



## Research papers

# Reactive iron and manganese distributions in seabed sediments near small mountainous rivers off Oregon and California (USA)

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## ABSTRACT

We examined the spatial distribution of sedimentary reactive iron ( $Fe_R$ ) and manganese ( $Mn_R$ ) along the continental shelf near the mouth of the Umpqua River, Oregon (USA). A well-defined muddy (silt + clay) depocenter of fluvial origin characterizes this part of the Oregon margin. Reactive Fe and Mn contents are elevated within the silt-rich landward edge of the depocenter. Away from this depocenter, sediments are predominantly sandy both along the inner-shelf (< ~100 m depth) and mid-shelf (~100–150 m depth) and have lower concentrations of reactive metals compared to the depocenter. Sediments are also muddy along the slope (> ~150 m depth) and have elevated  $Fe_R$  and  $Mn_R$ . Based on their correlation with sediment grain size, it appears that  $Fe_R$  and to a lesser extent  $Mn_R$ , are associated with mud size sediments. Reactive metal concentration is also positively correlated with organic carbon (OC) content, indicating a potentially common source. Seabed sediments from five other small, mountainous river systems (Klamath, Eel, Navarro, Russian, and Salinas) located south of Umpqua show the same general relationship between  $Fe_R$  and OC. Although both  $Fe_R$  and  $Mn_R$  exhibit similar relationships to grain size and OC, the relationships with  $Mn_R$  exhibit considerable scatter. Comparison of Umpqua River suspended sediment data with the seabed data suggests that  $Mn_R$  is more prone to loss from sediment particles during transit to the seabed as compared to  $Fe_R$ , and this difference explains why  $Fe_R$  maintains a reasonably tight relationship with organic carbon and particle size along the seafloor relative to  $Mn_R$ .

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## 1. Introduction

Iron (Fe) and manganese (Mn) are two important micronutrients that control primary productivity in parts of the open and coastal oceans (Sunda et al., 1981; Martin and Fitzwater, 1988; Sunda and Huntsman, 1988; Martin et al., 1990). One potential source of Fe and Mn is continental shelf sediments (Johnson et al., 1992; Shiller, 1997; Poulton and Raiswell, 2000; Elrod et al., 2004; Moore et al., 2004), which in turn derive their Fe through local rivers from terrestrial environments (e.g., Milliman and Syvitski, 1992; Colbert, 2004; Chase et al., 2007; Wetz et al., 2006; Lippiatt et al., 2010). These river-derived sediments are rich in reactive Fe (e.g., Aller et al., 1991; McKee et al., 2004; Poulton and Raiswell, 2005), where the term ‘reactive’ refers to the fraction of total sedimentary Fe (and Mn) that is highly reactive to sulfides and consists primarily of amorphous and poorly crystalline Fe

(and presumably Mn) metal hydroxides and oxides (Canfield, 1989; Poulton and Raiswell, 2002; Anderson and Raiswell, 2004; Poulton and Canfield, 2005). The presence of these reactive metals makes river-dominated margins potential ‘hotspots’ of micronutrient supply to the coastal ocean (e.g., Poulton and Raiswell, 2002; Severmann et al., 2010; McManus et al., 2012). The importance of river-dominated margin sediments as potential Fe and Mn sources to the overlying ocean is highlighted by recent studies that have shown atypically high benthic Fe and Mn fluxes from these systems compared to other shelf settings (Berelson et al., 2003; Elrod et al., 2004; Severmann et al., 2010; McManus et al., 2012).

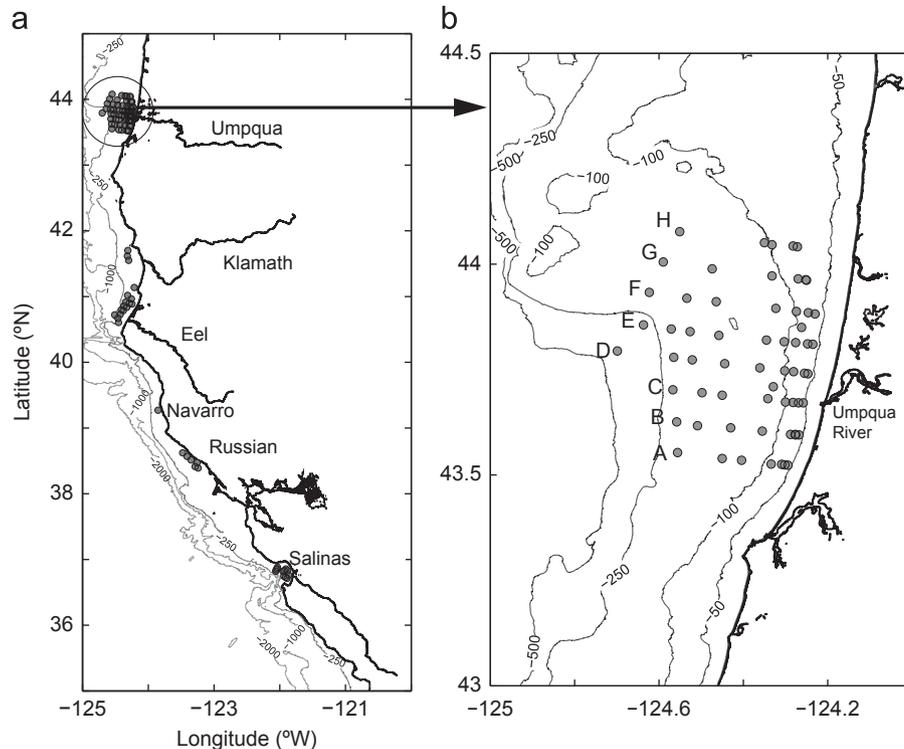
Fe and Mn rich shelf sediments may also enhance organic carbon (OC) preservation (e.g., Kaiser and Guggenberger, 2000; Poulton and Raiswell, 2005; Lalonde et al., 2012). From a mechanistic perspective, Lalonde et al. (2012) suggest that co-precipitation, or chelating between OC and Fe, or both of these processes forms macromolecular domains of Fe–OC complexes resistant to dissolution. Based on measurements from a wide range of aquatic environments, these authors estimated that about 22% of global sedimentary OC is preserved by reactive Fe phases (Lalonde et al., 2012).

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Sediment grain size may also play an important role in the transport of reactive Fe and OC from the terrestrial to the marine environment. Although the role of grain characteristics on OC transport and distributions has been well studied (e.g., Keil et al., 1994; Mayer, 1994a,b; Bergamaschi et al., 1997; Keil et al., 1998; Gordon and Goñi, 2004; Bianchi, 2007), there is a limited but

growing body of literature addressing the connection between grain size and reactive metal transport. (e.g., Whitney, 1975; Keil et al., 1994; Hedges and Keil, 1995; Poulton and Raiswell, 2005). One of these studies showed that finer fractions of suspended riverine sediments have four times higher reactive Fe compared to relatively coarser fractions (see Poulton and Raiswell, 2005).



**Fig. 1.** Study sites are shown including (a) locations of the sites near the six river-mouths shown by dots and (b) locations of transects near the Umpqua River mouth. In panel (b) sample locations are shown by dots.

**Table 1**  
Regional geologic and climatic characteristic of six rivers. Data are from Benke and Cushing (2005), Wheatcroft and Sommerfield (2005), Walsh and Nittrouer (2009), and Kniskern et al. (2011).

	Umpqua	Klamath	Eel	Navarro	Russian	Salinas
<b>Geology</b>	Eocene turbidities and volcanics	Serpentinite and granite of Paleozoic	Cretaceous to lower tertiary Franciscan melange		Franciscan melange	Mesozoic granitics overlain by metamorphic and marine sedimentary rocks Mediterranean <sup>a</sup>
<b>Climate</b>	Wet temperate <sup>a</sup> mountain forest <sup>c</sup>	Temperate, mountain forest, dessert <sup>c</sup>	Temperate, <sup>a</sup> temperate mountain forest <sup>c</sup>	Temperate mountain forest <sup>c</sup>	Temperate mountain forest <sup>c</sup>	
<b>Rainfall (cm/yr)</b>	200–230 <sup>a</sup> 115 <sup>c</sup>	85 <sup>c</sup>	130–175 <sup>a</sup> 133 <sup>c</sup>		105 <sup>c</sup>	25–65 <sup>a</sup> 36.4 <sup>c</sup>
<b>Basin size (km<sup>2</sup>)</b>	9534 11,800 <sup>a</sup> 12,133 <sup>c</sup>	21,950 40,608 <sup>c</sup>	8063 9300 <sup>a</sup> 9456 <sup>c</sup>	785	3452 3728 <sup>c</sup>	11,000 <sup>a</sup> 10,983 <sup>c</sup>
<b>Avg. discharge (m<sup>3</sup>/s)</b>	212 211 <sup>c</sup>	233 501 <sup>c</sup>	208 210 <sup>c</sup>	15	76 66 <sup>c</sup>	12.7
<b>Annual sed. load (x 10<sup>9</sup> kg)</b>	1.4	0.4	18 19 <sup>a</sup> 24 <sup>b</sup>	0.24	0.27	1.7–3.3 <sup>a</sup>
<b>Sed. yield (x 10<sup>3</sup> kg/km<sup>2</sup>/yr)</b>	147	252	2232	(300)	318	
<b>Shelf width (km)</b>	~30 <sup>a</sup>		~20 <sup>a</sup> 16 <sup>b</sup>			from 7 km to canyon <sup>a</sup>
<b>Shelf slope (m/km)</b>	0.04 <sup>a</sup>		0.03 <sup>a</sup>			0.02 <sup>a</sup>
<b>Depth of nearest maximum shelf depocenter (m)</b>	70–80 <sup>a</sup>		55 <sup>a</sup> 60 <sup>b</sup>			40 <sup>a</sup>

<sup>a</sup> Indicates reported values from Kniskern et al. (2011).

<sup>b</sup> Indicates reported values from Walsh and Nittrouer (2009).

<sup>c</sup> Indicates values from Benke and Cushing (2005) and unmarked values are from Wheatcroft and Sommerfield (2005).

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