Science of the Total Environment 568 (2016) 402–414

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

The impact of urban expansion and agricultural legacies on trace metal accumulation in fluvial and lacustrine sediments of the lower Chesapeake Bay basin, USA

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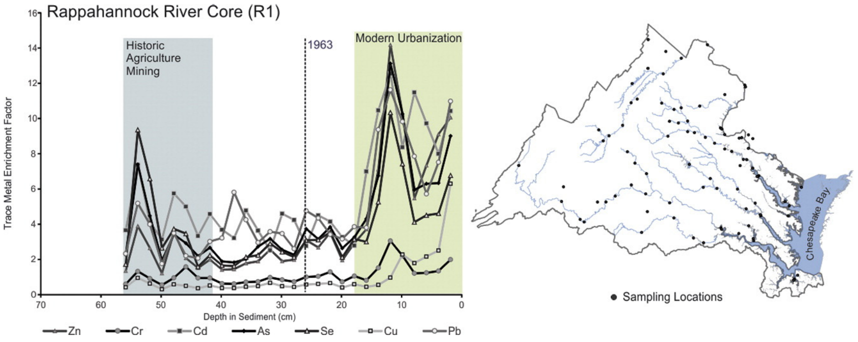
HIGHLIGHTS

- Metals analyses presented from historic and contemporary sediments of study site
- 19th century anthropogenic enrichments persist in subsurface fluvial sediments.
- Lake sediments record reservoir construction disturbances, and land-use signals.
- Urban, atmospheric and agricultural legacy sources dominate contemporary sediments.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 January 2016
Received in revised form 3 June 2016
Accepted 4 June 2016
Available online xxxx

Editor: F.M. Tack

Keywords:
Chesapeake Bay
Trace metals
Enrichment factor
Legacy sediments

ABSTRACT

The progressively declining ecological condition of the Chesapeake Bay is attributed to the influx of contaminants associated with sediment loads supplied by its largest tributaries. The continued urban expansion in the suburbs of Virginia cities, modern agricultural activities in the Shenandoah Valley, the anthropogenic and climate driven changes in fluvial system hydrodynamics and their potential associated impacts on trace metals enrichment in the bay's tributaries necessitate constant environmental monitoring of these important water bodies. Eight ^{210}Pb and ^{137}Cs dated sediment cores and seventy two sediment grab samples were used to analyze the spatial and temporal distributions of Al, Ca, Mg, Cr, Cd, As, Se, Pb, Cu, Zn, Mn, and Fe in the waterways of the Virginia portion of the Chesapeake Bay basin. The sediment cores for trace metal historical fluctuation analysis were obtained in lower fluvial-estuarine environments and reservoirs in the upper reaches of the basin. The trace metal profiles revealed high basal enrichment factors (EF) of between 0.05 and 40.24, which are interpreted to represent early nineteenth century agricultural activity and primary resource extraction. Surficial enrichment factors on both cores and surface grab samples ranged from 0.01 (Cu) to 1421 (Cd), with Pb, Cu, Zn, and Cd enrichments a plausible consequence of modern urban expansion and industrial development along major transportation corridors. Contemporary surficial enrichments of As, Se, and Cr also ranged between 0 and 137, with the higher values likely influenced by lithological and atmospheric sources. Pearson correlation analyses suggest mining and agricultural legacies, coupled with aerosol deposition, are responsible for high metal concentrations in western lakes and

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http://dx.doi.org/10.1016/j.scitotenv.2016.06.022

headwater reaches of fluvial systems, while metal accumulation in estuarine reaches of the major rivers can be attributed to urban effluence and the remobilization of legacy sediments.

1. Introduction

The aquatic systems of the southern Chesapeake Bay watershed display disrupted sedimentation, declining water quality, and altered ecologies resulting from anthropogenic alterations (Yesilonis et al., 2008; Dauer and Alden, 1995; Conrad and Chisholm-Brause, 2004; Conrad et al., 2007; Odhiambo and Ricker, 2011). These environmental aquatic degradations will continue to be exacerbated as basin's human population and urban expansion modify fluvial aggradation, degradation and contaminant dispersal processes. Globally, basins that once drained extensive areas of resource extraction and agriculture are rapidly being converted to urban-industrial centers and “mega-cities” (Taylor and Owens 2009; Duran et al., 2012). Therefore rapidly developing/industrializing and more economically developed countries are progressively going to be encountering the impact of contaminant laden legacy sediment in the associated fluvial basins and coastal zones (Ekeanyanwu et al., 2010; Taylor and Owens, 2009; Bhatt and Gardner, 2009; Singh et al., 2005; Liu and Xiaoming, 2011; Dhivert et al., 2016).

The accumulation of trace metals in aquatic systems lies at the intersection of natural geological processes and anthropogenic effluences. The pathways through which trace elements enter aquatic systems are diverse. Natural non-point sources like weathering of local geology and deposition of volcanic fallout provide significant inputs of trace metals via runoff or atmospheric deposition (Alloway, 2013). On a spatial basis, lithological degeneration is the dominant factor in determining the total concentration of heavy metals in world soils. Sediments derived from formations composed of black shales, coals, limestones, ultramafic rocks and sedimentary ironstones are regularly enriched in several heavy metals, although content can vary (Alloway, 2013; Table 1). During weathering, these deposits undergo dissolution and oxidation, and metals are dispersed in regional soils, transported long distances via Aeolian or fluvial transport and/or leached into groundwater (Alloway, 2013; Sweet et al., 1989; Roen, 1984; Tuttle et al., 2009).

Although innate sources of trace metals can dominate overall accumulation values, the prevalence and intensity of anthropogenic activities has altered natural processes. Point sources for metal pollution include municipal sewage discharges, power plant effluence, industrial releases, and acid mine drainage (Alloway, 2013; Andren et al., 1975). The disposal of mine tailings in proximity to aquatic systems correlates with environmental degradation (Odhiambo et al., 1996), eventually exacerbating the biological uptake of metals associated with mine waste (Axtmann and Luoma, 1991). Decaying automobile parts and concrete contributes significantly to trace metal concentration as water flows through landscapes (Rice, 1999; Wang and Bjorn, 2014; Karuppiah and Gupta, 1998; Yesilonis et al., 2008). Agricultural sources of heavy metal pollution include the use and subsequent runoff of pesticides, fertilizers and biosolids as well as the rearing of livestock whose manure is enriched in trace metals (Alloway, 2013; Karuppiah and Gupta, 1998).

Unlike many industrial and agricultural sources which contribute metals to local catchments, atmospheric deposition can transport particles long distances while simultaneously acting as a confined source of contamination (Kim et al., 2000; Scudlark et al., 2005; Mason et al., 1997). Airborne contaminant sources are widely varied and range from the industrial - smelters, coal fired power generation, foundries - to the domestic - emissions from heating, corrosion of metal structures, and dust from automobile wear (Kim et al., 2000; Petti, 1989; Scudlark et al., 2005). In addition to aerosol deposition, the erosion of contaminated soils and remobilization of fluvial sediments enriched in metals provide an extensive supply of trace metals to fluvial systems. Sediments eroded from upland areas during periods of intensive land clearing reflect landscape scale disturbances that continue to impair environments (Niemitz et al., 2013; Walter and Merritts, 2008; Donovan et al., 2015; Smith and Wilcock, 2015). Erosion of soil containing agricultural and industrial contaminants has accelerated in many modern landscapes due to the prevalence of impervious surfaces accompanying extensive urbanization and the subsequent acceleration of runoff during storm events (Niemitz et al., 2013; Pizzuto and O'Neal, 2009; Hupp et al., 2013). Trace metal adsorption is positively correlated with increases in particle surface area, allowing finely grained organic matter particles and clays to become leading chelators for metals in surface water bodies (Axtmann et al., 1997; Kuwabara et al., 1989; Sinex and Helz, 1981). Trace metals are predominantly present on the surface of sediments and are often found bound to organic or Fe-Mn oxyhydroxide coatings. Once introduced into an environment, trace metals persist distributed in the water column until they accumulate in benthic sediments (Fitchet et al., 1998; Axtmann et al., 1997; Wang and Rainbow, 2008; Rattner et al., 2008).

Previous localized studies within the Chesapeake Bay basin highlighted trace metal concentrations in the estuarine sediments of (Sinex and Helz, 1981; Rule, 1986; Hartwell and Hameedi, 2007) or metal transport in small fluvial or lacustrine sub-basins (Odhiambo et al., 2013; Clark et al., 2014); few contemporaneous studies exist that attempt to reconcile past land uses and metal concentrations with contemporary concentrations and sources on a macro or multi-basin scale. Fluvio-estuarine and lacustrine ^{210}Pb and ^{137}Cs dated cores were used in temporal analysis of anthropogenic metal inputs over the study area's history, and abundance of spatially diverse surface

Table 1
Mean metal concentrations in Earth's crust, Virginia soils, and all the sediment cores used in this study (μg g^{-1} except Al, Fe, Ca, Mg).

	Zn	Cu	Pb	Cr	Cd	As	Se	Mn	Al %	Fe %	Ca %	Mg %
Average crust[a]	70	55	12.5	100	0.2	1.8	0.05	950	8.23	5.63	4.15	2.33
Virginia soils[b]	29	6.5	34	16.01	0.04	4.6	1.2	1007	4.14	1.4	0.27	0.21
R1	84.8	15.2	27.9	29.4	23.0	18.5	14.7	221	3.54	0.2	0.31	1.48
P1	12.4	4.6	6.3	15.3	2.7	20.1	17.1	661	1.87	0.16	0.95	0.87
J1	56.9	12.8	15.3	38.4	45.9	28.5	22.6	441	3.23	0.18	1.01	0.28
J2	53.0	25.1	32.1	59.7	47.2	25.1	32.1	416	1.52	0.15	1.65	0.64
P-L-1	88.7	86.6	23.7	26.6	10.2	17.4	12.5	554	1.51	0.06	0.05	0.9
P-L-2	88.9	46.9	26.0	25.3	19.2	28.3	4.1	564	2.2	0.09	0.68	0.57
J-L-1	90.2	31.5	15.9	25.4	16.7	27.7	4.7	275	2.1	0.2	0.89	0.3
J-L-2	88.8	50.4	25.0	24.2	25.6	18.1	11.5	484	1.15	0.12	0.93	1.76

[a] Taylor (1964).

[b] Smith (2006).