

Heavy metals in sediments of two Chesapeake Bay tributaries - Wicomico and Pocomoke Rivers

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Abstract

Aquatic sediments can be both sinks and sources of heavy metals. The objective of this study was to measure the concentrations of heavy metals in sediments and sediment-porewaters of two Chesapeake Bay tributaries — Wicomico (WR) and Pocomoke (PR) Rivers so as to better understand the contributions of point (sewage treatment plant — STP) or non-point (agricultural runoff) sources of pollution. Sediment samples from three different depths (3", 6" and 9") at four different sites (one mile before, adjacent to, one and two miles after the STP) on each of the two rivers were collected. This part of WR is residential and receives only STP effluent; whereas this part of PR gets effluents from both the STP and agricultural runoff including runoff from a poultry production farm that generates and stores large amounts of litter. The samples were analyzed for zinc (Zn), lead (Pb), copper (Cu), cadmium (Cd) and arsenic (As) using atomic absorption spectrophotometer (AAS). The concentrations of metals in sediment were normalized against organic carbon content and the correlation coefficient was found to be high in all cases. Concentrations of these metals were significantly higher in the second (near the STP outlet) and third (near the poultry farm) sampling sites in WR and PR, respectively. Metal concentrations decreased significantly ($p \leq 0.05$) with depth in both the rivers. High concentrations of ammonia and nitrate in the WR indicate STP as the source of pollution, whereas a large amount of organic matter in PR sediment points toward agricultural runoff (from the poultry farm). As there was no baseline or earlier data on metal concentrations in these rivers the exact anthropogenic metal input could not be estimated.

Keywords: Heavy metal; Wicomico River; Pocomoke River; Chesapeake Bay tributaries; Sediment; Porewater; Agricultural runoff; Sewage treatment plant

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1. Introduction

Metals are natural constituents of rocks, soils and sediments. The accumulation of metals has been well documented in fresh water sediments [1]. Sediments are an important storage compartment (sink) for the metals and can also become a source by releasing these metals into the overlying waters. Because of their ability to sequester metals, sediments can reflect water quality and record the effects of anthropogenic emissions [2]. Metal accumulations in sediments occur from point sources of pollution such as metal smelters, chemical manufacturing plants and sewage effluents [3]. Metals discharged into estuarine and coastal areas are likely to be removed by particles and settle out as sediments. Concentrations of metals in sediments can be normalized against organic carbon, grain size, aluminum, etc., to understand the factors affecting the distribution and variation of metals between different locations [4]. Heavy metals (Zn, Cu and Pb) from agricultural (non-point sources of pollution) and municipal sources have been reported in the Chesapeake Bay and its tributaries [5]. Sediments and mollusc tissues collected from the St. Martin River, which is near (about 40 miles) the area of this study, had high concentrations of Pb, Cu and mercury (Hg) [6].

The WR and PR are two Chesapeake Bay tributaries on the Eastern Shore of Maryland that run through the populated (25,000) city of Salisbury and city (4,000) of Pocomoke, respectively. A small amount of industrial effluents (discharged in to the STP) and municipal sewage wastes are the main sources of contaminants to the WR whereas PR, in addition to the small STP, is also contaminated with agricultural non-point sources, including a poultry production farm that generates and stores large amounts of poultry litter. Salisbury and Pocomoke STPs receive effluents from many small scale industries (227,000 Lpd and 100,000 Lpd, respectively). The metals present in the municipal, industrial and non-point source waste discharges have tendencies to associate with the sediments [7]. Various metals (As, Cd, Cu and Pb) occur in different oxidized forms and interact differently with different components depending upon pH [8]. Kerhin et al., [9] reported that staurolite was the major mineral found in the area of this study and minerals associated with manganese (Mn) were absent. The data for iron and Mn for WR and PR are not available from the USGS database [10]. Thus WR and PR sediments (polluted by point and non-point sources) enriched with metals can act as a source of metal contamination (EPA priority pollutants — Zn, Pb, Cu, Cd and As) into the Chesapeake Bay. Little information is available on the heavy metal contents of tidal rivers' (such as WR and PR) sediments, porewaters and water columns.

2. Objective

The objective of this study was to measure the concentrations of heavy metals in WR and PR sediments and porewaters with the aim of learning the impacts of STP effluents and agricultural runoff on the accumulation of heavy metals in the sediments.

3. Materials and methods

3.1. Sample collection

The four study sites were one mile before the STP (WR1, PR1), at the STP outlet (WR2, PR2), one mile downstream from the STP (WR3, PR3), and two miles downstream from the STP (WR4, PR4) on WR (Fig. 1) and PR (Fig. 2), respectively. Chesapeake Bay is 6 and 9 miles downstream from sites WR2 and PR2, respectively.

Sediment samples were collected on July 17 (WR) and 19 (PR), 1995, respectively. Peterson classmate dredge was used from a boat to collect the sediment samples. The sediment samples were separated into 3", 6", and 9" depths (significantly different toxicity results were observed in the porewaters from these three depths in preliminary studies), stored (5 kg per sample) in polythene ziplock bags and shipped on ice to the

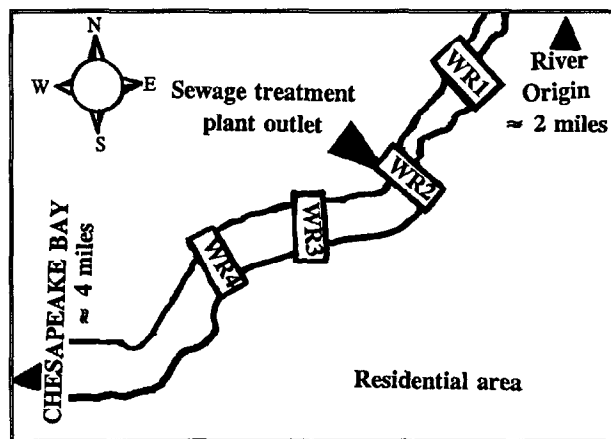


Fig. 1. Sampling sites in Wicomico River (WR).

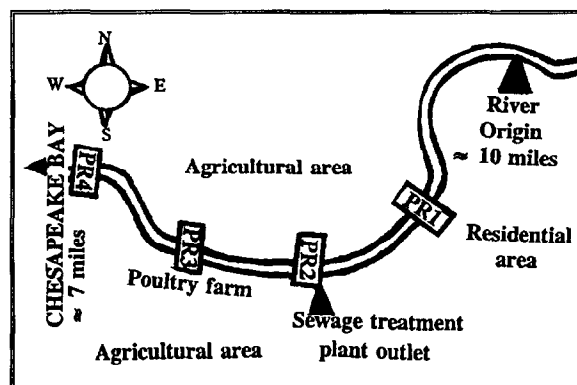


Fig. 2. Sampling sites in Pocomoke River (PR).

University of Maryland Eastern Shore Environmental Sciences Research Lab. The porewater and sediment were separated (within 24 h of sampling) by centrifugation in an IEC (Needham Heights, MA) Model 2K centrifuge at 5000G for 30 min using teflon centrifuge bottles. Porewater and sediment were stored in plastic sample bottles at 4°C. The sediment and porewater were analyzed for their physico-chemical characteristics using standard methods [11].

4. Metal analyses

Metals were analyzed using Perkin-Elmer (Norwalk, CT) Atomic Absorption Spectrophotometer with graphite furnace and auto sampler (detection limits for Pb, Cu, Cd and As were 0.05, 0.02, 0.003 and 0.2 $\mu\text{g L}^{-1}$, respectively) or flame emission (detection limit for Zn was 0.1 mg L^{-1}) [11], within 5 d after collection. Nitric acid digestion procedure was used for analyzing the heavy metals in sediment and porewater [7].

5. Statistical analysis

Randomized complete block [12] was used as the experimental design; ANOVA, LSD, Pearson's correlation and linear regression coefficients ($p \leq 0.05$) were calculated using SAS [13]. All experiments were replicated three times.

6. Results

6.1. Metals in porewater

The WR (Fig. 1) porewater was slightly alkaline and average salinity was 0.03% (Table 1). High concentration of ammonia (58 mg L^{-1}) was present in this porewater. Site WR2 (3" depth) porewater had highest metal concentrations among all the sites in WR (Figs. 3–7). Concentrations of Zn, Pb, Cu and Cd in the WR porewaters ranged from 0.48–9.91, 0.13–5.12, 0.004–0.039 and 0.001–0.026 mg L^{-1} , respectively. Porewater from this site also had a small amount of As (0.001 mg L^{-1}). Concentration of all the heavy metals in the porewater decreased with depth at all sites in WR (Figs. 3–7).

The PR porewater was slightly acidic and the average salinity was 0.05%. Porewater from site PR3 had the highest metal concentrations (Figs. 3–7). Concentrations of Zn, Pb, Cu and Cd ranged from 1.39–4.62, 0.57–0.74, 0.017–0.108 and 0.001–0.025 mg L^{-1} , respectively. Arsenic was found at sites PR3 (3" and 6" depth) and PR4 (3" depth) ranging from 0.004–0.007 mg L^{-1} . Porewater from site PR2 had higher concentrations of metals (except Pb) than the porewater from site PR1 but lower than the porewater from site PR3. Porewater from site PR4 had higher concentration of

Table 1
Physico-chemical characteristics of sediment and porewater (mean of 36 values)

Porewater	Wicomico River (WR)	Pocomoke River (PR)
pH	7.6 ± 0.15^a	6.3 ± 0.21
Conductivity (mS cm^{-1})	0.777 ± 0.009	0.748 ± 0.006
Turbidity (NTU)	4 ± 0.70	3 ± 0.83
Dissolved oxygen (mg L^{-1})	0.8 ± 0.04	0.21 ± 0.02
Salinity (%)	0.03 ± 0.01	0.05 ± 0.03
$\text{NH}_3\text{-N}$ (mg L^{-1})	58 ± 21.95	6 ± 2.55
$\text{NO}_3\text{-N}$ (mg L^{-1})	8 ± 0.22	0.8 ± 0.42
Oxid. Red. Potential (mv)	264 ± 32.61	87 ± 2.54
Hardness (mg L^{-1} of CaCO_3)	1.33 ± 1.24	1.84 ± 0.43
Total chlorine (mg L^{-1})	0.35 ± 0.004	0.88 ± 0.45
Sulfides (mg L^{-1})	0.53 ± 0.007	0.91 ± 0.56
Phosphates (mg L^{-1})	1.56 ± 1	3.53 ± 0.53
Sediment		
Porewater content (%)	61 ± 0.47	45 ± 0.82
Solid phase (%)	39 ± 0.47	55 ± 0.82
Bulk density ^b (g cm^{-3})	1.321 ± 1.13	1.537 ± 0.64
Organic matter (%)	2.1 ± 1.13	6.2 ± 0.64

^a standard deviations

$$\text{Bulk density} = \frac{\text{Wet weight of the sediment}}{(\text{dry wt. of sediment}/2.72) + \text{wt. of water}} \quad [9]$$

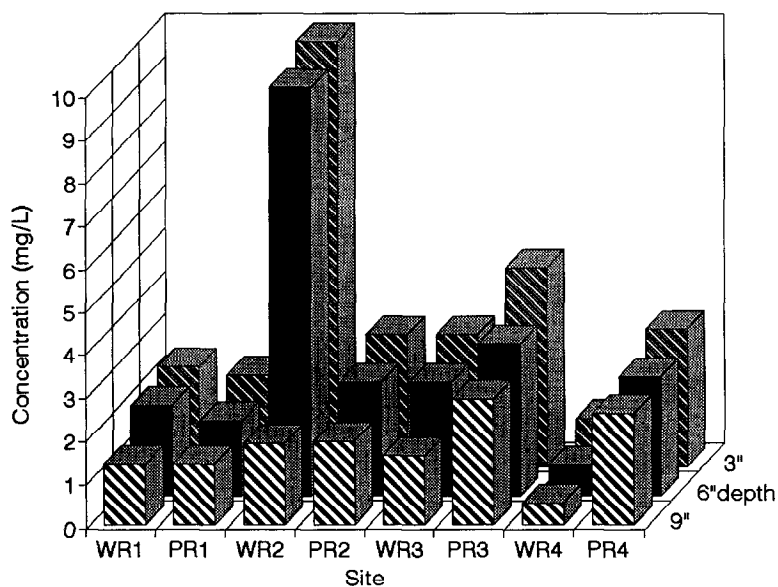


Fig. 3. Zn concentrations in WR and PR porewaters.

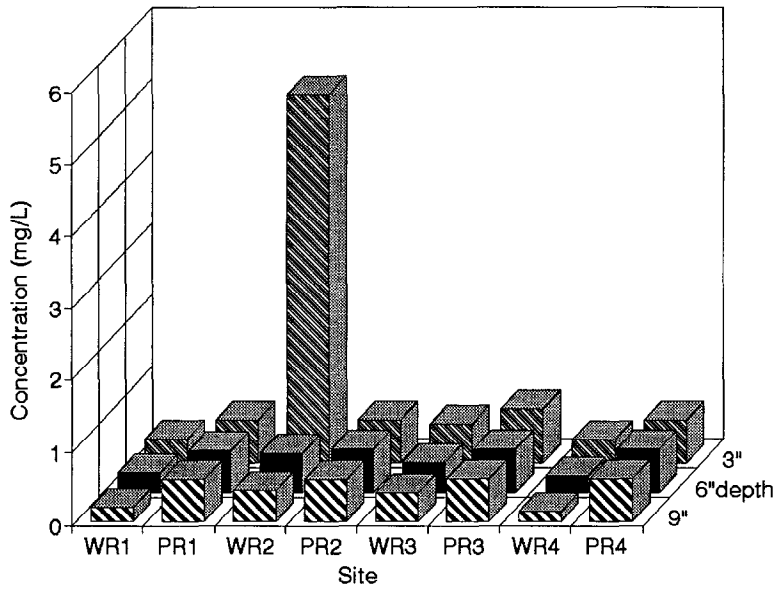


Fig. 4. Pb concentrations in WR and PR porewaters.

metals than the porewater from site PR1. Concentrations of metals decreased with depth at each of the sites (Figs. 3–7). Concentration of all the metals were higher in the porewater at site PR4 compared to site WR4.

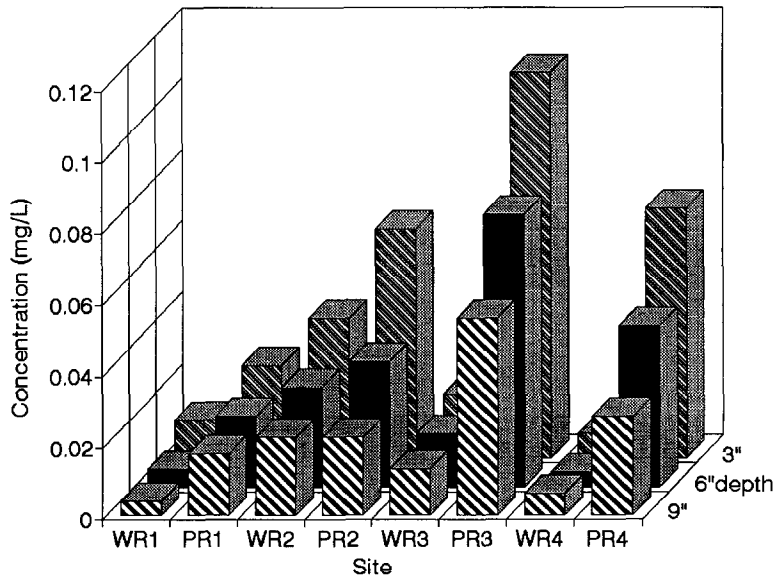


Fig. 5. Cu concentrations in WR and PR porewaters.

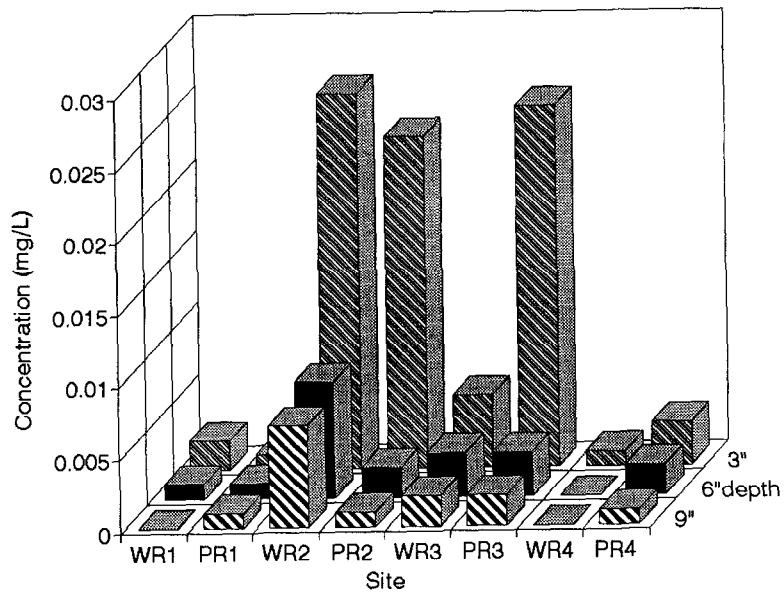


Fig. 6. Cd concentrations in WR and PR porewaters.

6.2. Metals in sediment

The amount of the solid phase in WR whole sediment was less than the PR sediment (Table 1). Higher amounts (3 times) of organic matter in PR sediment than WR

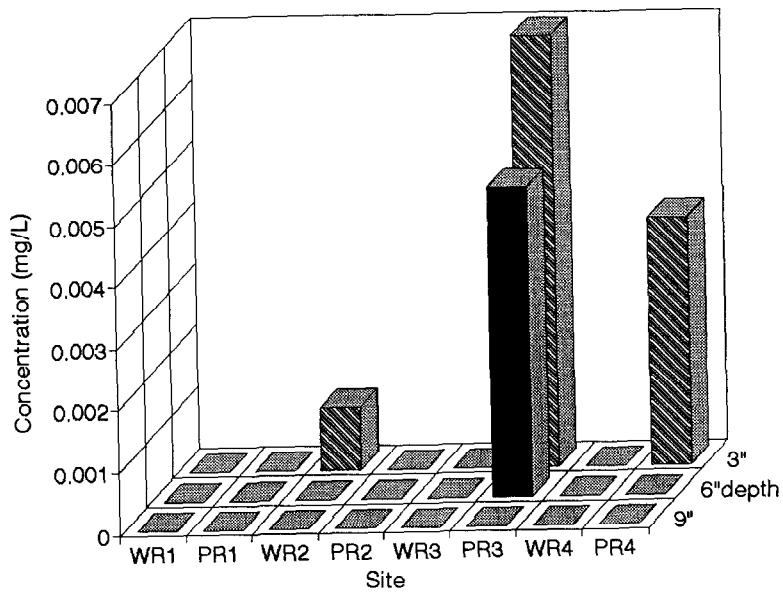


Fig. 7. As concentrations in WR and PR porewaters.

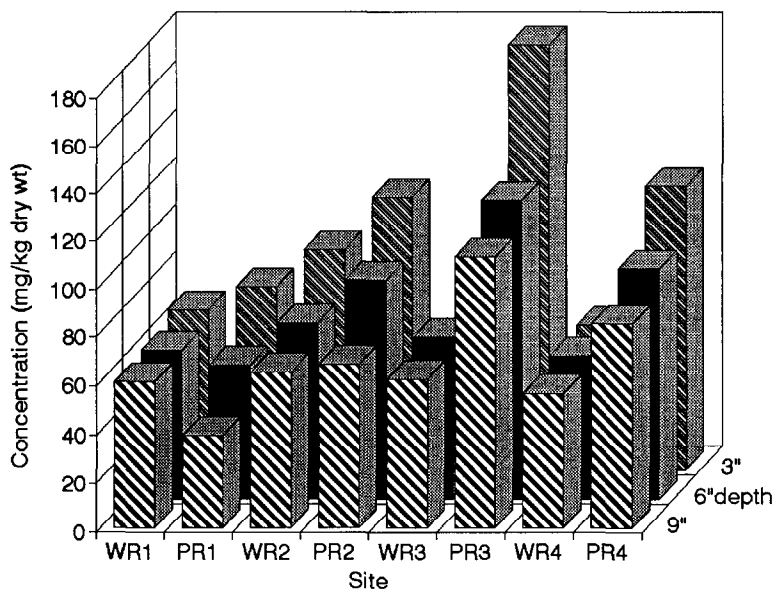


Fig. 8. Zn concentrations in WR and PR sediments.

sediment point towards agricultural runoff mostly from the poultry farm in PR. Metal concentrations in the sediments were several times higher than the porewater metal concentrations in both the rivers (Figs. 3–12). High concentrations of Zn followed by

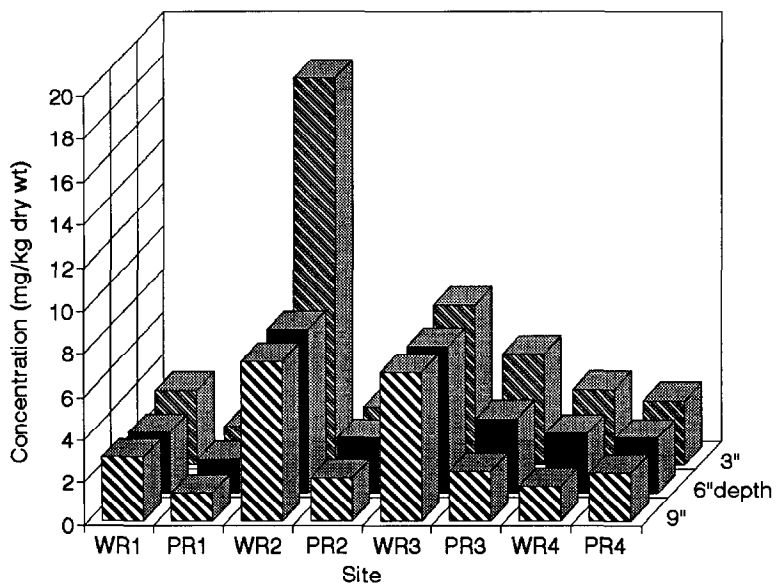


Fig. 9. Pb concentrations in WR and PR sediments.

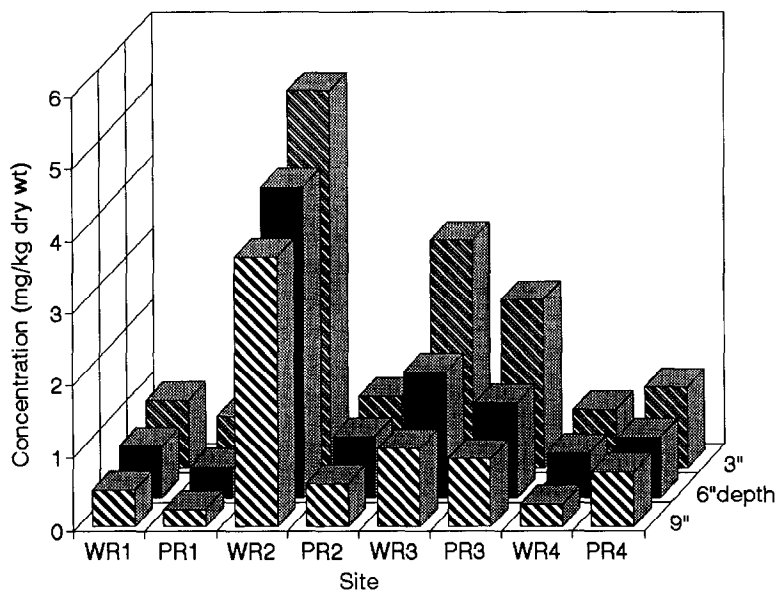


Fig. 10. Cu concentrations in WR and PR sediments.

Pb, Cu, As and Cd were found in both the river sediments. Zinc was higher in PR sediments; all the other metals were found to be higher in WR sediments. Pearson's correlation coefficient for all the metals against organic carbon ranged from 0.71 to 0.87

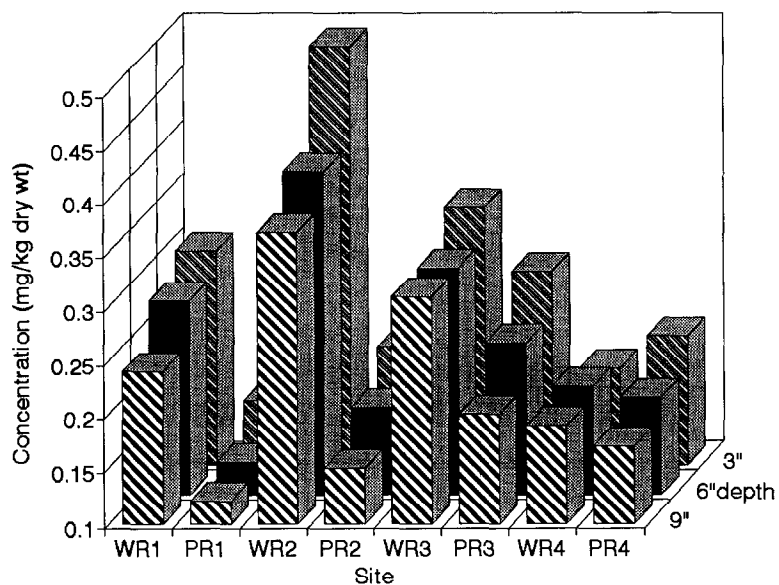


Fig. 11. Cd concentrations in WR and PR sediments.

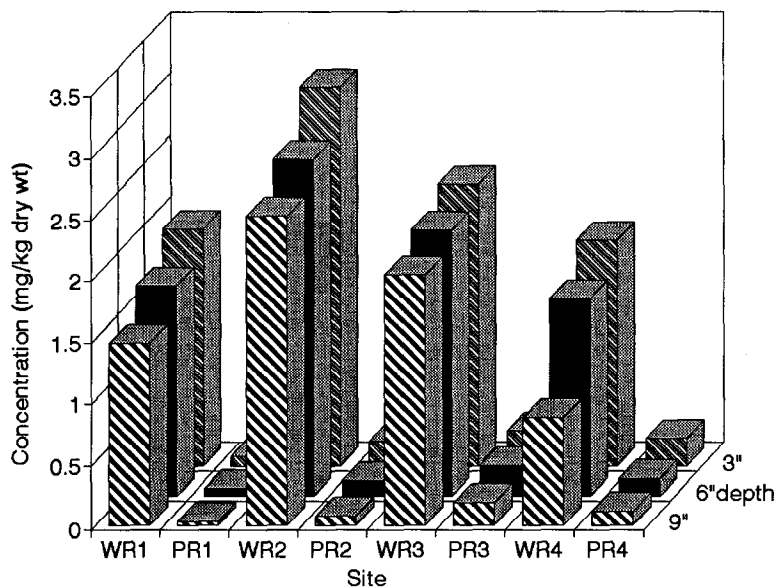


Fig. 12. As concentrations in WR and PR sediments.

for WR and from 0.79 to 0.94 for PR (Table 2). For all the metals analyzed, linear regression coefficient against the normalizing factor (organic carbon) was significant, ranging between 50% to 77% (WR) and 75% to 88% (PR) (Table 2).

7. Discussion

High concentration of ammonia present in WR porewater indicates recent pollution from the STP; Russo [14] reported that ammonia can enter natural water systems from industrial wastes and sewage effluents and it exists in unionized (NH_3) form at alkaline conditions. Phelps [15] reported high concentrations of ammonia in Anacostia Estuary sediments due to effluents from several combined storm sewer runoff. Pocomoke River

Table 2

Pearson's Correlation Coefficient and Regression Coefficient of sediment metal content against organic carbon

Metal	Pearson's Correlation Coefficient (r)		Linear Regression Coefficient (r^2)	
	WR	PR	WR	PR
Zn	0.81	0.92	0.66	0.85
Pb	0.71	0.88	0.50	0.77
Cu	0.79	0.79	0.61	0.75
Cd	0.87	0.94	0.77	0.88
As	0.83	0.90	0.67	0.82

porewater was slightly acidic; possibly from (excess) usage of chlorine and sulfur dioxide (the PR STP has only a primary settling tank and then heavy treatment with disinfectants), used as disinfectant and dechlorinating agents. Chlorine hydrolyses to form hydrochloric and hypochlorous acids and sulfur dioxide forms sulfurous and sulfuric acids [16,17]. The amount of dissolved oxygen and nitrate is lower in PR porewater than in the WR porewater (Table 1). High amounts of ammonia and nitrate in WR porewater indicate the impact of the STP effluent (from a populated city).

In WR, site WR2 is near the STP outlet (that receives effluents from industrial plants including beverage, food and poultry processing) which is the major source of heavy metal input into the river. Gaunlett [18] reported that incompletely treated sewage contributes various pollutants including heavy metals to the rivers. A municipal STP in Akron contributed high concentrations of Zn (600 mg L^{-1}) and low concentrations of Cu and Cd into Cuyahoga River water [19]. Site WR1 is only about 2 miles downstream from the origin of WR passing through residential area. The amounts of heavy metals in site WR1 porewater were higher than the amounts in site WR4 porewater. The porewater from site WR3 has higher amount of heavy metals than site WR1 and WR4, possibly because of the proximity (downstream) to the STP outlet. Heavy metals from site WR2 do not appear to have been transported downstream with tidal water to site WR4. The amount of pollutants in freshwater is modified by certain characteristics of running water especially by transporting, dispersing and diluting the pollutants from their source [20]. Presence of the small amount of As in the porewater of site WR2 (3" depth) only and higher amounts of Cd (at this site at all depths compared to other sites) confirm the STP outlet as the source of pollution [21]. The pH (7.6 ± 0.15) is not expected to influence the metal distribution, particularly Cd, as Cd interactions occur at $\text{pH} > 8$ [8]. Concentration of heavy metals in the porewater decreased with depth at all sites in WR.

In PR, As was found in sites PR3 and PR4; As is present both in herbicides [20] and poultry litter [22]. Site PR3 is one mile downstream from the STP outlet but adjacent to a poultry farm which may be the source of heavy metals into the river along with other agricultural runoff. Berndtsson [23] studied metal accumulation in sediments receiving sewage effluents and extensive drainage from agricultural areas in River Hoje, Sweden, and found high concentrations of Zn (1700 ppm), Pb (180 ppm) and Cu (740 ppm). The Delmarva Peninsula, where the rivers in this study are located, is ranked 4th in the nation in poultry and litter production (9,500 tons per day); land disposal of large amounts of poultry litter can contribute heavy metals (Cu, Cd and As) to waters and sediments after precipitation [22]. A ton of poultry litter contains approximately 320 ppm Cu, 35 ppm As and Pb each and smaller amounts of Cd and Hg [24].

Porewater from site PR2 had higher concentrations of metals than the porewater from site PR1 but lower than the porewater from site PR3. This increase in the metal contents at site PR3 can be from both the transport of metals from site PR2 (STP) and from the poultry and agricultural farm runoff. Porewater from site PR4 had higher concentration of metals (except Pb) than the porewater from site PR1. Concentration of metals decreased with depth at each of the sites indicating a reduction in anthropogenic sources of pollution with increasing time. Concentration of all the metals was higher in the porewater at site PR4 compared with site WR4 possibly from the transport of metals

from site PR3 (poultry and agricultural farm runoff). High concentrations of Cd at only 3" depth at sites WR2, PR2 and PR3 suggest point sources of pollution of relatively recent origin [21].

The sedimentation rate in Chesapeake Bay ranges from 1.6 mm to 12.6 mm yr⁻¹ [9]. Higher amounts (3 times) of organic matter in PR sediment than WR sediment point towards agricultural runoff mostly from the poultry farm. Shine et al., [4] reported organic carbon as the important carrier phase for metals (Zn, Pb, Cu and Cd) in New Bedford Harbor sediments, with a positive correlation coefficient of 0.80, 0.87, 0.83 and 0.65 respectively, against organic carbon. Similar positive correlation coefficients between metals and organic carbon in WR and PR point towards organic binding sites for the metals.

Porewater of both the rivers had less than 5% of metals (mean of all depths and sites) except Pb compared to the metal concentration in the sediments. Swartz et al., [25] reported that metals are usually bound to sediment and only < 5% dissolve in porewater. No correlation was seen between the mean concentrations of heavy metals in sediment and porewaters; similar observations were reported for Detroit River [26]. High concentrations of Zn followed by Pb, Cu, As and Cd were found in both the river sediments. Zinc was higher in PR sediments and all the other metals were found to be higher in WR sediments. The Maryland Department of Environment [10] reported the concentrations of heavy metals in the top 3 cm of WR sediment (near the river mouth on Chesapeake Bay) as Zn (60.84), Pb (18.32), Cu (8.87), Cd (0.44) and As (11.78) mg kg⁻¹ (average of data from 1986–1994); the concentrations of Zn, Pb and Cd are comparable to these results but the concentrations of Cu and As were very low in our study. Berndtsson [23] reported high amounts (1,700 ppm) of Zn in River Hoje (Sweden) sediments which receives extensive drainage from agricultural land. Muller et al., [2] reported extremely high values for Zn in the sediments of Rhine (2,000 ppm) and Elbe (2,450 ppm) rivers. The WR and PR are of recent origin compared to Rhine and Elbe and are located in a rural area.

The data by Stigliani et al., [27] indicate that the amount of Zn, Pb and Cd in the Rhine Basin from agricultural sources is 40, 60 and 35 times higher, respectively, than from sewage effluents. The discharge of effluents from many small scale industries (in compliance with the EPA pretreatment limit of 2.61 ppm Zn) into the STP, corrosion of galvanized steel, ships and barges on the river and storm water runoff are the major sources of Zn; Cd occurs both as a trace impurity in Zn additives and in phosphate fertilizers; As is also found in phosphate fertilizer and is used as a herbicide; Cu compounds are used as molluscicides and algicides; Pb (other than the atmospheric deposition from leaded gasoline and paints) usually comes from battery acid disposal [20]. Shine et al., [4] reported mean values (ppm) for Zn, Pb, Cu, Cd as 74.6, 25.7, 9.62 and 0.08, respectively in the cleaner sediment of Buzzard Bay, MA.

Anthropogenic emission deposition of heavy metals is relatively lower on the Eastern Shore of Maryland (Wye site) and is in the order of Zn > Pb > Cu > Cd [28]. Cadmium is known to accumulate around sewage outfalls and other sources of aquatic pollution [21]. Cadmium concentration of upto 45 mg kg⁻¹ sediment has been reported from point and non-point sources of pollution [29]. Muller et al., [2] reported upto 126 ppm Cd in rivers Gail and Drau in Austria. The metal concentrations in the sediments decreased

Table 3

Comparison of metal concentrations in WR and PR sediment-porewater with EPA freshwater acute criteria and priority pollutant range in sediment porewater ($\mu\text{g L}^{-1}$)

Metal	Mean conc. of metals in WR porewater (3" depth)	Mean conc. of metals in PR porewater (3" depth)	Freshwater acute criteria [33]	Sediment-porewater Range[34]
Zn	4080	3240	120	90–330
Pb	1570	600	83	30–400
Cu	19	7	18	11–49
Cd	9	8	4	2–7

with depth in both the rivers. Most studies indicate that the concentrations of heavy metals decline with depth and are lower in the deeper accumulated sediments [3,4,30,31].

Anthropogenic input of metals is either studied by comparing metal concentrations from previous studies at the same site or from baseline metal concentrations [32]. No previous data is available on metal concentrations in WR and PR and thus the exact anthropogenic metal input could not be calculated; upstream data cannot be used for comparison because of the tidal nature of these rivers. Berigan and Ankley [1] observed Zn, Pb, Cu, Cd and As concentration (mg L^{-1}) in an Illinois River tributary porewater, containing a complex mixture of contaminants from point and non-point sources of pollution, as 0.38, 0.134, 0.096, 0.006 and 0.005, respectively. Hoke et al., [7] reported toxicity of porewater of Grand Calumet River, IN, contaminated by municipal, industrial and non-point source waste discharges, containing Zn, Pb, Cu, Cd and As ranging from 0.019–0.49, 0.020–0.054, 0.005–0.18, 0.005–0.016 and 0.050–0.321 mg L^{-1} , respectively. The concentrations of Zn and Pb in WR and PR porewaters were higher than reported by Berigan and Ankley [1] and Hoke et al., [7] whereas concentrations of Cu and Cd were in the same range and As was lower. The WR porewaters had higher concentrations of Zn, Pb, Cu and Cd and the PR porewaters had Zn, Pb and Cd higher than the fresh water acute criteria for protection of aquatic life [33] and also the range of these priority pollutants in sediment-porewater [34] (Table 3).

Phelps [15] found Zn, Pb, Cu, Cd and As in Anacostia River Estuary sediments at 105, 1.2, 25.2, 1.2 and 3.8 mg kg^{-1} sediment, respectively. The WR and PR sediments had similar concentrations of Zn, Pb, Cd and As, but low concentrations of Cu. Helz and Huggett [5] reported Zn, Cu and Pb as 225, 65 and 70 mg kg^{-1} sediment in samples collected from a site roughly equidistance from Baltimore and Norfolk in the Chesapeake Bay; this site is close to the area in this study. The concentrations of metals in aqueous sediments are known to vary to a great extent depending upon the location and the nature of water. Zinc, Pb and Cu in river, estuarine and coastal sediments have been reported to vary from 263–1420, 94–960, 38–251 mg kg^{-1} [35]. The concentrations of Zn, Pb and Cu in WR and PR sediments were lower than these ranges.

8. Conclusions

The following conclusions can be made from this study:

- (1) High concentrations of metals were found in the site adjacent to the STP outlet in WR and in the site adjacent to a poultry farm in PR.
- (2) The metal concentrations decreased with depth both in sediment and porewater of both the rivers.
- (3) High concentrations of ammonia and nitrate in the WR indicate STP as the source of pollution, whereas large amount of organic matter in PR sediment points towards agricultural runoff (poultry farm).
- (4) The site downstream from the STP in WR was cleaner than the site upstream (possibly from tidal action) but in case of PR the downstream site had higher concentration of heavy metals, both from the STP and the poultry farm runoff.

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