Chronological changes in toxicity of and heavy metals in sediments of two Chesapeake Bay tributaries

Makesh Karuppiah, Gian Gupta [*]

Department of Natural Sciences, University of Maryland Eastern Shore, Princess Anne, MD 21853, USA

Abstract

Sediments are storage compartments for many toxicants and act as indicators of pollution. The objective of this research was to study the chronological changes in the toxicity and heavy metals concentrations in the sediments of Wicomico River (WR) and Pocomoke River (PR)—two Chesapeake Bay tributaries. The sediments were collected from four sites in both the rivers; sediment and porewater were separated and analyzed for toxicity using the marine luminescent bacteria—*Vibrio fischeri* (Microtox®). The most toxic site from each river was used for studying the chronological changes in toxicity and heavy metals concentrations. A mean sedimentation rate (7.5 cm/yr) was used for calculating the time scale. The sediments were collected at a depth of 23.0 cm and divided into three 10-yr periods. The sediment collected from the depth corresponding to the years 1965–1975 was the least toxic and contained the lowest amount of metals in both the rivers. The toxicity and heavy metal concentrations from this depth were used as the baseline data. Five heavy metals—all EPA priority pollutant—zinc, lead, copper, cadmium and arsenic were identified and measured both in the sediment and porewater. The results show an increase in both the toxicity and input of metals over the next 20 yr compared to the baseline data for both the rivers. The increases in toxicity and heavy metals concentrations appear to be related to increase in industrial and agricultural activity around WR and PR, respectively. © 1998 Elsevier Science B.V.

Keywords: Sediment; Porewater; Toxicity; Microtox®; Heavy metals; EPA priority pollutants; Chesapeake Bay tributaries

---

[*] Corresponding author. Tel.: +1 410 651 6030; fax: +1 410 651 7739.

1. Introduction

Aqueous sediments originate from weathering and erosion of rocks and end up in the water bodies with runoff. Sediments are storage compartments for many toxicants; because of their ability to sequester pollutants they can record the effects of both natural and anthropogenic inputs and act as indicators of pollution [1]. Sediments are complex in nature and their composition changes with the nature and concentration of various chemical inputs in to the water body. The distribution of pollutants in sediments sampled from industrialized estuaries has been used as an indicator of past and present pollution events [2].

The Chesapeake Bay is the largest estuary in the United States with 150 tributaries. The rivers and streams that feed into the bay transport huge quantities of sediments [3]. The WR and PR are two tributaries of Chesapeake Bay on the Eastern Shore of Maryland, that receive the municipal sewage treatment plant (STP) effluents from the cities of Salisbury and Pocomoke, respectively. Municipal wastewaters contain pollutants from variety of sources such as industries, hospitals and atmospheric fall-out [4].

Wastewaters consist of both organic and inorganic materials including metals such as As, Cd, Cu, Pb and Zn [5]. These metals are EPA priority pollutants and can also be found in natural waters. Sediments tend to accumulate metal pollutants especially near sewage outfalls. Agricultural runoff can also contribute these metals [6] to a water body. The objective of this research was to study the chronological changes in toxicity of and heavy metals (toxicants that contribute to the toxicity of both WR and PR porewaters) concentrations in the sediments of WR and PR.

2. Material and methods

2.1. Study site

The four study sites (Figs. 1 and 2) were 1.6 km upstream of the sewage treatment plant (WR1, PR1), at the sewage treatment plant outlet (WR2, PR2), 1.6 and 3.2 km downstream of the sewage treatment plant (WR3, PR3 and WR4, PR4), respectively. Sediment samples were collected on July 17 (WR) and 19 (PR), 1995 to a depth of 23.0 cm and separated into 0–7.5 cm, 7.5–15.0 and 15.0–23.0 cm depths using Peterson classmate dredge. Significant differences in toxicities and toxicity inducing substances of the sediments from these depths have been reported in previous studies [7,8]; the samples were stored in polythene Ziplock bags (with little redox changes as measured using a Fisher Scientific (Pittsburgh, PA) Accumet pH meter), and shipped on ice to the University of Maryland Eastern Shore Environmental Sciences Research Lab. The porewater and solid phase sediment were separated in an IEC (Needham Heights, MA) Model 2K centrifuge at $5000 \times g$ for 30 min using teflon centrifuge bottles. Porewater and sediment were then stored in glass and plastic sample bottles, respectively at 4°C.

2.2. Microtox® toxicity test

Microtox® is a bacterial assay using luminescence bacteria developed by Beckman Instruments [9]. Based on the reduction in bioluminescence of the marine bacterium
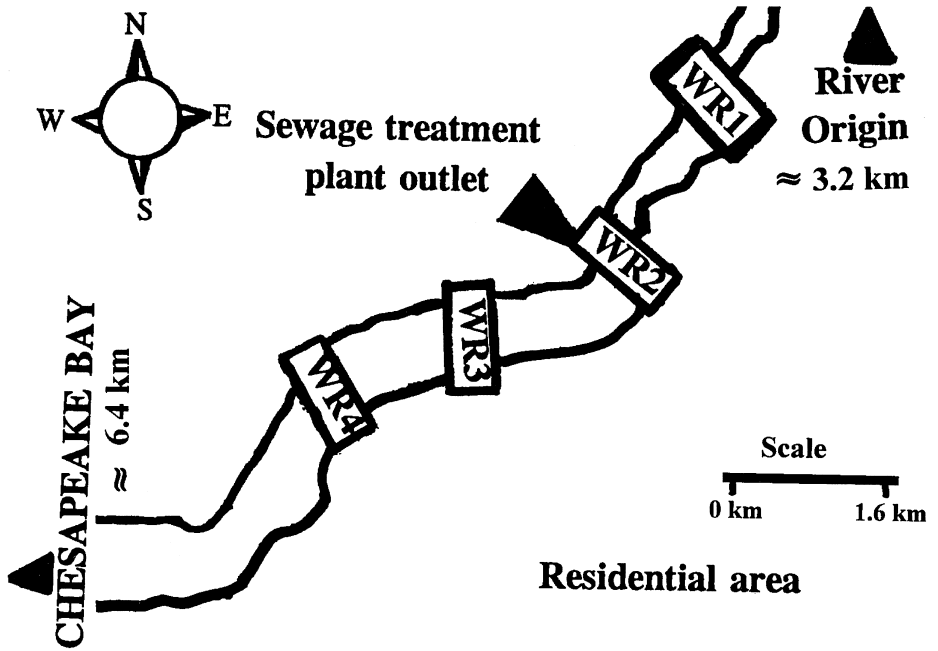
Fig. 1. Sampling sites in Wicomico River (WR).

Vibrio fischeri by toxicants, the toxicity ($EC_{50}\%$) of porewater was measured using the Microtox® Toxicity Analyzer 2055. The lower the $EC_{50}\%$ value the more toxic the substance is. Some inconsistencies with the use of Microtox® were reported by Ankley
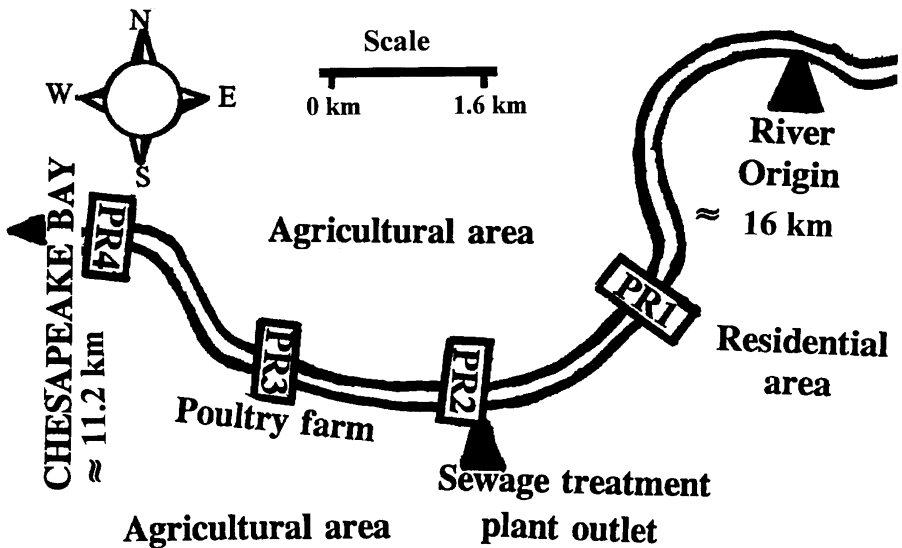

Fig. 2. Sampling sites in Pocomoke River (PR).

et al. [10] and Dieter et al. [11] but Hoke et al. [12] and Toussaint et al. [13] have shown that the results of this test compare favorably with toxicity tests using both fish and invertebrates for a large number of compounds.

2.3. Heavy metals analyses

Metals were analyzed using Perkin–Elmer (Norwalk, CT) Atomic Absorption Spectrophotometer with graphite furnace and auto sampler (detection limits for As, Cd, Cu and Pb were 0.2, 0.003, 0.02 and 0.05 μg/l, respectively) or flame emission (detection limit for Zn was 100 μg/l). Nitric acid digestion procedure was used for preparing the samples for analyzing the heavy metals in sediment and porewater [12].

3. Statistical analyses

Randomized complete block was used as the experimental design to minimize the error due to sediment heterogeneity; analysis of variance (ANOVA) and least significant differences (LSD) were calculated using SAS$^{\circledR}$ [14] to compare the means of three replicates sampled at each site.

4. Results and discussion

Chronological study on anthropogenic input of pollutants is done either by comparing pollutant concentrations from previous studies at the same site or from baseline concentrations [15]. The sedimentation rates in the WR and PR regions are known to range from 0.25 cm–1.25 cm/yr [16]. Using the mean value of 0.75 cm/yr, the time scales for the sediments collected from different depths were estimated and along with the corresponding changes in human population density are shown in Table 1. The data for the lowest (15.0–23.0 cm) depth sampled may be considered as the baseline data for

Table 1
Sediment depths from Wicomico River and Pocomoke River and corresponding population data

Sediment sample depths (cm)	Estimated periods	Salisbury population[a]	Wicimico River sewage treatment plant influent (1/day)	Pocomoke population[a]	Pocomoke River sewage treatment plant influent (1/day)
15.0–23.0	1966–1975	16,302	1.2×10^7	2187	5×10^5
7.5–15.0	1976–1985	20,592	1.3×10^7	3500	1×10^6
0–7.5	1986–1995	25,000	1.6×10^7	4000	1.2×10^6

[a]Source: Maryland Community Profile [Maryland Community Profile—Lower Eastern Shore, Wicomico County, MD—Community Profile, 1996, Internet Homepage http://www.skipjack.net/swed/pop.html; Maryland Community Profile—Lower Eastern Shore, Worcester County, MD—Community Profile, 1996, Internet Homepage http://www.skipjack.net/le_shore/Worcester/audit.].

Table 2
Porewater toxicity (Microtox$^{\circledR}$ EC$_{50}$%)mean values with sediment depth

Depth (cm)	Estimated periods	Sites				LSD[a]
		1	2	3	4	
Wicomico River						
15.0–23.0	1966–1975	60	28	62	96	2.62
7.5–15.0	1976–1985	51 (15)[b]	24 (14)	55 (11)	84 (12)	6.24
0–7.5	1986–1995	42 (18)	21 (13)	43 (22)	78 (7)	3.74
	LSD	5.43	5.84	9.17	4.69	
Pocomoke River						
15.0–23.0	1966–1975	97	71	39	62	2.43
7.5–15.0	1976–1985	92 (5)	63 (11)	25 (33)	46 (25)	1.52
0–7.5	1986–1995	85 (8)	58 (8)	13 (50)	37 (20)	3.62
	LSD	2.48	2.92	3.26	2.49	

[a] Least significant difference ($p \leq 0.05$).
[b] Values in parentheses indicate the % decrease in Microtox$^{\circledR}$ EC$_{50}$% from previous years.
Lower EC$_{50}$% value equates with higher toxicity.

toxicity and metals concentrations in this study because the toxicity of the samples from this depth were the lowest of all the samples tested from both rivers. The most toxic sites were WR2 (adjacent to STP outlet) and PR3 (1 mile downstream of STP and adjacent to a poultry farm) in WR and PR, respectively (Table 2).

The volumes of influent to STPs during the three 10-yr periods are shown in Table 1. The daily average effluent concentrations from the WR-STP (October–December, 1995) for Zn, Pb and Cu were 50, 8 and 25 μg/l, respectively. Site WR2 porewater (15.0–23.0 cm depth) had an EC$_{50}$% value of 28 and metal concentrations of Zn = 1.85, Pb = 0.42, Cu = 0.022, Cd = 0.007 mg/l during 1966–1975 (Table 3). The relative increases (%) in the concentration of metals during the period 1976–1985 were Zn = 414, Pb = 28, Cu = 27 and Cd = 14. Also during this period, the toxicity (Microtox$^{\circledR}$ EC$_{50}$%) and human population increased by 15% and 26%, respectively. Metal fabrication, metal finishing and water conditioning industries are possibly the major contributors of Zn to WR STP [17]. Domestic wastes, non-process wastewaters, stormwater runoff, ships and barges and accidental spills to storm sewer system also contributed Zn to WR [7]. Studies have shown that municipal wastewater contains Zn along with other metals and organic pollutants from variety of sources such as industries and atmospheric fallouts [4,5]. Along with a human population increase, there was an increase in industrial activity mainly from shipbuilding and barges [7] during this period.

The subsequent increases (%) in the concentration of metals during the period 1986–1995 compared to the period 1976–1985 were quite small except in the case of Pb and Cd. The main sources for Pb are from industries that finish metal or use metal salts and commercial establishments such as photography and print shops, auto repair shops, X-ray laboratories and dentists (E. Ludy, The City of Salisbury Wastewater Treatment Plant. Personal Communication, March 11, 1996.). Cadmium occurs as an impurity in Zn additives and it tends to accumulate in sediments around sewage outfalls [18].

Table 3
Changes in metal concentrations in sediment (mg/kg) and porewater (mg/l) samples in the Wicomico (WR2) and Pocomoke (PR3) rivers with depth

Depth (cm) (estimated period-yr)	Zn		Pb		Cu		Cd		As	
	Sediment	Pore water	Sediment	Pore water	Sediment	Pore water	Sediment	Pore water	Sediment	Pore water
Wicomico River (WR2)										
0–7.5 (1986–1995)	90.75[a]	9.91[a]	18.01[a]	5.12[a]	5.23[a]	0.039[a]	0.49[a]	0.026[a]	3.07[a]	0.001
7.5–15.0 (1976–1985)	72.16[b]	9.50[b]	7.60[b]	0.54[b]	4.30[b]	0.028[b]	0.48[b]	0.008[b]	2.73[b]	ND
15.0–23.0 (1966–1975)	63.75[c]	1.85[c]	7.43[b]	0.42[c]	3.73[b]	0.022[c]	0.37[c]	0.007[b]	2.50[c]	ND
LSD	3.12	0.13	0.54	0.01	0.60	0.002	0.01	0.001	0.12	
Pocomoke River (PR3)										
0–7.5 (1986–1995)	176.42[a]	4.62[a]	5.14[a]	0.74[a]	2.33[a]	0.108[a]	0.28[a]	0.025[a]	0.29[a]	0.007[a]
7.5–15.0 (1976–1985)	123.26[b]	3.51[b]	3.51[b]	0.59[b]	1.29[b]	0.076[b]	0.24[ab]	0.003[b]	0.24[b]	0.005[b]
15.0–23.0 (1966–1975)	111.64[c]	2.89[c]	2.35[c]	0.59[b]	0.92[c]	0.055[c]	0.20[b]	0.002[b]	0.18[c]	ND
LSD	10.81	0.12	0.19	0.004	0.09	0.006	0.05	0.005	0.03	0.001

ND = Not detected.
LSD = Least significant difference ($p \leq 0.05$).

Atmospheric deposition ($mg/m^3/yr$) of heavy metals on the Eastern Shore of Maryland (Wye site) is in the order of Zn (4.70 ± 0.56–48.20 ± 6.70) > Pb (0.32 ± 0.20–13.60 ± 0.98) > Cu (0.31 ± 0.23–9.24 ± 0.71) > Cd (0.01 ± 0.01–0.43 ± 0.04) [19]. The toxicants input increased from 1966 to 1995 due to the increase in human population and industrial activities. Various other factors such as water and sediment equilibrium, tidal actions, rainfall, efficiency of STP and EPA regulations can influence the toxicants input, storage and transport.

The concentrations in the WR sediments of Zn, Pb, Cu, Cd and As showed a slight increase during 1976–1985 from the baseline values (Table 3). During the years 1986–1995 the concentrations of these metals further increased significantly; the concentration of Pb increased by 137%. The proposed criteria for Pb for STP effluent, set by the state of Maryland, is a weekly average of 4.9 $\mu g/l$ but the daily average concentration of the effluent from WR-STP is 8 $\mu g/l$. During the years 1986–1995 the number of various industries (such as metal fabrication and finishing, food industries, poultry processing, microwave, water treatment, plastic, pharmaceuticals) and other sources (such as hospitals and printers) contributing Pb and Cd to STP increased significantly leading to the increases in sediment and porewater concentrations of Pb and Cd in WR [E. Ludy, The City of Salisbury Wastewater Treatment Plant. Personal Communication, March 11, 1996.].

Site PR3 porewater (15.0–23.0 cm depth) had an $EC_{50}\%$ value of 39 and metal concentrations of Zn = 2.89, Pb = 0.59, Cu = 0.055, Cd = 0.002 mg/l during the

baseline period (1966–1975) (Table 3). The lands around the sampling sites in PR are mostly used for agriculture (Fig. 2) while the WR runs through residential areas. Site PR3 is 1.6 km downstream from the STP outlet but adjacent to a poultry farm (started during 1971) which may also be the source of heavy metals into the river along with other agricultural runoff. The relative increases (%) in the concentration of metals during the period 1976–1985 were Zn = 21, Cu = 38 and Cd = 50 (Table 3). Also, during this period, the toxicity and human population in the PR region increased by 33% and 60%, respectively. About 4.05×10^5 hectares are used as farmland in Worcester county where PR is located. Agricultural crop production (corn and soybean yield), use of pesticides and fertilizers have increased significantly with time. Also, poultry production increased from 2.5×10^5 birds in 1976–1985 to 2.85×10^6 birds during 1986–1995 in this area [20]. Increased agricultural activities including runoff from the poultry farms likely contributed the toxicants found in the PR sediments. Poultry litter contains metals such as Zn (320 mg/kg), Cu (320 mg/kg), Cd (35 mg/kg) and As (35 mg/kg) [21]. Subsequent increases (%) in the concentration of metals during the period 1986–1995 were small except Cd which increased by 733%. Cadmium is also present in small amounts in phosphate fertilizers and it accumulates in coastal sediments from different sources of aquatic pollution [18].

The concentrations of Zn, Pb, Cu, Cd and As in the PR sediments showed increases (%) equal to 53, 95, 121, 37 and 54, respectively, from the baseline values (Table 3). Zinc and Pb accumulates in sediments receiving extensive drainage from agricultural areas [22]. In addition to poultry litter, molluscicides, herbicides, fertilizers and algicides contain Cu, Cd and As [23]. The increase in metal concentrations in PR sediments may be related to increased agricultural activities including the runoff from poultry farms in the region.

5. Conclusions

The following conclusions can be made from this study: (1) Due to increase in population, increased industrial activities, and increase in the volume of the sewage treatment plant influent, both the metals concentrations and toxicity of sediment increased significantly with time (1966–1995) in WR. (2) Due to the increase in agricultural activities including poultry farms, the metals concentrations and toxicity of sediments have steadily increased with time (1966–1995) in PR. (3) Lead concentration increased significantly in WR sediment and porewater possibly due to an increase in various industrial activities, commercial facilities that use lead compounds and through atmospheric deposition.

References

[1] J.P. Shine, R.V. Ika, T.E. Ford, Multivariate statistical examination of spatial and temporal patterns of heavy metal contamination in New Bedford Harbor marine sediments, Environ. Sci. Technol. 29 (1995) 1781.

[2] M. Ravichandran, M. Baskaran, P.H. Santschi, T.S. Bianchi, History of trace metal pollution in Sabine–Neches estuary, Beaumont, TX, Environ. Sci. Technol. 29 (1995) 1495.

[3] United States Environmental Protection Agency, Chesapeake Bay, Introduction to an Ecosystem, EPA Chesapeake Bay Program, Washington, DC, 1989, pp. 1–33.

[4] E.A. Stetar, H.L. Boston, I.L. Larsen, M.H. Mobley, The removal of radio active cobalt, cesium and iodine in a conventional municipal waste water treatment plant, Water Environ. Res. 65 (1993) 630.

[5] B.R. Ravishanker, J.F. Blais, H. Bemhoussa, R.D. Tyagi, Bioleaching of metals from sewage sludge: elemental sulfur recovery, J. Environ. Eng. 120 (1994) 462.

[6] W.M. Stigliani, P.R. Jaffe, S. Anderberg, Heavy metal pollution in the Rhine Basin, Environ. Sci. Technol. 27 (1993) 786.

[7] G. Gupta, M. Karuppiah, Toxicity study of a Chesapeake Bay tributary—Wicomico River, Chemosphere 32 (1996) 1193.

[8] G. Gupta, M. Karuppiah, Toxicity identification of Pocomoke River porewater, Chemosphere 33 (1996) 939.

[9] A.A. Bulich, in: D. Liu, B.J. Dutka (Eds.), Toxicity Screening Procedures Using Bacterial Systems, Marcel Dekker, New York, NY, 1984, pp. 55–64.

[10] G.T. Ankley, G.S. Peterson, J.R. Amato, J.J. Jenson, Evaluation of sucrose as an alternative to sodium chloride in the microtox assay: comparison to fish and cladoceran tests with freshwater effluents, Environ. Toxicol. Chem. 9 (1990) 1305.

[11] C.D. Dieter, S.J. Hamilton, W.G. Duffy, L.D. Flake, Evaluation of the Microtox® test to detect phorate contamination of wetlands, J. Fresh Water Ecol. 9 (1994) 271.

[12] R.A. Hoke, J.P. Giesy, M. Zalik, M. Unger, Toxicity of sediments and sediment–porewaters from the Grand Calumet River—Indiana Harbor, Ecotoxicol. Environ. Safety 26 (1993) 86.

[13] M.W. Toussaint, T.R. Shedd, W.H.V. Schalic, G.R. Leather, A comparison of standard acute toxicity tests with rapid-screening toxicity tests, Environ. Toxicol. Chem. 14 (1995) 907.

[14] SAS® Statistics, SAS® User's Guide: Version 5, 1985, SAS Institute, Cary, NC.

[15] A.J. deGroot, K.H. Zschuppe, W. Salomons, Standardization of methods of analysis for heavy metals in sediments, Hydrobiologia 92 (1982) 689.

[16] R.T. Kerhin, J.P. Halka, D.V. Wells, E.L. Hennessee, P.J. Blakeslee, N. Zoltan, R.H. Cuthbertson, The Surficial Sediments of Chesapeake Bay, Maryland. Physical Characteristics and Sediment Budget, Dept. of Natural Resources, Maryland Geological Survey, 1988, Report 48.

[17] G. Gupta, M. Karuppiah, Heavy metals in sediments of two Chesapeake Bay tributaries—Wicomico and Pocomoke rivers, J. Hazard. Mater. 50 (1996) 15.

[18] R.C. Swartz, G.R. Ditsworth, D.W. Schults, J.O. Lamberson, Sediment toxicity to a marine infaunal amphipod: cadmium and its interaction with sewage sludge, Marine Environ. Res. 18 (1985) 133.

[19] J.E. Baker, T.M. Church, J.M. Ondov, J.R. Scudlark, Chesapeake Bay Atmospheric Deposition Study Phase I, July 1990–June 1991, Dept. of Natural Resources, Chesapeake Bay Research and Monitoring Division, MD, 1994.

[20] Maryland Agricultural Statistics, Annual Summaries, Maryland Department of Agriculture, 1966–1995, Annapolis, MD.

[21] G.C. Gupta, P. Kelly, Toxicity comparisons of some animal wastes, Water, Air, Soil Pollut. 53 (1990) 113.

[22] R. Berndtsson, Transport and sedimentation of pollutants in a river reach: a chemical mass balance approach, Water Resour. Res. 26 (1990) 1549.

[23] J.M. Hellawell, Toxic substances in rivers and sediments, Environ. Pollut. 50 (1988) 61.