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A New Focus on Groundwater–Seawater Interactions
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Influence of groundwater discharge through a coastal sandy barrier in southern Brazil on seawater metal chemistry

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Abstract Sandy barriers developed during the Holocene transgressing sea are common features of many coastal regions throughout the world. We present here the results of the study of groundwater–surface water interactions associated with a 600-km barrier which created the Mirim-Patos Lagoon system, the largest in South America. Results show that the composition of the groundwater discharge to the ocean from these permeable sands differs significantly in metal concentrations from those of surface freshwater–seawater mixtures, primarily as a result of redox processes. Estimates of the volume of freshwater transport and seawater cycling through the sands, and metal concentrations in surface waters and in groundwaters, were used to estimate metal fluxes between compartments of this system and indicate that iron, manganese, cobalt and perhaps vanadium, cadmium, copper and zinc are being enriched in adjacent coastal waters, whereas uranium and perhaps molybdenum are being depleted.

Key words metals; coastal ocean; groundwater discharge; Brazil

INTRODUCTION

There is a growing body of evidence indicating the importance of groundwater pathways for the transport of solutes in permeable sediments and aquifers at the land-sea boundary. Inputs may consist of freshwater, seawater-freshwater mixtures and/or recirculated seawater; these are collectively referred to as submarine groundwater discharge (SGD). Whether SGD originates in freshwater aquifers or includes or is dominated by infiltrated seawater, its composition can be quite different from surface waters and its effect on the coastal ocean can be significant. Groundwater discharge from coastal aquifers can transport material to the ocean from land, in addition to rivers, and often at much higher concentrations.

We have been involved in a study of groundwater–surface water interactions associated with Patos Lagoon (Fig. 1), on the extreme southern coast of Brazil, in an attempt to understand better the exchange processes involving groundwater pathways in permeable sediments. The Patos Lagoon system is the largest in South America and is relatively pristine, with little human development surrounding it, especially on the barrier spit separating it from the sea. Given the geological and hydrological characteristics of the Patos Lagoon system, we hypothesized that a relatively large
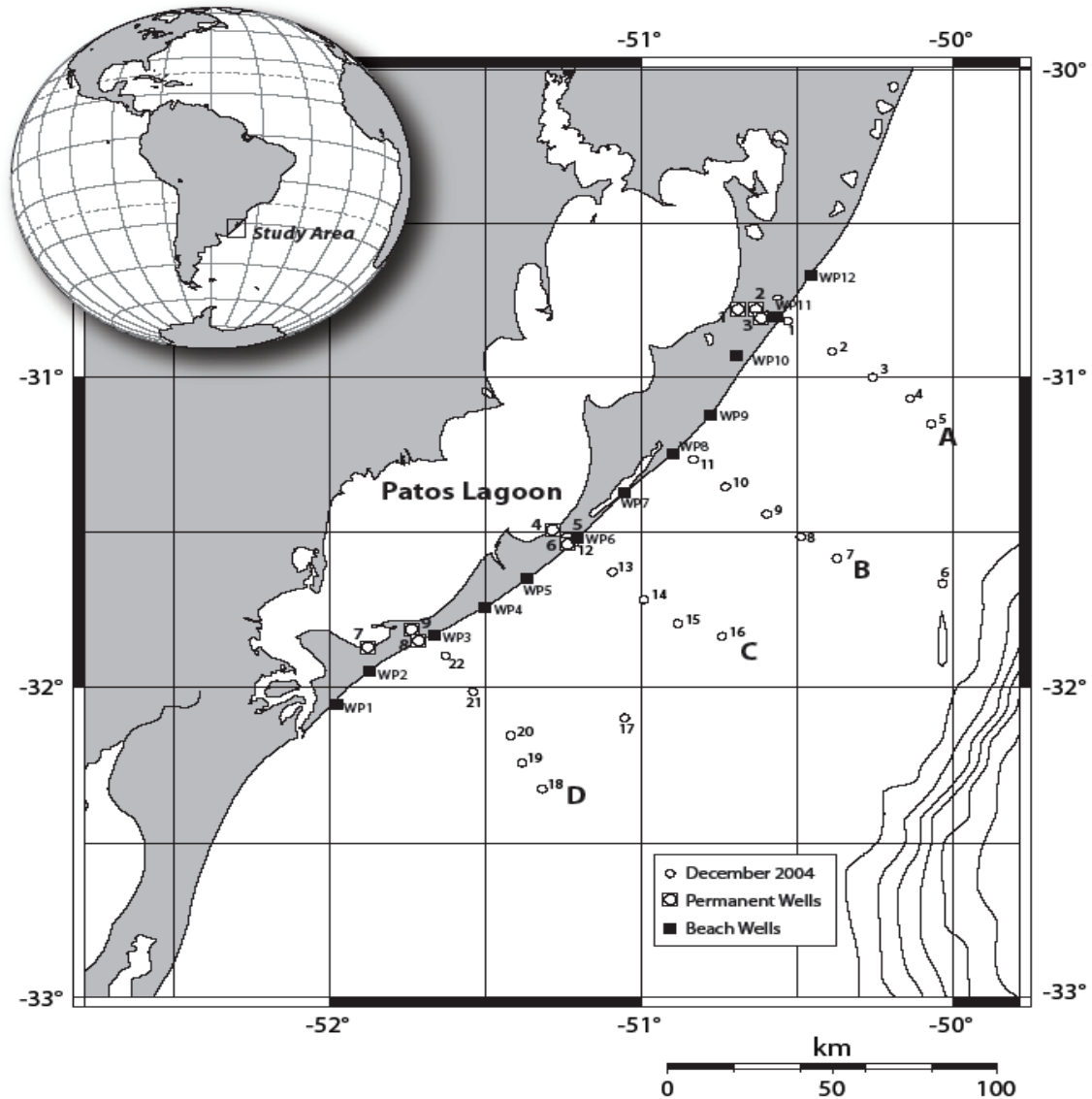
Fig. 1 Patos-Mirim Lagoon system. The Mirim Lagoon is partially shown in the lower left corner of the figure. Its only outlet to the ocean is through the Patos Lagoon. Map of the study area shows locations of permanent wells, beach groundwater and surf zone stations and offshore hydrographic and water sampling stations. The latter are located along four transects referred to in the text, starting from the north, as Transects A, B, C and D.

amount of freshwater flow must occur through the barrier, where it mixes with seawater within the permeable sediments underlying the barrier spit. Here we report the results of trace metal (Fe, Mn, Co, U, V, Mo, Cu, Cd, and Zn) analyses of groundwater recovered from permanent wells installed within the lagoon barrier and from temporary well points deployed along the adjacent beach face. These results are compared to metal concentrations measured in surface waters in the region to assess the impact of SGD on them. Constrained by previously reported Ra measurements (Windom *et al.*, 2006), a simple conceptual model is used to estimate metal fluxes in this groundwater–surface water system.

The Patos-Mirim Lagoon system represents the major coastal expression of a Holocene Post-Glacial Marine Transgression barrier complex (Dillenburg *et al.*, 2002; Fig. 1). It covers an area of over 10 000 km^2. The major surface contact with the sea is a relatively small inlet (approx. 800 m wide) near the city of Rio Grande. This also provides the major surface outlet for Mirim Lagoon, which drains through the Sao Goncalo Channel, into the Patos Lagoon.

High discharge to the lagoon occurs in the winter (June–August) during which the entire lagoon system is fresh. During these periods, circulation within the Patos Lagoon is driven by fresh water discharge whereas wind drives circulation at other times (Möller *et al.*, 1996). Tides (generally about 0.5 m) exert little control on circulation or water level within the lagoon except at its entrance near Rio Grande. But winds and freshwater discharge can result in seasonally significant up-set and down-set of water levels. Generally, however, the water level of the lagoon is always 0.5 m or more above sea level over most of the lagoon.

METHODS

Field sampling campaigns were conducted during the Austral summer (November 2003 and December 2004) when freshwater discharge to the Patos Lagoon is minimal and the salinity of the outflow at its mouth is high (Windom *et al.*, 1999). Data on wind direction and velocity for one week prior and the week during our field campaigns were obtained from a meteorological station at the Fundação Universidade Federal do Rio Grande (FURG) near the mouth of the lagoon. During the November, 2003 campaign mean wind direction was onshore for 4 days with maximum velocities of 6 m s^{-1}, from the south 2 days at less than 2 m s^{-1}, and from the north 9 days at approx. 3 m s^{-1}. During the December 2004 campaign, mean wind direction was onshore 4 days at 2–4 m s^{-1} and 10 days from the north at 2–5 m s^{-1}. The Rio de la Plata discharge is also lowest during the Austral summer and the southward along-shore wind stress further minimizes the intrusion of any freshwater from this source into the study area under these conditions (Piola *et al.*, 2005). This also applies to the discharge from Patos Lagoon.

Sampling methods have been described elsewhere (Windom *et al.*, 2006) and included the following types of samples:
– Permanent wells across three transects of the Patos Lagoon barrier (PLB) with each transect consisting of three sets of wells, one near the lagoon, one in the interior and one near the beach front. Each set generally included three wells screened nominally at 5, 10 and 15 m (Fig. 1).
– Beach groundwater using a drive-point peizometer system (Charette & Sholkovitz, 2006) to sample along the beach of the PLB down to a maximum depth of 8 m, but most samples were collected at shallower depths of a metre or two. Sampling sites were spaced at ~20 km intervals on the southernmost 240 km of the PLB ocean beach (Fig. 1).
– Surf zone samples collected at the same sites as the beach groundwater samples were taken.
– Offshore surface seawater samples collected in December 2004 along four transects perpendicular to shore using the research vessel Atlantico Sul (Fig. 1).

  − Surface water samples collected along a salinity gradient starting in Patos Lagoon and extending through its inlet to offshore just south of Transect D (Fig. 1) during June 2001 when freshwater discharge is high and surface water metal variations should be influenced more by river–seawater mixing end members.

Details of metal analyses have been previously described (Windom & Niencheski, 2003; Windom *et al*., 2006) and involved ultra clean techniques to minimize contamination. Detections limits are generally at least an order of magnitude below the lowest concentration reported below and precision of analysis at concentrations typical of seawater concentrations are generally better than ±10%.

RESULTS

The mean and median metal concentrations in the various compartments of this groundwater–surface water system (Table 1) indicate considerable groundwater enrichment of Fe, Mn and Co above typical levels in surface waters whereas the

Table 1 Summary of average and median metal concentrations in waters of the study area collected in November 2003 and December 2004 compared to average ocean values taken from Bruland (1983).

|	Salinity	Fe (µM)	Mn (nM)	Co (nM)	U (nM)	V (nM)	Mo (nM)	Cu (nM)	Cd (pM)	Zn (nM)
Permanent wells										
2003										
Average	0.55	12.7	4351	21	0.27	12.0	6.3	1.7	163	15
Median	0.1	1.7	2781	4	0.13	7.0	2.2	1.2	92	10
2004										
Average	0.2	21.2	2041	24	0.14	9.2	3.5	1.7	57	19
Median	0.1	4.4	1461	4	0.11	5.5	1.2	1.4	42	16
Beach wells										
2003										
Average	11.1	27.8	4324	2.4	1.47	10.6	41.1	1.1	59	11
Median	8.3	22.6	2146	1.9	0.21	6.05	38.2	0.7	41	10
2004										
Average	22.9	24.1	4395	4.5	3.00	9.5	45.2	2.3	54	8
Median	24.5	20.8	3733	1.8	2.47	7.5	54.1	2.3	46	8
Surf zone										
2003										
Average	30.5	4.2	101.3	1.0	10.0	34.8	68.4	5.0	153	9.7
Median	30.3	1.2	60.5	0.8	11.7	35.4	74.0	5.5	143	7.3
2004										
Average	33.6	1.0	27.5	1.0	11.9	39.6	70.2	7.4	175	7.6
Median	34.1	1.0	26.6	1.0	11.6	41.1	67.5	7.4	143	6.7
Shelf										
Average	35.5	0.06	2.3	0.4	13.5	25.9	91.8	2.2	41.8	0.6
Median	35.5	0.04	1.9	0.4	13.3	26.6	93.5	2.1	42.6	0.6
Ocean										
Average		0.001	0.5	0.02	13.8	30	110	4.0	700	6
Surf. depleted		0.0001	0.2	0.01		20		0.5	1	0.05
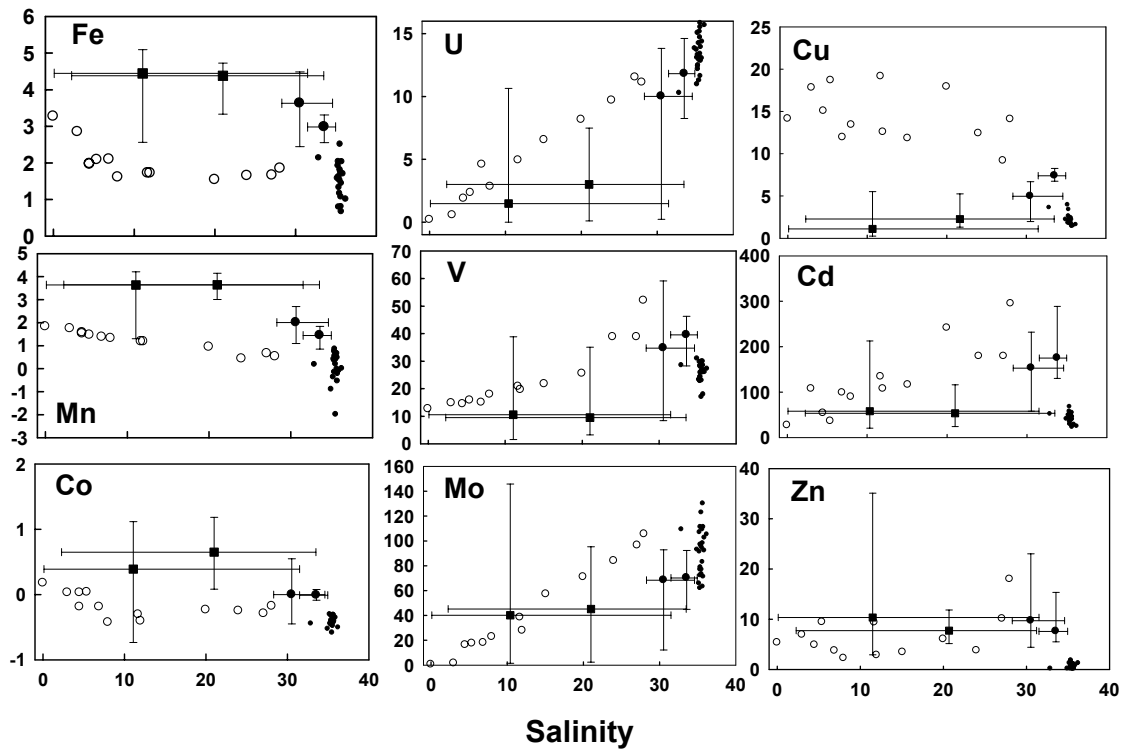
Fig. 2 Mean and range of metal concentrations (in nM except for Cd which is in pM) in beach groundwater (filled squares), and surf zone samples (filled circles, left is 2003 and right is 2004) compared to those in samples collected along a salinity transect in June 2001 (open circles) and shelf water samples collected in December 2004 (filled circles).

concentrations of the other metals, with the exception of Cu, are similar to uncontaminated surface freshwater levels or equivalent surface freshwater–sea water mixtures. Copper concentrations in groundwaters are almost a factor of ten lower than natural surface freshwater values.

Mean concentrations and ranges of metal concentrations in beach groundwater and in samples from the adjacent surf zone for the summer 2003 and 2004 sampling campaigns are shown in Fig. 2 in relation to concentrations observed for surface water samples collected along a salinity gradient during the winter 2001, and for surface shelf water samples collected from offshore transects during December 2004. Results indicate that groundwater concentrations of Fe, Mn and Co (Fig. 2) are virtually always greater than equivalent surface freshwater–sea water mixture. Groundwater U, V, Cu and Cd concentrations (Fig. 2) are generally always less than equivalent surface waters, while Mo and Zn concentrations in ground waters overlap those of surface waters.

DISCUSSION

We use the results presented above, along with the estimates of submarine groundwater discharge (SGD) from Windom *et al.* (2006), based on radium isotopic tracers, to estimate metal fluxes between compartments of this coastal groundwater–
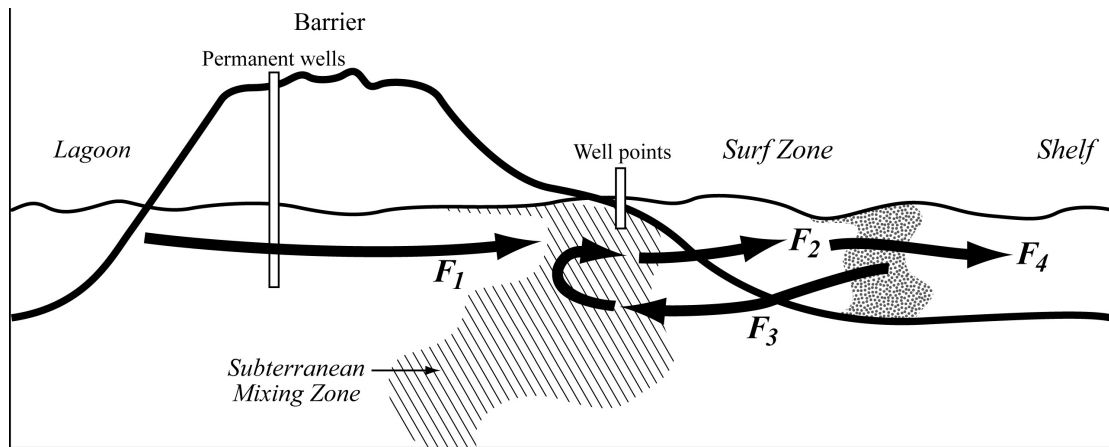
Fig. 3 Conceptual model of groundwater–surface water system.

surface water system. Our conceptual model of how this system operates is as follows is shown in Fig. 3. This is similar to the subterranean estuary studied by Charette & Sholkovitz (2006). By knowing the SGD water flux we can estimate the relative fluxes shown in the conceptual model shown in Fig. 3 starting with the SGdD flux (F_2) which was estimated by Windom *et al.* (2006) using radium isotope tracers as summarized below and based on groundwater and surface water data collected during the December 2004 campaign:

Windom *et al.* (2006) used radium isotopes as tracers to estimate the SGD flux following the method used by Moore (2003). For this estimate they assumed that radium additions to coastal surface waters occurs only in the near-shore zone due to SGD, net cross-shelf advection is zero, cross-shelf mixing is constant and the system is steady state. Given these assumptions, the cross shelf radium isotope gradients in the upper stratified layer of transects A and B must be balanced by the near-shore SGD flux of radium and radioactive decay (there are no additional inputs from the bottom). Using a model based on these assumptions and the average ^{228}Ra concentration of beach groundwater, Windom *et al.* (2006) estimated the SGD to be 8.5×10^7 m^3 d^{-1} for the 240 km study coastline. The average salinity of the SGD was assumed to be 22.9, the average of the beach groundwater, while that of the surf zone was 34.6. Thus, based on salt balance, 3.1×10^7 m^3 d^{-1} is the freshwater component (Q_{fw}) of the SGD. The remainder (5.4×10^7 m^3 d^{-1}) must be balance by recirculated seawater, so that:

$$SGD = Q_{fw} + Q_{sw}$$

where Q_{sw} is the seawater flux into the permeable sands that is ultimately recycled in the SGD. And for mass balance, assuming steady state, the net offshore transport of water due to mixing must equal Q_{fw}.

Referring to the conceptual model presented in Fig. 3, we can estimate the metal flux associated with the various water fluxes discussed above. These fluxes, which would include those in the freshwater moving toward the ocean (F_1), in SGD (F_2), in seawater recirculated through permeable sediments (F_3), the flux to the inner shelf (F_4), and the flux (not shown in Fig. 5) necessary to sustain the observed mean concentrations of metals observed in inner shelf waters (F_5). These can be estimated using the following equations:

$$F_1 = [C]_{fw} \times Q_{fw} \tag{1}$$

$$F_2 = [C]_{bgw} \times SGD \tag{2}$$

$$F_3 = [C]_{sz} \times (SGD - Q_{fw}) \tag{3}$$

$$F_4 = \{[C]_{bgw} \times SGD\} - \{[C]_{sz} \times (SGD - Q_{fw})\} = F_2 - F_3 \tag{4}$$

$$F_5 = [C]_{shelf} \times (V_{surface\ layer}/\tau) \tag{5}$$

where $[C]_{fw,}$ $[C]_{bgw}$ $[C]_{sz}$ and $[C]_{shelf}$ are the mean concentrations of a given nutrient in permanent wells, beach groundwater, surf zone, and inner shelf, respectively; $V_{surface\ layer}$ is the volume of the inner shelf surface layer (240 km × 22 km × 10 m) used by Windom *et al.* (2006) to calculate a residence time, τ, of 8.3 days using radium isotopic tracers. Because we only have radium tracer data from our December 2004 campaign, from which we can estimate SGD, the flux estimates presented below are based only on the results from samples collected during that campaign. Table 2 gives the results of these calculations along with estimated metal fluxes from the nearby Parana River based on average metal concentrations in world rivers (Martin & Whitfield, 1981; Martin & Windom, 1991) and an average discharge of 14 000 m^3/s. From these data we make the following conclusions:

The estimated fluxes of Fe, Mn and Co in SGD, F_2, cannot be sustained by the F_1 flux to the freshwater–seawater mixing zone represented by beach groundwater. The estimated sea water flux back to the groundwater, F_3, is small and leads to the implication that the F_4 flux to the shelf is more than sufficient to maintain observed metal concentrations. We must therefore conclude that a large part of the SGD flux of these metals is removed relatively rapidly in the near shore to reconcile these flux estimates. The accumulation of iron associated with the fresh-sea water boundary in subterranean mixing zone has been demonstrated by Charette *et al.* (2005) and Windom *et al.* (2006) have shown that the concentrations of iron in surface waters of this region decrease exponentially going offshore. Nonetheless, the data plotted in Fig. 2, demonstrate that the groundwater source provides and important third end-member input, along with surface freshwater and ocean end members, necessary to explain observed surface shelf water Fe, Mn and Co concentrations. The SGD flux for these three metals is also about twice that estimated for the Parana.

Flux estimates for U suggest that this metal is being removed in the near shore (i.e. more is entering the groundwater system in recirculated sea water than is being removed in SGD). And while this estimated removal rate is on the order of one percent

Table 2 Estimated fluxes, as identified in Fig. 5, compared to those for the Parana River. Underlined flux estimates likely having the greatest uncertainty.

Fluxes Moles/day	Fe 10	Mn ×10⁴	Co	U	V	Mo	Cu	Cd	Zn
F1	<u>66</u>	<u>6.3</u>	<u>740</u>	<u>4.0</u>	<u>280</u>	<u>110</u>	<u>53.0</u>	<u>17.0</u>	<u>590</u>
F2	205	<u>37</u>	<u>380</u>	<u>250</u>	<u>810</u>	<u>3850</u>	190	4.5	660
F3	5.1	0.1	50	640	2140	3790	400	10.0	410
F4	200	<u>37</u>	<u>3300</u>	<u>−390</u>	<u>−1330</u>	<u>60.0</u>	−210	−5.5	250
F5	36.4	1.5	20000	86000	16600	58600	14000	267000	4000
Parana	87	18	2000	1200	24000	7000	28000	120	11000

of the flux necessary to maintain the observed mean shelf concentration, the results shown in Fig. 2 for the U-salinity relationship, suggests that this removal may be affecting shelf water concentrations more than the calculations in Table 2 reflect. A similar conclusion was made by Charette & Sholkovitz (2006) for a coastal system along the northeast Atlantic coast of the USA.

For V, Cd and Cu, results of flux calculations suggest that these metals are being removed in the near shore. Unlike U, which is conservative in the ocean, V, Cd and Cu are depleted in surface waters. During the Austral summer, the influence of the Brazil current on shelf waters was significant (Windom *et al.*, 2006) and the ocean water end member of surface waters in this region should be depleted in these three elements (Bruland, 1983) and the results shown in Fig. 2 (for V) and Fig. 4 (for Cu and Cd) indicate a low ocean end member and suggest that SGD acts as a source for these elements. A likely explanation is that these metals are relatively insoluble in suboxic groundwater (Cu and Cd as sulphides) and the resuspension of particles in the near-shore leads to their remobilization. Thus redox processes in the near shore would invalidate the flux calculations for these elements, suggesting that processes associated with SGD provided a sink for these elements when, in fact, this system acts as a source providing a third end member for the surface water concentrations shown in Fig. 2. It is interesting to note that the estimated Cd flux from the Parana is clearly insufficient to support the shelf (F5) flux, suggesting another source, whereas its Cu and Zn fluxes are of the order of magnitude.

For Zn, the flux calculations suggest that SGD is a source and the relation between surface water concentrations shown in Fig. 2 suggests this source provides a third mixing end member similar to the results shown for V, Cu and Cd.

The calculated flux to the shelf, F_4, suggests that that SGD may provide a positive input of Mo. But as indicated in Table 2, this calculation has a high uncertainty, while results shown in Fig. 2 suggest that the near shore acts as a sink, similar to the U results. Windom & Neincheski (2003) demonstrated that U and Mo, which are conservative in the ocean, were depleted in groundwater mixtures of freshwater and seawater and attributed this removal as being mediated by microbial processes.

CONCLUSIONS

The results reported here show that SGD may provide both sources and sinks for metals in coastal ocean regions characterized by permeable sediments such as barriers of coastal lagoons. They also suggest that the subterranean transport pathway may be important in explaining surface water mixing relationships of metals. Although flux calculations based on water balance are informative regarding the magnitude of fluxes, they do not take into account processes occurring at interfaces. Groundwater transport, seawater cycling through permeable coastal/shelf sediments and SGD along the coast of southern Brazil is a complex process deserving greater attention both here and in other coastal areas dominated by permeable sands.

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