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GEOCHEMICAL FACTORS COMPLICATING THE USE OF *AUFWUCHS* AS A BIOMONITOR FOR LEAD LEVELS IN TWO NEW JERSEY RESERVOIRS

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Abstract—Material accumulating on glass slides was sampled monthly from two reservoirs for 1 year. Monthly changes in lead concentration in these samples were correlated with fluctuations in associated iron plus manganese concentration. Correlation with changes in algal cell density was also significant ($\alpha = 0.05$), yet not as important in the statistical model as iron plus manganese concentration.

Upon microscopic examination, it was evident that the majority of the material removed from the slides was a rust-colored matrix. X-ray analysis revealed that the majority of the lead in the material scraped from the slides was associated with this iron and manganese-rich matrix surrounding the microflora, not with the microflora itself. As a result the material scraped from the slides (often defined as *aufwuchs* in biomonitoring efforts) could not be considered a valid biomonitor of lead levels in these reservoirs. The local geochemistry, not the biota, was the dominant factor affecting the lead concentrations in the material accumulating on the glass slides. The findings of this study indicate a potential for misinterpretation of biomonitoring efforts employing procedurally defined *aufwuchs*.

INTRODUCTION

Algal species may accumulate high levels of various trace elements (Keeney *et al.*, 1976; Patrick, 1978; Trollope & Evans, 1976). Such phenomena have led to concern about the possibility of bioaccumulation by primary consumers utilizing algae as a food source (Gale *et al.*, 1973). For example, Denny & Welsh (1979) have indicated that zooplankton may accumulate lead by ingestion of phytoplankton which had concentrated the element to a level 100,000 times the concentration in the water. It has also been suggested that lead sequestered by sediments can be made available to grazing species via ingestion of epipelic algae (Milne & Dickman, 1977).

The ability of algae to accumulate trace elements has also led to the increased use of algae as biomonitors for the presence of trace elements in aquatic systems (Trollope & Evans, 1976; Johnson *et al.*, 1978; Friant & Koerner, 1981). Research on two small reservoirs with different degrees of lead contamination revealed that *aufwuchs* (procedurally defined as the material scraped from glass slides) could concentrate lead over 100,000 times levels found in the water column (Newman & McIntosh, 1982). In this study, lead concentrations in this material far exceeded those in any of the biota sampled. However, the associated lead did not accurately reflect differences in lead levels found at the two sites. In addition, regression analyses suggested that grazing gastropods did not readily accumulate lead from this material, despite the high concentrations present in this potential food source. This paper examines more closely the nature of the procedurally defined *aufwuchs*-associated lead at the two study sites.

MATERIALS AND METHODS

Study sites

The two sites on Lawrence Brook (Middlesex County, New Jersey) have been described earlier (Newman & McIntosh, 1982). Both are eutrophic impoundments containing dense stands of the macrophytes, *Cabomba* sp. and *Myriophyllum* sp. during summer months. Sediments and waters at the Weston's Mill pond site had higher lead concentrations (490 $\mu g\ Pb\ g^{-1}$ dry wt and 2.0 $\mu g\ Pb\ l^{-1}$† respectively) than those of the Farrington Lake site (210 $\mu g\ Pb\ g^{-1}$ dry wt and 1.3 $\mu g\ Pb\ l^{-1}$). Both had soft waters (hardness: 33 $mg\ l^{-1}$ as $CaCO_3$; total alkalinity: 15 $mg\ l^{-1}$ as $CaCO_3$) in which the pH fluctuated due to photosynthetic activity.

Local geological features include the Brunswick formation (soft, hematite-stained shale with sandstone beds) and the Magothy and Raritan formation (sand and clay) (Department of Conservation and Economic Development Geological Map of New Jersey, Atlas Sheet No. 40 and Wolfe, 1977).

Monthly sampling

Material was allowed to accumulate on glass slides suspended vertically in plastic frames 0.5 m below the water surface. The entire frame of slides was allowed 2 months to accumulate growth before sampling began. Each month, three slides were selected randomly from each site and placed into acid-cleaned, Nalgene™ tubes containing water from the sampling site. Within 1 h, the material was

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†Averaged after the elimination of one anomalous set of samples taken in July 1979.

scraped from all but one side of the slides, pooled and dried in a desiccator. The material on the intact side was preserved with Lugol's fixative (APHA, 1975) and permanently mounted for later examination. Diatom frustules from acid digests were mounted and used for microscopic identification. These slides were examined under a phase contrast microscope to ascertain the composition of the associated community. Ten random fields on each slide were chosen for examination. Densities were expressed in cells mm^{-2} of surface.

The material was subjected to nitric acid digestion (Feng & Ruddy, 1975) and analyzed for lead, iron and manganese by atomic absorption spectrophotometry. Details of the analyses were reported elsewhere (Newman & McIntosh, 1982). Samples were analyzed by the methods of standard additions initially to check for matrix effects. No significant effects were noted.

Spatial distribution of trace elements

Additional slides were taken from the Weston's Mill Pond site in July and March 1980 to determine the spatial distribution of lead and other selected metals associated with the material coating the slides. After freeze-drying, portions of the slides and the associated material were mounted on spectroscopically pure, fused carbon planchets and sputter coated with carbon for X-ray elemental analyses (15 min at 12 mA).

An ETEC Autoscan scanning electron microscope with a Canberra Model 8100 energy dispersive X-ray fluorescent spectrometer was used for examination of the material. The X-ray analyzer was calibrated with the copper $L_{\alpha 1}$ (0.928 keV) and K_α (8.040 keV) peaks collected from a small piece of copper tape also placed onto the carbon planchets. The microscope was operated at 20 kV, with a 150 μ objective aperture, 12 mm working distance, 45° tilt angle and fixed condensor current for all samples. The spectrometer resolution at the manganese K_α peak was 162 eV, with approx. 12 eV channel and covering a spectral range from 0 to 12 keV. A rather long X-ray collection time of 20 min for each sample area was used to improve the detection and statistical reliability of the elemental peaks.

Data analysis

The maximum R^2 improvement program of the SAS statistical package (Helwig & Council, 1979) was used for regression analyses. Lead concentration associated with the material coating the slides was regressed against the associated iron plus manganese concentration, dissolved (passing through a 0.45 μ filter) lead concentration in the water column and cell density on the slide surface. Due to the introduction of large amounts of lead-laden silt and runoff from construction activities, data from Weston's Mill Pond in July and August 1979 samples were omitted from statistical analyses.

RESULTS

Diatoms dominated the microfloral communities at both sites. Algal blooms were seen in spring while lowest cell densities were experienced in late fall and winter (Figs 1 and 2). Cell densities were generally higher at the Weston's Mill Pond site. A rust-colored matrix in which the microflora were interspersed made up a large proportion of the mass on slides from both sites.

Atomic absorption spectrophotometry revealed that iron and manganese comprised $10.6 \pm 4.0\%$ (Weston's Mill Pond samples) and $8.3 \pm 5.6\%$ (Farrington Lake samples) by weight of the material scraped from the slides during the year of sampling. Monthly changes in the associated lead concentrations at each site appeared to parallel changes in the amount of iron plus manganese per gram of material (Figs 1 and 2). In the statistical model, change in the amount of iron plus manganese was the most significant factor ($P = 0.001$) in accounting for the observed changes in associated lead concentrations. When this contribution of iron plus manganese was accounted for in the statistical model, changes in cell density were also shown to have a significant, positive correlation with changes in associated lead concentrations ($P = 0.044$). The July and August samples from the Weston's Mill Pond were omitted from these analyses as the July sample had anomalously high dissolved lead concentrations and the August samples has anomalous material-associated lead concentrations. Both were judged to be nonrepresentative and, as such, not suitable for comparison with other monthly samples. In the statistical model generated from the remaining 22 sets of data, changes in iron plus manganese concentration contributed 47% of the variation in associated lead concentration while cell density contributed only 11%. Dissolved lead concentrations in the water did not contribute significantly to the statistical model.

Examination of a secondary electron micrograph of the material sampled in July 1979 (Fig. 3) shows that, despite the presence of 300 cells mm^{-2}, the majority of the material coating the slides is a smooth matrix with frequent elevated areas resembling pock marks. In a high magnification micrograph of the same area (Fig. 4), the matrix can be seen clearly around the microflora. To determine the relative abundance of lead in the matrix and biota, X-ray spectra were collected in similar fashion on random areas of matrix and biota. Net integrated intensities at 1.2 FWHM (full width at half maximum) were obtained for the elements of interest (lead, iron, manganese, zinc and silicon); differences in composition are considered relative, particularly since a partial contribution due to matrix occurred when obtaining spectra from the biota. As the silicon peak intensity of the matrix was the same for both samples, the results were normalized to a silicon matrix count of 1000 for ease of comparison. The relative abundance of selected elements on the slides (Table 1) indicates that the matrix contained considerably more lead, zinc, iron and manganese than any of the microfloral species examined. This greater abundance of these metals occurred for both the July 1979 and March 1980 samples.

DISCUSSION

The information generated during the study provided insight into the nature of the lead on the slides. The majority of the material scraped from the slides and often defined as *aufwuchs* (Johnson et al., 1978;

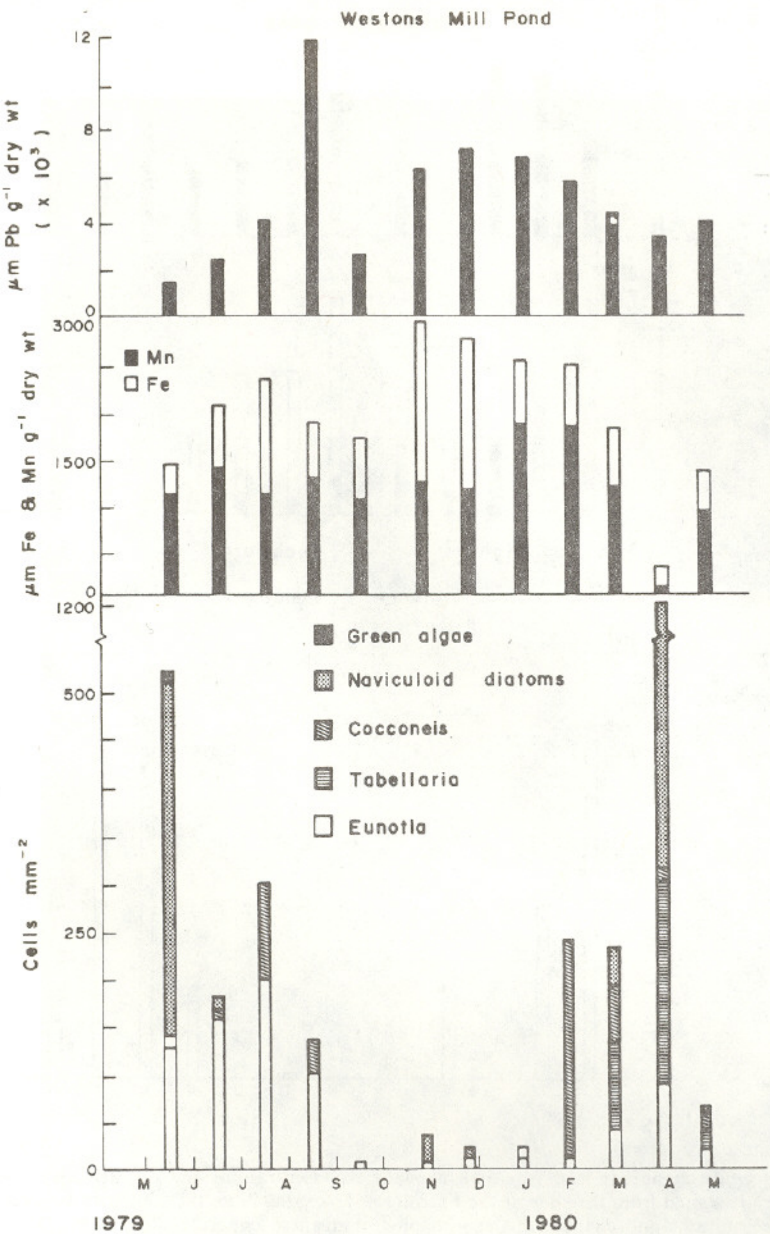

Fig. 1. Monthly changes in lead, iron and manganese concentrations and cell densities associated with the material scraped from the slides at the Weston's Mill Pond site. Note the very high lead concentrations in the August 1979 sample. This sample is considered anomalous, resulting from the introduction of a large amount of lead-laden silt and water from roadside construction during the previous month. With this exception, the changes in lead concentration seem to parallel the changes in iron plus manganese concentrations.

Friant & Koerner, 1981) was actually a rust-colored matrix. X-ray fluoresence analysis showed this material to be rich in iron and manganese; local geological formations (red shale) act as a ready source of both these elements. This abiotic matrix contained more lead (and zinc) per unit area than any of the microfloral species examined.

Atomic absorption elemental analysis of the samples revealed that a large amount of the sample was composed of iron and manganese. Regression analyses showed that changes in lead concentration of this material were most strongly correlated with iron plus manganese concentration. This correlation may result from the avid binding of lead to the iron and manganese oxides coating the slides. Previous research has indicated that this binding by oxides may be direct (Jenne, 1977; Vuceta & Morgan, 1978) or in combination with organic ligands (Davis & Leckie, 1978).

Microchemical analysis (SEM) showed that iron

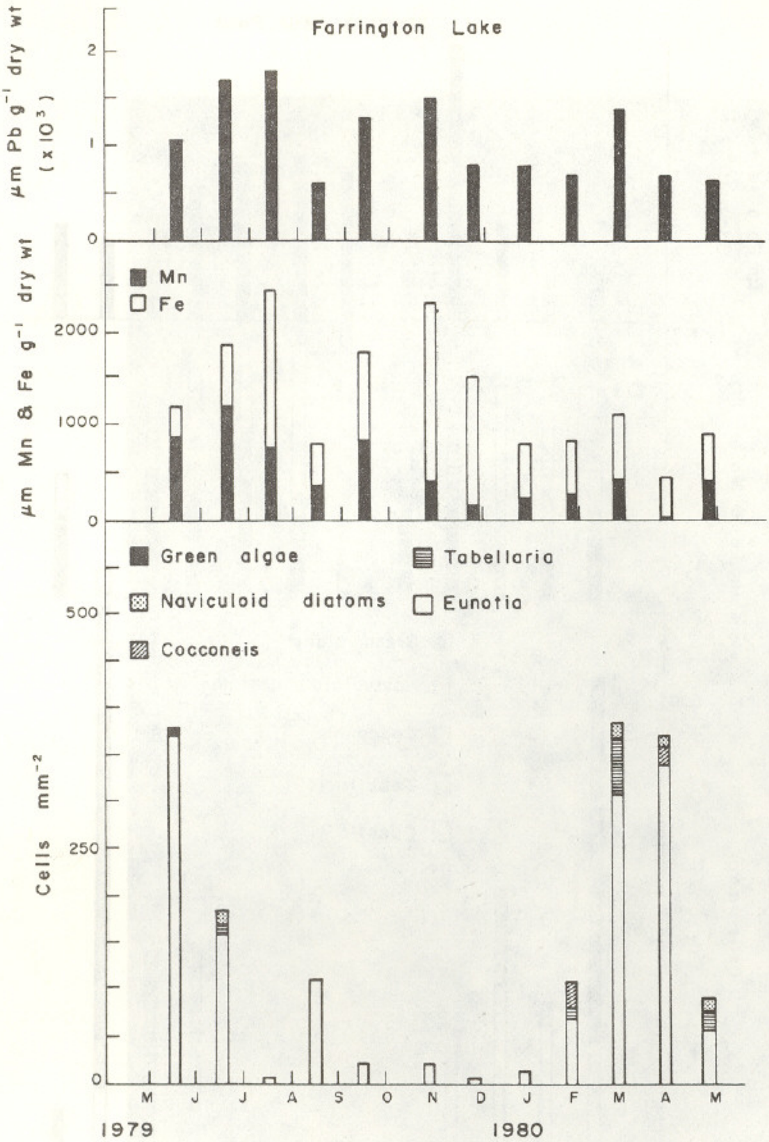

Fig. 2. Monthly changes in lead, iron and manganese concentrations and cell densities associated with the material scraped from the slide at the Farrington Lake site. Note the similarity between changes in lead concentrations and changes in the iron plus manganese concentrations. As with Weston's Mill Pond samples, no clear relationship is apparent between lead concentrations and cell densities.

and manganese-rich matrix covered more area of the slides than the microflora. The matrix also contained more lead per unit area of surface than the biota. Although changes in algal cell density did correlate significantly with changes in lead concentration in this material, this correlation was not as strong as that for iron plus manganese concentration to lead concentration. The results of this study strongly suggest that the local geochemistry of the two systems is the dominant factor determining the lead concentrations in the material scraped from the slides and frequently designated as *aufwuchs*-associated lead.

Although it is well documented that algae do concentrate heavy metals (Denny & Welsh, 1979) and this characteristic can be utilized in biomonitoring efforts (Kenney *et al.*, 1976; Johnson *et al.*, 1978), the present study represents a case in which there is much potential for misinterpretation of data generated during efforts utilizing procedurally defined *aufwuchs*. Phillips (1977) suggested that ideal biomonitoring organisms should reflect the amount of toxic metal available to the aquatic biota. Yet, regression analyses (Newman & McIntosh, 1982) suggest that the lead associated with the procedurally defined *aufwuchs* from these sites is not as available for bioaccumulation as was first suspected. Additionally, the majority of the material-associated lead was not contained in the biota but, rather, the abiotic matrix surrounding

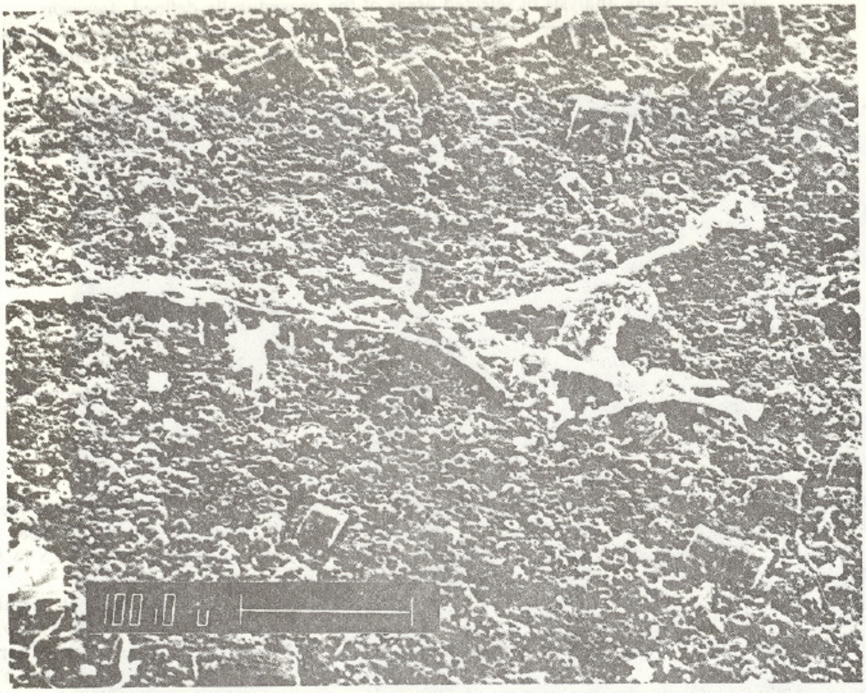

Fig. 3. A scanning electron micrograph (×90) of a typical area of the July 1979 sample from Weston's Mill Pond. A large portion of the material coating the slide is an amorphous matrix. Frequent elevated areas are apparent in this material.

the microfloral species. Phillips (1977) also suggested that a biomonitoring organism should reflect a moving, time-averaged estimate of heavy metal levels in the environment. The average concentration in the material scraped from the slides maintained at the two sites did not reflect consistently the differences seen in the general habitat contamination at the two sites.

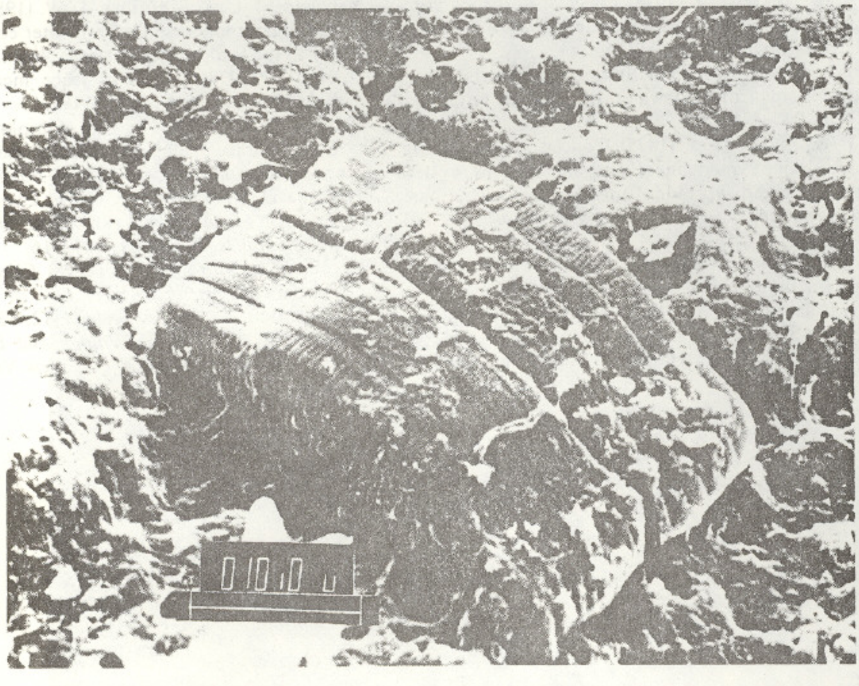

Fig. 4. A scanning electron micrograph (×900) of the same area seen in Fig. 3. Note the amorphous nature of the matrix surrounding the microflora. Almost the entire surface of the slide is covered with this material which appears rust-colored under the light microscope.

Table 1. X-ray analysis of selected areas of the procedurally defined *Aufwuchs*

		Counts collected in 20 min (arbitrary units)				
Date	Sample area	Si K_α	Mn K_α	Fe K_β	Pb $L_{\alpha 1}$	Zn K_α
July 1979	Matrix	1000	274	22	6	12
	Cocconeis	1109	66	2	1	3
	Eunotia	991	45	5	ND	1
March 1980	Matrix	1000	824	32	7	35
	Green filamentous algae	896	104	4	ND	5
	Tabellaria	836	33	3	ND	2

ND = none detected.

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