Estuarine, Coastal and Shelf Science 99 (2012) 31–41

Contents lists available at SciVerse ScienceDirect

Estuarine, Coastal and Shelf Science

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

Calculation of river-seawater endmembers and differential trace metal scavenging in the Columbia River plume

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ARTICLE INFO

Article history:
Received 24 May 2011
Accepted 7 December 2011
Available online 27 December 2011

Keywords:
river plume
trace metals
model
water mixing
conservative mixing
Columbia river

ABSTRACT

A simple model is presented for calculating river and seawater mixing zone endmembers. This model allows construction of a conservative mixing line with respect to trace metals scavenged from surface waters, in the absence of direct endmember sampling. Results of the model suggest a transition from non-conservative to conservative behavior of the trace metals gallium (Ga) and zirconium (Zr) along a transect extending offshore of the Columbia River, indicating environmental controls on differential scavenging. Mechanistic explanation of observed differential scavenging is supported by wind data indicating northward transport of Columbia River plume waters, followed by southwest, offshore, transport. Columbia River plume waters transported to the southwest at the time of sample collection were therefore flanked offshore by aged plume waters returning from the north. While upwelling conditions provide nutrients during southerly transport of plume waters, northward plume transport is associated with downwelling, low nutrient conditions. Low phytoplankton abundance during periods of northward plume transport reduces trace metal scavenging, therefore dilution of river waters with ocean surface waters of comparatively low Ga and Zr concentrations results in near-conservative mixing of Ga and Zr in offshore, aged, plume waters. Results of this work suggest dynamic modification of trace metal residence time within close geographic proximity established by physical and biologic controls, dictated by local winds. Lower trace metal scavenging rates, resulting in a longer residence time, are suggested during northward transport of Columbia River plume waters, compared to higher scavenging rates, and thus shorter residence times, during southerly transport of plume waters. Gallium, demonstrating high analytical precision, reduced contamination risk, and decreased complications of upwelled sources relative to Zr, is proposed to provide identification of aged Columbia River plume waters.

1. Introduction

Trace metal flux to the ocean from rivers is altered within the mixing zone between the freshwater and seawater endmembers as dilution and removal processes are initiated within dynamic estuarine environments (Boyle et al., 1977; Sholkovitz, 1978; Godfrey et al., 2008). Modification of trace metal concentrations continues beyond the estuary within plume waters of the mixing zone as a function of chemical, physical, and biological processes during mixing with the seawater endmember.

Physical processes control mixing within estuaries and as river plumes are transported offshore. Local winds result in the dynamic transport of plume waters (Hickey et al., 2009) and influence upwelling, establishing nutrient availability for phytoplankton growth. Phytoplankton contributes to trace metal removal through both cellular uptake and sorption onto cell surfaces. Scavenging of trace metals within the surface and photic zone is therefore enhanced by increased particulate surface area provided by phytoplankton.

Upon sinking of particulate matter through the water column, trace metals removed from the surface may exhibit characteristics associated with scavenged or nutrient type profiles. Elements demonstrating nutrient type profiles are remineralized during heterotrophic respiration, returning to the dissolved phase, and therefore accumulating as a function of increasing water mass age. Alternatively, elements maintaining association with the particulate phase are removed by settling through the water column, resulting in scavenged type profiles.

Aluminum represents the archetypal scavenged element (Orians and Bruland, 1985), demonstrating rapid scavenged removal from the water column, including scavenging of Al by diatoms (Moran and Moore, 1988; Gehlen et al., 2002; Middag et al., 2009). Gallium (Ga) exhibits similar behavior, however, scavenging occurs more slowly relative to the rapid loss of Al from the water column (Orians and Bruland, 1988a). Gallium therefore represents

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doi:10.1016/j.ecss.2011.12.013

an analog of Al, providing a greater geographic and temporal range from a common elemental point source. Zirconium (Zr) concentrations increase with depth and exhibit enrichment along thermohaline transport (McKelvey and Orians, 1993; Godfrey et al., 1996; Firdaus et al., 2011).

Dilution of trace metal concentrations sourced from a river results in conservative mixing with respect to salinity. Conservative mixing is exemplified by linear elemental concentration as a function of salinity, given a two endmember steady state system of fresh river water mixing with seawater. Deviation from linearity indicates source or removal processes. Positive deviations from a linear conservative mixing line indicate a source during mixing. Conversely, negative deflections from linearity are indicative of trace metal removals during mixing of river and seawater endmembers (Boyle et al., 1974, 1977; Liss, 1976; Officer, 1979; Rattray and Officer, 1979).

Chemical properties of trace metals determine the extent of source, removal, or conservative behavior during transition from river to seawater as a function of differential chemical reactivities. Definition of the mixing zone will therefore be unique to individual trace metals, and to the environment sampled. Behavior of trace metals within the mixing zone may be defined given sampling along a transect extending from a riverine endmember, $S = 0$, across the mixing zone, to a salinity associated with a mixing zone endmember, allowing for connection of a conservative mixing line (Holiday and Liss, 1976). However, mixing zones covering a broad extent, extending 50–100 km offshore (Brown and Bruland, 2009), may hinder acquisition of samples explicitly defining the two endmembers and rather samples acquired may all be from within the mixing zone, thus complicating identification of the endmembers.

This work therefore presents a method for the definition of river and seawater endmembers based on samples acquired from within the mixing zone. Further, connection of these endmembers produces a conservative mixing line, allowing for evaluation of trace metal removal behavior from a riverine source during mixing of river and seawater endmembers.

Concentration data for Ga and Zr from three transects associated with the Columbia River plume will be utilized in this work, representing the first publication of this data. Ocean sampling and analysis is described in Section 2, Methods. Trace metal concentrations are reported in the Results Section 3.1, followed by hydrography (Section 3.2). Model development is a direct result of interpreting trace metal concentrations, and is therefore presented in the Results, Section 3.3. Constraints governing application of the model are outlined in Section 3.4. Results of the model applied to Ga and Zr concentrations associated with the Columbia River plume are described in Section 3.5.1 and 3.5.2 for Ga and Zr, respectively. Description of a mechanism supporting observed trace metal concentrations as predicted by the model, based on winds associated with the sampling period is presented in the Discussion (Section 4). Finally, results and discussion are summarized in the Conclusion (Section 5).

2. Methods

Oceanic sampling for trace metals was conducted aboard the R/V *Point Sur* in June and July 1997. Samples for trace metal analysis were acquired via a Teflon pump from a 'fish' towed at a depth of 1–2 m, samples were collected with established trace metal clean sampling techniques and acidified with 2 mL HCl.

Analysis of Ga and Zr were conducted by ICP-MS following concentration on Chelex-100 resin. Samples were adjusted to pH = 2 and 1000 mL were loaded onto 1.5 mL Chelex-100 at a flow rate of 0.2 mL/min, a method optimized for Zr by McKelvey and Orians (1998). Gallium concentrations analyzed by this method utilizing Chelex-100, at pH = 2, calculated based on an internal standard (Rh) are supported based on agreement with results from the method of Orians and Boyle (1993) utilizing 8-hydroxyquinoline resin at pH = 4 calculated via standard addition, Precision for Ga and Zr are 5% and 13% and limits of detection are 0.24 and 6 pmol/kg, for Ga and Zr respectively (Lanthier, 1999).

Hydrographic properties, temperature and salinity, acquired continuously along each transect were provided by Ken Bruland's group at University of California Santa Cruz. Wind data, presented in the Discussion, was accessed from the National Oceanic and Atmospheric Administration (NOAA) National Data Buoy Center.

3. Results

3.1. Trace metal concentrations

Measured trace metal concentrations of Ga and Zr (Lanthier, 1999) are presented in Table 1.

3.2. Hydrography

Brief interpretation of hydrographic data along the cruise transects is instructive in interpreting model results and application of the endmember calculation method presented in Section 3.3. Transect 9 (T9) extended from the mouth of the Columbia River, while transects 8 (T8) and 7 (T7) are south along the Oregon coast (Fig. 1a). Stations at which trace metal samples were acquired are numbered based on increasing distance from the coast.

Temperature and salinity data collected continuously along transects indicate distinct characteristics among the three transects in T-S space (Fig. 1b). Trace metal stations are indicated along each transect and may be referenced to Fig. 1a. Transect T9 demonstrates the influence of the Columbia River plume, as stations 1–4 occupy the lowest salinity values among the three transects (Fig. 1b). Salinities decrease from stations 1 to 4, and the lowest salinities of the core waters of the plume occur ~30 km offshore (Fig. 1c).

Table 1
Temperatures and salinity and Ga and Zr concentrations.

Transect	Station	*S*	*T*	Ga	Zr
			°C	pM	pM
T9	1	25.413	16.78	28	48
	2	24.669	16.55	36	63
	3	23.791	16.45	42	81
	4	22.624	16.5	49	86
	5	28.564	17.9	16	29
	6	28.31	19.36	72	65
	7	29.277	18.88	43	54
T8	1	31.605	13.92	10.7	53
	2	31.277	15.17	11.8	39
	3	30.112	15.77	14.7	42
	4	30.142	15.76	12.7	35
	5	30.121	16.17	11.6	28
	6	28.372	18.3	20	42
	7	27.364	18.71	23	34
	8	29.38	18.73	16	29
	9	31.647	17.85	7.5	16
T7	1	27.888	16.57	19	45
	2	26.953	17.66	24	46
	3	26.469	17.89	27	47
	4	25.903	18.04	26	39
	5	25.751	18.07	31	48
	6	26.058	18.38	29	57
	7	26.482	18.10	26	45
	8	25.507	18.35	33	46
	9	25.989	18.28	30	52
	10	26.293	18.29	27	49
	11	26.98	18.14	25	45