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Importance of seasonal variability and coastal processes on estuarine manganese and barium cycling in a Pacific Northwest estuary

Debbie Colbert, James McManus*

Oregon State University, College of Oceanic and Atmospheric Sciences, 104 Ocean Admin Building, Corvallis, OR 97331, USA

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Abstract

Dissolved and particulate manganese (Mn) and barium (Ba) within the Tillamook Bay estuary are examined over seasonal cycles under a range of river discharge conditions from January to December 1999. Based on estuarine distributions and box model calculations, Mn and Ba behavior within the estuary is best quantified by considering two dominant factors: interaction with suspended particulate material (adsorption/desorption reactions) and input from benthic sources. Seasonal differences in elemental concentration patterns are dominated by variations in the relative importance of these two variables. While Mn exhibits estuarine behavior typical for this element, Ba shows an uncharacteristic lower estuary source. We hypothesize that this source results from the benthic dissolution of ocean-derived particulate Ba.

The fluxes of dissolved Mn and Ba from the river to the coastal ocean are related to river discharge rates with the high fluxes observed under winter conditions. These winter flux maxima occur despite estuarine removal processes that also occur under winter conditions. During all other seasons, box model calculations indicate that the total (dissolved plus particulate) river fluxes of Mn and Ba to the coastal ocean are enhanced by internal estuarine processes—i.e., by transport across the sediment–water interface. On an annual basis, dissolved Mn and Ba fluxes to the coastal ocean are enriched by 390% and 170%, respectively, over what is expected from riverine inputs alone. The results of this research underscore the importance of estuarine processes in modifying the riverine flux of these elements to the ocean and the necessity of temporal sampling in evaluating processes controlling elemental distributions and delivery to the coastal ocean. Measurements of both the dissolved and particulate phases are also essential for describing and modeling these elemental budgets.

Keywords: Manganese; Barium; Estuary; Particulate; Dissolved; Flux; USA; Oregon; Tillamook Bay

*Corresponding author. Tel.: +1 541 737 8285; fax: +1 541 737 2064.
E-mail address: mcmanus@coas.oregonstate.edu (J. McManus).

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1. Introduction

The importance of estuaries in modifying the riverine flux of trace and alkaline-earth elements to the oceans is well documented (Hanor and Chan, 1977; Morris et al., 1982; Shiller, 1997). Changes in pH, ionic strength, and redox potential alter the adsorption potential of suspended particles, creating surfaces for scavenging, precipitation, and flocculation (Millward, 1995; Morris et al., 1982). Such geochemical processes can, in turn, affect the partitioning between the particulate and dissolved phases of elements such as Mn (Callaway et al., 1988) and Ba (Li and Chan, 1979).

The variety of hydrodynamic and physicochemical conditions occurring in estuaries gives rise to a range of element behavior among estuaries (Owens et al., 1997) and temporally within a given estuary (Stecher and Kogut, 1999). For example, dissolved manganese can behave conservatively (Moore et al., 1979; Muller et al., 1994), exhibit mid-estuarine maxima (Callaway et al., 1988; Laslett and Balls, 1995), or undergo removal at low salinities (Morris and Bale, 1979; Yan et al., 1990). Within the water column, dissolved Mn sources include release via bacterial reduction of Mn-oxides (Klinkhammer and McManus, 2001) and addition from anthropogenic sources (Klinkhammer and Bender, 1981; Owens and Balls, 1997). Mid-estuary peaks in dissolved Mn have been attributed to benthic sources either as diagenetic remobilization from bottom sediments (Laslett and Balls, 1995), injection of sediment pore fluids into the water column (Morris et al., 1987, 1982; Paucot and Wollast, 1997), or desorption from resuspended particles (Callaway et al., 1988). Removal of dissolved Mn at low salinities has been attributed to suspended particle interactions (Morris and Bale, 1979; Yan et al., 1990) and flocculation processes (Church, 1986). The extent to which these biogeochemical processes influence estuarine Mn distributions may, in turn, depend on estuarine flushing time (Callaway et al., 1988; Laslett and Balls, 1995; Muller et al., 1994), which can vary seasonally with river discharge.

While manganese cycling exhibits a broad range of behavior in estuaries, barium distributions have typically exhibited non-conservative behavior with barium production generally occurring at low salinities (Edmond et al., 1978; Hanor and Chan, 1977; Li and Chan, 1979). Desorption of Ba from riverine particles occurs as seawater cations substitute into clay matrices at the freshwater–saltwater boundary (Hanor and Chan, 1977). However, this riverine particle source does not adequately account for Ba enrichment observed in some estuaries (Carroll et al., 1993; Coffey et al., 1997; Moore, 1997; Shaw et al., 1998). In these systems, excess barium is attributed to seasonal salt intrusion with release of barium from barium-rich sediments stored in upper estuaries (Carroll et al., 1993) or from coastal aquifers (Moore, 1997; Shaw et al., 1998). These latter studies suggest that additional Ba sources within estuaries may be important for constructing geochemical budgets for this element, especially over seasonal cycles. Barium cycling within estuaries is further complicated by seasonal removal of Ba in association with phytoplankton production (Guay and Falkner, 1998; Nozaki et al., 2001; Stecher and Kogut, 1999) and via adsorption onto Fe and Mn oxy-hydroxides (Coffey et al., 1997; Ingri and Widerlund, 1994).

The variety of Mn and Ba behaviors highlights the need for further understanding how these elements are affected by seasonal changes in estuary hydrodynamics. Furthermore, few studies have examined trace and alkaline-earth element distributions within Pacific Northwest estuaries (Callaway et al., 1988; Klinkhammer and McManus, 2001), particularly over seasonal timescales. We measured dissolved and particulate Mn and Ba in the Tillamook Bay estuary and five rivers feeding the estuary from January to December 1999. Our goal was to examine the distributions and partitioning of these elements within the estuary over a range of river discharge conditions and quantify their input to the coastal ocean.

2. Methods

2.1. Study area

Tillamook Bay estuary is located 80 km south of the Columbia River. The bay receives freshwater