3	2.4	<3.7	146	4.5	0.3	1.8
March A	—	1.8	<9.1	872	0.7	—	2.0
April A	—	1.5	<4.2	90	0.9	—	1.7
April B	—	2.7	<8.9	363	1.7	—	2.0
May A	0.3	2.3	<5.3	179	6.5	0.3	1.7
May B	—	3.4	<12	547	13	—	2.9
June	—	2.2	84	544	16	—	5.3

$${}^a\text{E.F.} = \left(\frac{\text{trace element concentration}}{\text{Ce concentration}} \right)_{\text{sample}} \bigg/ \left(\frac{\text{trace element concentration}}{\text{Ce concentration}} \right)_{\text{soil}};$$

soil ratios from Bolton et al. (1974).

^bA and B refer to the first and second halves (sampling periods) of each month.