Radium-228 as a tracer of dissolved trace element inputs from the Peruvian continental margin


To cite this version:

V. Sanial, L.E. Kipp, P.B. Henderson, P. van Beek, J.-L. Reyss, et al.. Radium-228 as a tracer of dissolved trace element inputs from the Peruvian continental margin. Marine Chemistry, 2018, 201, pp. 20-34. 10.1016/j.marchem.2017.05.008 . hal-02007361

HAL Id: hal-02007361
https://hal.science/hal-02007361
Submitted on 10 Apr 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Radium-228 as a tracer of dissolved trace element inputs from the Peruvian continental margin


Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA
Laboratoire d’Études en Géophysique et Océanographie Spatiales (LEGOS), CNRS-CNRS-IRD-UPS, Observatoire MidiPyrénnées, 31400 Toulouse, France
Environnements, Dynamiques et Territoires de la Montagne (EDYTEM), Université de Savoie Mont Blanc, CNRS, 73373 Le Bourget du Lac, Cédex, France
Department of Earth Sciences, University of Southern California, Los Angeles, CA 90089-0740, USA
Joint Institute for the Study of the Atmosphere and the Ocean, NOAA-Pacific Marine Environmental Laboratory and the University of Washington, Seattle, WA, USA
Department of Ocean, Earth and Atmospheric Sciences, Old Dominion University, Norfolk, VA 23529, USA
Department of Earth and Ocean Sciences, University of South Carolina, Columbia, SC 29208, USA

Keywords:
- Radium isotopes
- Sediment inputs
- Trace elements
- GEOTRACES

ABSTRACT

Continental margins play a central role in the composition of seawater by being an important source of trace element essentials to the functioning of the ocean ecosystems. Here, we measured long-lived radium isotopes ($^{226}$Ra, $^{228}$Ra) along a zonal transect at 12°S (US GEOTRACES GP16) in the eastern tropical South Pacific Ocean. We used $^{228}$Ra to quantify the trace element and isotope (TEI) fluxes (DMn, DFe, and DCo) delivered from the Peruvian continental shelf and slope. First, elevated $^{228}$Ra activities were measured in surface water over the entire transect (~8500 km), evidence that the continental shelf is an important source of sediment-derived TEIs not only to coastal areas, but to central Pacific Ocean waters. Modeled $^{228}$Ra shelf fluxes combined with water column dissolved TEI/$^{228}$Ra ratios were used to quantify the shelf-ocean input rates (normalized to shelf-area) for DMn (3.3 × 10$^4$ μmol m$^{-2}$ y$^{-1}$), DFe (1.5 × 10$^4$ μmol m$^{-2}$ y$^{-1}$), and DCo (1.0 × 10$^3$ μmol m$^{-2}$ y$^{-1}$). Second, co-occurring plumes of $^{228}$Ra, DFe, and DMn extended over 1800 km from the margin at 1000–2500 m depth, indicative of a continental slope sediment TEI input to the intermediate water column. The $^{228}$Ra gradient allowed us to derive an effective horizontal eddy diffusion coefficient ($K_h$) of 46 m$^2$ s$^{-1}$, which in turn permitted the calculation of slope sediment DMn (6.4 × 10$^4$ μmol m$^{-2}$ y$^{-1}$) and DFe (5.9 × 10$^4$ μmol m$^{-2}$ y$^{-1}$) fluxes based on their offshore concentration gradients. On the scale of the South Pacific continental margin between 0–20°S, the DMn shelf flux is approximately 2–3 orders of magnitude higher than the slope flux, while the DFe shelf/slope flux is ~3. Both shelf and slope sediment derived DMn was transported over a significant distance towards the ocean interior, while DFe concentration gradients were steep, consistent with longer water column residence time for DMn as compared to DFe in marine systems. These findings highlight the importance of considering the continental slope-ocean boundary in the oceanic budgets of biologically-important trace elements.

1. Introduction

Continental margins, at the interface between land and ocean, play a central role in marine primary productivity through the supply of biologically-essential trace elements to the ocean. They comprise a shelf region with a gentle bathymetric gradient, and a much steeper slope area that extends to the deep ocean abyssal plain. In the eastern tropical South Pacific Ocean, the margin hosts a highly productive coastal upwelling system (Pennington et al., 2006) that drives high rates of primary production responsible for as much as 10% of the world’s fish catch (Chavez et al., 2008). The upwelling is most intense between 4°S and 16°S. Though its strength may exhibit seasonal variability, it is a permanent feature due to persistent alongshore winds (Chavez et al., 2008). With high productivity comes intense respiration of sinking organic matter, which, combined with weak ocean ventilation, leads to the formation of an OMZ (oxygen minimum zone) (Karstensen et al., 2008), one of the most extensive OMZs in the world ocean (Paulmier and Ruiz-Pino, 2009). While upwelling supplies significant quantities of macronutrients, phytoplankton growth can be limited by the availability of the micronutrient iron.

* Corresponding author.
E-mail address: vsanial@whoi.edu (V. Sanial).

http://dx.doi.org/10.1016/j.marchem.2017.05.008
Received 16 December 2016; Received in revised form 5 May 2017; Accepted 27 May 2017
0304-4203/© 2017 Published by Elsevier B.V.
Along the coastal margin, major sources of trace elements like iron include rivers (e.g., Viers et al., 2009), dust (e.g., Jickells et al., 2005), submarine groundwater discharge (SGD; e.g., Moore, 1996) and diffusion from sediments (e.g., Dale et al., 2015). Dust deposition, a major source of iron to the ocean, as well as riverine inputs, are relatively low in the eastern South Pacific (Jickells et al., 2005; Milliman and Farnsworth, 2011). This is partly because the Peru coastal region is characterized by relatively low precipitation (Scholl et al., 1970), and dust deposition decreases rapidly away from the coast (Albani et al., 2014). Sediments may be an important source of trace elements in this setting, though they only recently have been fully considered as a source term in ocean mass balances (Erold et al., 2004; Jeandel et al., 2011; Moore and Braucher, 2008; Tagliabue et al., 2014; Windom et al., 2006).

The Peru OMZ impinges on the shelf and slope, which facilitates Fe (II) release from margin sediments into the overlying water column (Scholz et al., 2011). Thus, continental shelf sedimentary sources may be the primary source of iron that sustains the productivity of the Peru upwelling region (Johnson et al., 1999). The oxygen deficiency drives active biogeochemical cycles for many other trace elements, especially those that are redox sensitive (Codispoti et al., 2005). In particular, high concentrations of micronutrients such as dissolved cobalt (DCo) and manganese (DMn) have been observed in low oxygen waters (Hatta et al., 2015; Johnson et al., 1996; Noble et al., 2012) including in the Peru OMZ (Hawco et al., 2016; Resing et al., 2015).

Here, we use the naturally occurring radium isotopes $^{226}$Ra ($T_{1/2} = 1600$ y) and $^{228}$Ra ($T_{1/2} = 5.75$ y) as tracers of trace element and isotope (TEI) inputs from the Peruvian continental margin. Radium isotopes are continuously produced through the decay of thorium isotopes in sediments. Because radium isotopes are mobile in seawater in contrast to their thorium parents, advective input from coastal aquifers (Moore, 1996) and diffusion from marine sediments are the two major pathways by which Ra enters the ocean (Koczy, 1958; Kaufman et al., 1973; Moore, 1969a, 1969b). In this way, Ra isotopes help fulfill a central goal of the international GEOTRACES program: to identify processes and quantify fluxes that control the distribution of TEIs at the ocean boundaries. The distribution of $^{228}$Ra along a zonal section off Peru is used to identify what extent the dissolved TEI enrichments, with a focus on Mn, Co, and Fe, are derived from margin sedimentary sources. We also use $^{226}$Ra as a flux gauge to quantify TEI inputs from the Peruvian continental margin, including the shelf and slope. First, we describe the distributions of $^{226}$Ra and $^{228}$Ra over a zonal transect between Peru and Tahiti. Then, we present measurements of $^{228}$Ra slope and shelf fluxes. Finally, we combine the distributions of Mn, Co, and Fe with an application of $^{228}$Ra as a flux gauge to estimate the shelf and slope benthic fluxes of these TEIs.

2. Methods

Seawater samples for Ra isotope analysis were collected onboard the R/V Thomas G. Thompson during the U.S. GEOTRACES Eastern Pacific Zonal Transect (GP16; Oct 26th–Dec 23rd 2013; PI: C. German and J. Moffet) along 12’S between Peru and Tahiti, a distance of 8500 km (Fig. 1). The sampling and analytical methods were largely the same as those employed during the U.S. GEOTRACES North Atlantic Transect in 2010–2011 (GA03; Charette et al., 2015) with further details described in Henderson et al., 2013. A brief description is thus reported below.

2.1. Sample collection

Radium isotopes were preconcentrated from seawater using MnO$_2$ cartridges (“Mn-cartridges”) deployed on modified McLane in situ pumps (ISPs). The ISPs were further modified after the GA03 cruise by adding a second 5” cartridge holder for determining actinium-227 ($^{227}$Ac) cartridge yields. A spring was also added to each cartridge holder in order to minimize seawater bypass through the cartridge, improving the Ra scavenging efficiency. Ten inch cellulose cartridges (3M Micro-Klean RB series, G80B2) were cut to 4”, impregnated with MnO$_2$ and deployed on each ISP for scavenging dissolved (< 1 µm from the QMA and Supor prefiltrers) radium isotopes (Henderson et al., 2013). The ISPs were deployed at 23 stations with 16–24 depths sampled excluding shallower shelf stations. The ISP flow rates averaged ~6 L min$^{-1}$ over 4 h, which resulted in average filtration volumes of 1500 ± 200 L; lower volumes were usually associated with high particle loading that caused the prefilters to clog.

At these high ISP filtration rates, the Mn-cartridges do not scavenge 100% of the radium isotopes. Thus, at each sampling depth, separate samples (21 ± 2 L) were collected from a 30 L Niskin bottle mounted above the ISP (> 1000 m) or from a CTD rosette (< 1000 m). These samples were gravity filtered through acrylic fiber impregnated with MnO$_2$ (“Mn-fiber”) at < 0.5 L min$^{-1}$, which has been shown to quantitatively remove radium from seawater (Moore, 2008). The scavenging efficiencies of the Mn-cartridges were estimated by comparing the $^{226}$Ra activity measured on the cartridge with the $^{228}$Ra activity determined on the corresponding Niskin sample.

In addition to the ISP collection system, around 40 g of Mn-fiber was placed in a mesh bag and suspended in surface water (< 3 m) at each station. The mesh bags were deployed between 8 and 55 h depending on the ship’s time on station. The equivalent volume of seawater pre-concentrated on the Mn-fiber ranged from 230 to 2500 L, which was determined by comparing the $^{226}$Ra activity measured on the Mn-fiber with the $^{226}$Ra activity determined from the surface water Niskin bottle.

Water column and surface water samples for the analysis of dissolved manganese (DMn), dissolved iron (DFe), and dissolved cobalt (DCo) were collected and processed following GEOTRACES trace metal clean protocols, as described by Sedwick et al. (2015), Resing et al. (2015) and Hawco et al. (2016), respectively.

2.2. Laboratory analyses

The Mn-fibers from the mesh bags were rinsed with radium free water, ashed, epoxy sealed, and analyzed using high purity, well-type germanium detectors (HPGe) at the University of South Carolina. Radium-228 was quantified from gamma lines at 338 and 911 keV ($^{228}$Ra daughter of $^{228}$Ac), and $^{226}$Ra was measured through the 352 keV $^{214}$Pb peak. Mn-fiber ash standards of different heights were prepared from a NIST-certified $^{226}$Ra solution (SRM#4967A) and gravimetrically prepared $^{232}$Th solution (activity confirmed through MC-ICP-MS); these were used to determine the counts per minute to disintegrations per minute conversion factors for the samples (a combination of gamma ray intensity and detector efficiency at different geometries) (Moore, 1984).

The 10 g Mn-fibers from the small-volume Niskin bottles were rinsed with MQ water, partially dried using compressed air, and placed into 125 mL PVC cartridge holders (Peterson et al., 2009). The samples

---

(Blundel et al., 2005; Hutchins et al., 2002).

Fig. 1. Eastern Pacific Zonal Transect between Peru and Tahiti (US GEOTRACES GP16; Oct–Dec 2013; white circles). The position of stations from Chung (1980) are marked with solid squares.)
were flushed with He for 5 min at 250 mL min⁻¹, sealed and stored for a minimum of 12 days before analysis, which corresponds to at least 90% ²²²Rn ingrowth. The cartridge holders were then flushed for 15 min with He (250 mL min⁻¹) through a cryo-loop cooled with liquid nitrogen, which serves to trap the ²²²Rn. The cryo-loop was then isolated and heated, and the ²²²Rn was rapidly transferred from the cryo-loop into an alpha scintillation cell (Lucas Cell) with a He flow rate of 450 mL min⁻¹. The Lucas Cells were held for 3 h to allow the ²²²Rn daughters to reach secular equilibrium (Key et al., 1979), then counted for ~200 min on a radon counting system (Model AC/DC-DRC-MK 10-2). This method was calibrated using Mn-fibers loaded with ~20 dpm of ²²⁶Ra (NIST-certified SRM#4967A) and processed in the same way as the samples. These standards were processed at least once per month on each detector. Counting uncertainties typically range from 1 to 7% (1-σ), depending on the ²²²Ra content on the Mn-fiber. These were propagated with the ²²⁶Ra/²²²Ra gamma analysis analytical uncertainty (1-σ) in determining the uncertainties on the reported ²²⁸Ra activities.

The Mn-cartridges and Mn-fibers were ashed at 820 °C for 48 h and 24 h, respectively (Charrette et al., 2001, 2015). The ash was then transferred to polystyrene vials and sealed with epoxy to avoid ²²²Rn loss. Gamma analyses were conducted in an underground laboratory in the French Alps (Laboratoire Souterrain de Modane, LSM) protected from cosmic radiation by the mountain with 1700 m of rock overhead (Reyss et al., 1995), which permitted the detection of the generally low ²²⁶Ra activities. Samples were counted for 2-6 days on high purity, well-type germanium detectors. Six standards were used to calibrate the gamma detectors as described in Reyss et al. (1995). The ²²⁶Ra/²²²Ra activity ratios were determined only in samples collected on the first half of the transect (Stations 1–17; Fig. 1) and in the core of the hydrothermal plume (see Kipp et al. in this issue) using the ²²⁶Ra activities estimated from the ³³⁷Ac peaks (338, 911, and 969 keV) and the ²²⁶Ra activities estimated from the ²¹⁴Pb peaks (295 and 352 keV) and ²¹⁴Bi peak (609 keV).

The scavenging efficiency of radium on the MnO₂ cartridges was 66 ± 16% (1-σ) over the entire GP16 cruise (improved relative to the U.S. Atlantic GEOTRACES cruises: 52 ± 22%; Charrette et al., 2015). Given that the cartridge MnO₂ impregnation method and the average ISP flow rate was the same for both cruises, the introduction of the spring in the cartridge holder is likely the main factor explaining the increased extraction efficiency. Further, the lower standard deviation for GP16 is an indication that reproducibility has also been improved. The ²²⁶Ra and ²²⁸Ra data are available on the BCO-DMO website (http://www.bco-dmo.org/dataset-deployment/650344).

Dissolved manganese was determined at sea as described by Resing et al. (2015). Dissolved iron was determined post-cruise at Old Dominion University by flow injection analysis with in-line pre-concentration on resin-immobilized 8-hydroxyquinoline and colorimetric detection (Sedwick et al., 2015). Dissolved cobalt was determined post cruise following Hawco et al. (2016).

3. Results and discussion

3.1. Distribution of Ra isotopes along the US GEOTRACES GP16 transect

3.1.1. Radium-226 distribution: relationship with hydrography

The ²²⁶Ra activities measured during GP16 were lowest within the surface mixed layer with an average of 6.69 ± 0.36 dpm 100 L⁻¹ (1-σ). The highest ²²⁶Ra activity measured was 34.9 ± 1.28 dpm 100 L⁻¹ (station 13, 3754 m depth). Chung (1980) reported ²²⁸Ra profiles from 1969 and 1972 at stations located in close proximity to the GP16 transect (Fig. 2). In general, the ²²⁶Ra activities measured for GP16 overlap with these historical measurements, and any minor offset is likely due to the slight differences in the station locations. Surface data reported by Chung (1980) from the Peru coastal ocean between 10°S and 20°S averaged 7.2 ± 0.2 dpm 100 L⁻¹, which is consistent within the 1 sigma standard deviation of our data. The new data collected provide an important 40-year inter-calibration between the GEOSECS (1972) and GEOTRACES (SCOR Working Group, 2007) programs.

The “nutrient-like” profile of ²²⁸Ra and the higher activities in the Pacific versus Atlantic deep waters activities led Broecker et al. (1967) to conclude that the ocean ²²⁶Ra distribution is influenced by biogeochemical processes such as surface uptake and particle settling. It has been suggested that tests of siliceous phytoplankton play an important role in radium removal (Ku et al., 1970; Ku and Lin, 1976). As a result, the residence time of ²²⁶Ra in the upper 1000 m has been estimated at 400 years by Moore and Dymond (1991), which is less than expected based solely on its half-life. Chung (1980) reported a linear relationship between ²²⁶Ra and silicate in the upper 2000 m across the East Pacific Rise with a slope of 1.5 × 10⁻³ dpm Ra µmol Si⁻¹. This relationship was more variable below 2000 m, which Chung (1980) and others hypothesized was due to the diffusion of radium from sediments produced by ²³⁰Th decay (Cochran, 1980). The general pattern of ²²⁶Ra activities in the GP16 section is also similar to silicate, with homogeneous and low concentrations in the first 2000 m, an increase of the concentration with depth and an asymmetry between the eastern part and the western part of the transect below 2000 m (Fig. 3). This asymmetry in silicate concentrations and ²²⁶Ra activities is mainly the result of different deep water mass signatures for both ²²⁶Ra and Si.

The positions of the main water masses were identified by an Optimum Multiparameter Analysis (OMPA; Peters et al. in this issue; Fig. 3). Above 2000 m, the ²²⁶Ra distribution across the entire GP16 section was relatively homogeneous despite the presence of different surface and intermediate water masses (Fig. 3). Below 2000 m, a high contribution of Pacific Deep Water (PDW) in the eastern part of the transect suggests a strong influence from North Pacific waters flowing south, whereas the presence of the Antarctic Bottom Water (AABW) and the Lower Circumpolar Deep Water (LCDW) indicates a northward flowing water mass in the western part of the transect (Peters et al. in this issue; Reid, 1997). The PDW is one of the oldest water masses,

Fig. 2. Vertical profiles of ²²⁶Ra from US GEOTRACES GP16 (this study, open symbols) and from Chung, 1980 (closed symbols). Station locations are marked on Fig. 1.
while AABW is relatively young (DeVries and Primeau, 2011; Khatiwala et al., 2012). As a consequence, 226Ra activity increases from the deep Southern Ocean waters to the North Pacific waters (Broecker et al., 1967; Chung, 1974).

During GP16, only one sampling depth was located in the core of the AABW, characterized by low temperature (< 1 °C), high density ($\rho_0 > 27.81$ kg m$^{-3}$) and a 226Ra activity of $23.1 \pm 0.7$ dpm 100 L$^{-1}$ (station 36, 4733 m; Fig. 4). This is consistent with previous measurements of 226Ra activities in AABW, which range from 21 to 23 dpm 100 L$^{-1}$ (Chung and Craig, 1973; Ku and Lin, 1976). Pacific Deep Water has very distinct θ-S characteristics (27.75 kg m$^{-3} < \rho_0 < 27.78$ kg m$^{-3}$; Fig. 4). We observed PDW 226Ra activities in the range of 28.7 dpm 100 L$^{-1}$ (station 17, 2700 m) to 34.9 dpm 100 L$^{-1}$ (station 13, 3754 m). These are in agreement with the large range of values reported for PDW (28–47 dpm 100 L$^{-1}$; Chan et al., 1976; Chung and Craig, 1973). On the western half of the GP16 transect, PDW and AABW are mixed with Lower Circumpolar Deep Water (LCDW) (Fig. 3), which is consistent with the reported 226Ra activities given that the 226Ra in Circumpolar Deep Water ranges from 16 to 20 dpm 100 L$^{-1}$ (Hanfland, 2002; Ku and Lin, 1976; van Beek et al., 2008). The relatively high 226Ra activities in the AABW/LCDW, around 27.78 kg m$^{-3}$, are associated with samples collected particularly close to the seafloor at station 25 and 26 (< 20 m from the seafloor), and are likely due to diffuse input from deep sediments (Hammond et al., 1990; Huh and Ku, 1998).

3.1.2. Radium-228 distribution

Unlike 226Ra, oceanic 228Ra distributions are not strictly related to major water masses due to the shorter half-life (5.75 years). Radium activities in the Pacific Ocean are generally one order of magnitude lower than in the Atlantic Ocean, a result of dilution and decay in the significantly larger Pacific basin relative to its continental margin area (Charette et al., 2015; Knauss et al., 1978; Li et al., 1980; Moore, 1969a, 1969b; van Beek et al., 2007). Larger continental 228Ra inputs in the Atlantic Ocean could also play a role in the difference (Kwon et al., 2014). For the GP16 section, 228Ra ranged from below detection limit to 0.64 ± 0.08 dpm 100 L$^{-1}$, with the highest activity found on the Peruvian shelf (station 3, 13 m). Over the shelf, 228Ra activities increased with distance from shore, which is atypical given the expected strong source of 228Ra from terrestrial runoff and margin sediments. In the off-shelf surface water, 228Ra peaked at stations 7 and 9, after which activities decreased with the increasing distance from the coastline (Fig. 5).

The 228Ra activities measured during GP16 fall within the range of the few Pacific Ocean studies that have reported on this isotope (Huh and Ku, 1998; Kaufman et al., 1973; Knauss et al., 1978; Moore, 1969a, 1969b; Yamada and Nozaki, 1986). More precisely, station 7 (84°W), station 9 (89°W), station 13 (99°W), and station 25 (125°W) display very similar surface 228Ra activities as those from the 1960–1970s (Kaufman et al., 1973; Knauss et al., 1978; Fig. 5). We note, that in these previous studies, fixed 228Ra values of 6.5 dpm 100 L$^{-1}$ and 8.5 dpm 100 L$^{-1}$ were assumed in order to estimate the 228Ra activities, based on measured 228Ra/226Ra activity ratios in Knauss et al. (1978) and Kaufman et al. (1973), respectively. The average 228Ra activity in the mixed layer depth during GP16 was 6.69 ± 0.36 dpm 100 L$^{-1}$.

The difference in 228Ra activities between GP16 and historical values over the shelf (0.2–1.9 dpm 100 L$^{-1}$, collected in March 1973; Knauss et al., 1978) are probably due to a combination of seasonal and interannual variability in 228Ra inputs, along shore currents, and/or upwelling. The 228Ra activities measured during GP16 are in the lower range of the historical data. Seasonal variability in 228Ra has been observed in the U.S. North Atlantic coast with lower 228Ra excess activities relative to offshore waters in winter as compared to summer (Kelly and
The shallowness of the pycnocline, even such small variations in the surface during GP16. The passage of eddies (e.g. V. Sanial et al., 2016) can extend vertically down to 2000 m have also been identified in the eastern South Pacific (Chaigneau and Pizarro, 2005), which could potentially explain this deep 228Ra anomaly at station 9. However, no specific vertical features in temperature, salinity or nutrients have been identified at this station to confirm the presence of an eddy.

The 228Ra activities increased again close to the bottom, likely due to diffusive input from seafloor sediments (Hammond et al., 1990; Huh and Ku, 1998). Near-bottom 228Ra activities were especially high in the very narrow 6000 m deep Peru-Chile Trench (station 1) and at stations 7 and 9 (Fig. 6). In the case of station 1, these high activities may be a result of benthic input from both slopes of the trench. Sediment remobilization as indicated by the high concentration of lithogenic particles at the bottom of stations 7 and 9 and subsequent desorption could also potentially explain the high 228Ra activities at this location (Lam et al. in this issue).

3.2. Shelf and slope 228Ra fluxes

Kwon et al. (2014) developed an inverse model based on a global database of water column 228Ra measurements to derive the shelf 228Ra flux necessary to balance the upper ocean 228Ra inventory. Their 2° x 2°-resolution model results suggested that the sources of 228Ra to the South Pacific Ocean are relatively equally distributed between SGD, rivers, and sediments with an average combined 228Ra flux from the Peruvian Shelf (F-Ra

The eastern tropical Pacific is characterized by a shallow and strong permanent pycnocline that limits ventilation of subsurface waters resulting in very low subsurface oxygen concentrations (Fiedler and Talley, 2006). As a consequence, penetration of the 228Ra signal to intermediate waters is less than typically observed in other ocean basins (e.g. Charette et al., 2015). Seasonal variation in the pycnocline depth is quite small (± 10 m; Fiedler and Talley, 2006). However, because of the shallowness of the pycnocline, even such small variations in depth can impact 228Ra activities over the shelf.

The 228Ra activities decreased from the surface with increasing depth and were generally < 0.1 dpm 100 L−1 in the mid water column with the exception of stations close to the Peruvian margin, where significant 228Ra activities were observed between ~1000–2500 m up to 600 km from the slope (station 1; Fig. 7). Since the 228Ra activities decreased to near background values at 200 m, this mid water 228Ra must be derived from slope sediment input and horizontal transport along isopycnal surfaces (Sarmiento et al., 1982).

A relatively high 228Ra activity (0.127 ± 0.032 dpm 100 L−1) was measured at station 9, 1000 m, which can only be explained by recent contact with sediments (Bowman et al., 2016) found a similar anomaly for total mercury concentrations (HgT) at this station that extended down to 2000 m. Hawco et al., 2016 also reported high concentrations of dissolved and labile Co at station 9, likely due to a shelf source; however, this Co anomaly is located at shallower depths (100–200 m). The Peru upwelling system is well known for generating numerous eddies that are typically formed near the coast and move westward with temperature and salinity anomalies down to 800 m (Pegliasco et al., 2015); one of these may have transported shelf water and have generated the Co anomaly. Highly energetic mesoscale eddies that can extend vertically down to 2000 m have also been identified in the eastern Pacific (Chaigneau and Pizarro, 2005), which could potentially explain this deep 228Ra anomaly at station 9. However, no specific vertical features in temperature, salinity or nutrients have been identified at this station to confirm the presence of an eddy.
Given our assumptions that horizontal advection and vertical mixing are negligible, and that radium behaves conservatively, the only sinks would be horizontal diffusion and radioactive decay. The distribution of $^{228}\text{Ra}$ with distance from the slope can then be described as:

$$\frac{dc}{dt} = K_h \frac{\partial^2 c}{\partial x^2} - \lambda c$$  \hspace{1cm} (1)

where $C$ is the excess $^{228}\text{Ra}$ concentration (atoms m$^{-3}$), $t$ is time, $K_h$ is the horizontal eddy diffusion coefficient (m$^2$ s$^{-1}$), and $x$ is the zonal distance from the slope (Moore, 2000). While shelf inputs of $^{228}\text{Ra}$ may display seasonal variability due to variations in upwelling intensity or river inputs, the source of radium from the slope is probably relatively constant. This allows us to assume steady-state for Eq. (1) below 1 km, which is less likely at the surface considering the timescale over which $^{228}\text{Ra}$ integrates (Moore, 2015). Applying a boundary condition where $C$ decreases to zero as $x$ approaches infinity, Eq. (1) can be rearranged as follows:

$$C(x) = C_0 e^{-ax}, \text{ where } a = \sqrt{\lambda / K_h}$$  \hspace{1cm} (2)

Given the boundary condition noted above, $^{228}\text{Ra}$ must be corrected for the mid water column background concentration, which we determined from the average of the $^{228}\text{Ra}$ activities between 1000 m and 3000 m across 94°W to 110°W (stations 11–17; $n = 13$; $0.048 \pm 0.009$ dpm 100 L$^{-1}$ or $2.1 \pm 0.39 \times 10^6$ atoms m$^{-3}$). This background value is not an analytical blank; rather it is likely to reflect the average mid-water $^{228}\text{Ra}$ activity due to diapycnal mixing from the surface and deep ocean maxima or possibly from horizontal transport from distant, isolated topographic highs (not from in situ production from its parent $^{232}\text{Th}$, which contributes < 1% of the $^{228}\text{Ra}$ value used here; $-2.4 \times 10^{-4}$ dpm 100 L$^{-1}$ Lopez et al., 2015). The $^{228}\text{Ra}$ activities thus corrected for background activities are denoted as excess $^{228}\text{Ra}$ ($^{228}\text{Ra}_{\text{ex}}$).

Assuming that the exponential decrease of $^{228}\text{Ra}_{\text{ex}}$ concentrations between 1000 m and 2500 m with increasing distance from the margin is dominated by horizontal eddy diffusion, we use Eq. (2) to derive a mean $K_h$ of 46 m$^2$ s$^{-1}$ for this depth range (Fig. 8). Estimates of $K_h$ at specific depths 1200 m, 1800 m, and 2400 m were 94 m$^2$ s$^{-1}$, 24 m$^2$ s$^{-1}$, and 49 m$^2$ s$^{-1}$, respectively. The similar magnitude of $K_h$ estimates suggest a low spatial variability in mixing over the studied depth range. The $K_h$ calculated is two orders of magnitude lower than the $^{228}\text{Ra}$-based $K_h$ of Sarmiento et al. (1982) estimated for the abyssal
North Atlantic Basin, although mixing in their study area should be more vigorous than along the Peru slope, with a significant impact on horizontal eddy strength. Furthermore, the basin-wide scale of their study is significantly larger than our margin region, which fits the known trend of increasing $K_s$ with increasing mixing length scale (Okubo, 1971). A recent ocean-wide compilation of $K_s$ at scales of 300 km (Cole et al., 2015) based on salinity variations on isopycnals observed with Argo floats, reports regional values at 12°S in the 1–2 km depth range that are less than an order of magnitude greater than those calculated here. Regardless, the simultaneous observation of the TEI concentration field and the tracer-derived diffusivity should offer a more robust interpretation of the TEI fluxes to be calculated in subsequent sections.

The Peru-Chile upwelling system is well-known for generating numerous eddies. However, the mesoscale eddies generated by the eastern boundary upwelling system in the Peru-Chile area are limited to the first 600 m of the water column (e.g. Pegliasco et al., 2015). The influence of mesoscale surface and subsurface eddies is thus very limited in the depth range of 1000–2500 m. Some horizontal jets have been identified at 1000 m and 1500 m in the Tropical Pacific Ocean but they are likely stronger on the western side of the basin and tend to disappear as they approach the South American coast (Cravatte et al., 2012). We think an advection-dominated system is less likely than a diffusion-dominated system due to the linear gradient in dissolved Mn, which will be discussed later. In shallower waters, between 300 and 1000 m, it may be that the offshore diffusive transport of $^{228}$Ra is suppressed by an onshore component of advection, explaining the absence of an excess in these depths. However, this is speculative; the required velocities would be difficult to detect by direct measurement or geostrophy. Finally, and perhaps most importantly, the mixing rate calculated above is an important component of advection, explaining the absence of an excess in these depths. This speculation may reflect a combination of three factors. First, the upwelling of isopycnals above this horizon suggests that a component of onshore flow must be present, limiting offshore transport of Ra. Second, at each station, horizons below 500 m were closer to the shelf than the horizons sampled above. Third, the compilation of Cole et al. (2015) suggests that horizontal eddy diffusivity should decrease with depth, perhaps causing the modest benthic input in the 100–500 m depth range to be so diluted by rapid transport that the concentration approaches detection limits.

\[ F_{R-slope} = \lambda \sin \theta \]

where $I$ is the inventory of $^{228}$Ra$_{shelf}$ over the depth range of interest and $\theta$ is the inclination of the slope (2.06°). The inventory of $^{228}$Ra between 1000 m and 2500 m is equal to the area under the curve in a plot of $^{228}$Ra concentration against distance from the slope (Fig. 8); in practice, it is estimated by taking the integral of Eq. (2), where $C_{0}/a = I (8.9 \times 10^{11} \text{ atoms m}^{-2})$. Substituting $I$ into Eq. (3) gives a $F_{R-slope}$ of $1.0\times 10^{-2} \text{ m}^{-1} (3.8 \times 10^{6} \text{ atoms m}^{-2} \text{ y}^{-1})$, which is comparable to $^{228}$Ra slope fluxes estimated by Hammond et al. (1990) for the San Nicolas (335 atoms m$^{-2}$ s$^{-1}$,oxic conditions) and San Pedro (166 atoms m$^{-2}$ s$^{-1}$, anoxic conditions) Basins located offshore from Southern California (USA).

The same approach could be used to estimate the $F_{R-shelf}$ since the offshore $^{228}$Ra inventory must be supplied by coastal inputs and transport via diffusion and advection. The weighted $^{228}$Ra activities were estimated from stations 5 through 17 for all samples above the 26 kg m$^{-3}$ isopycnal and were plotted as a function of the distance from the shelf (Fig. 9). The $^{228}$Ra inventory is estimated at $6.8 \times 10^{12}$ atoms m$^{-2}$. Considering an inclination of the shelf of 0.38° and using the Eq. (3), the $F_{R-shelf}$ is $0.6 \times 10^{10}$ atoms m$^{-2} \text{ y}^{-1}$, within a factor of three of the Kwon et al. (2014) estimate. While there is some concern about the validity of the assumptions used in deriving the 1D diffusion-decay model for the upper ocean, the relatively good agreement with the global-scale model of Kwon et al. (2014) suggests these assumptions may be reasonable. Nonetheless, the $F_{R-shelf}$ from Kwon et al. (2014) inverse model will be considered in the rest of the manuscript since this approach may incorporate $^{228}$Ra sources from beyond the Peruvian shelf while the global model does not, and it takes into account the global ocean circulation and seasonal variability in shelf inputs.

The per unit area $F_{R-slope}$ is about 25% of the shelf flux; the lower slope rate may reflect differences in the composition of sediments and/or the processes transporting radium from pore fluids to overlying waters. In terms of total $^{228}$Ra inputs, the ocean flux from the margin is dominated by the shelf input, in part because of the higher flux per unit area, but also because the shelf area is much greater than the area of the upper slope. This difference alone would cause the rapid decrease in $^{228}$Ra with depth seen in the profiles below 100 m. The subsequent rise in $^{228}$Ra activities below 500 m is less easily explained, though we argue that this pattern may reflect a combination of three factors. First, the upwardly tilting isopycnals above this horizon suggest that a component of onshore flow must be present, limiting offshore transport of Ra. Second, at each station, horizons below 500 m were closer to the margin than the horizons sampled above. Third, the compilation of Cole et al. (2015) suggests that horizontal eddy diffusivity should decrease with depth, perhaps causing the modest benthic input in the 100–500 m depth range to be so diluted by rapid transport that the concentration approaches detection limits.

3.3. TEI distributions relative to $^{228}$Ra in the upper water column

Ocean dissolved TEI concentrations are controlled by a balance between their sources (e.g. sediments, hydrothermal vents, rivers, SGD, aeolian depositions) and sinks (e.g. biological uptake, precipitation, scavenging; Bruland and Lohan, 2003). The TEI distribution depends on the rates of each process including mixing and transport (Noble et al., 2012). Among the TEIs, dissolved manganese (DMn), cobalt (DCo), and iron (DFe) are important micronutrients that are redox active and present in seawater at extremely low concentrations (nM-pM) due to scavenging and low solubility (McManus et al., 2012; Saito et al., 2004). Each is affected by internal biogeochemical cycling processes occurring at different rates. For instance, DFe is rapidly scavenged from the upper ocean (Landing and Bruland, 1987), while scavenging removal of DCo is relatively slow (Noble et al., 2012). In addition, biological processes play an essential role in the geochemical cycling of Co (Sunda and Huntsman, 1995b), Fe (Sunda and Huntsman, 1995a), and Mn (Sunda et al., 1983), with dissolved Fe exhibiting the most nutrient like behavior (Johnson et al., 1997). Manganese, Co, and Fe are co-factors in enzymes and structural elements in proteins. As a consequence, their extremely low concentrations in seawater may actively control the rate of the photosynthesis (Morel and Price, 2003). Due to biological uptake, DFe and DCo are depleted at the surface. In contrast, DMn concentrations are maximum at the surface because of the photochemical reduction of Mn oxides to soluble Mn (Sunda and Huntsman, 1988).

The $^{228}$Ra plume in the upper 200 m extends from the Peru margin to the open ocean (Fig. 6) and provides evidence of recent contact of shelf waters with sediments. Most of these upper ocean waters contained high concentrations of dissolved oxygen; thus, this shelf plume is situated above the Peru OMZ (Fig. 10a). Similarly, the highest DMn

![Fig. 9. Distribution of weighted average of $^{228}$Ra (stations 1, 5–17) between the surface and the 26 kg m$^{-3}$ isopycnal as a function of the distance from the shelf.](image-url)
concentrations were measured within the shelf plume, suggesting a common source with $^{228}$Ra. Note that a secondary DMn maximum was observed below the shelf plume along the oxycline near 95°W (Fig. 10b), which likely results from remineralization of organic matter rather than reduction of manganese oxides (Vedamati et al., 2015).

Dissolved Co and DFe displayed very different patterns compared with DMn. Whereas relatively high DCo concentrations were measured in the shelf plume, a broad DCo maximum was found in subsurface waters (Fig. 10c) suggesting an intense water column remineralization source (Hawco et al., 2016). In general, DFe concentrations were low within the shelf plume, though high DFe concentrations were found in the near bottom samples (Fig. 10d). A rapid decrease of DFe concentrations across the Peruvian shelf was previously reported by Bruland et al. (2005). They showed that shelf-derived DFe was not transported beyond 81°W (~300 km from the coast), which is in agreement with the highly particle-reactive behavior of Fe (Landing and Bruland, 1987; Boyd and Ellwood, 2010). Vedamati et al. (2014) also reported an abrupt decrease in DFe and Fe(II) along three different transects across the Peruvian shelf break, and suggested oxidative scavenging was the main removal process, which is consistent with the more rapid westward decrease in DFe in the oxygenated surface waters along GP16, compared with DCo and DMn (Hawco et al., 2016; Heller et al., 2017). Nitrate-mediated Fe(II) oxidation might also contribute to the rapid decrease in Fe across the margin-ocean boundary in the Peruvian anoxic region (Scholz et al., 2016). In addition, Moffett (1997) demonstrated that the upper water column of the equatorial Pacific was characterized by slow Mn oxidation rates, which resulted in a relatively long residence time for Mn in surface waters, thereby facilitating long-range transport to the open ocean. Taken together, these observations indicate that the shelf sediments were a source of Fe but, in contrast to Mn, scavenging prevented its off shelf transport.

Because the Peru shelf waters are enriched in DMn, DCo and DFe as well as in $^{228}$Ra (Fig. 10), we propose the use of $^{228}$Ra as a tool to estimate the shelf to ocean fluxes of these key TEIs following Charette et al. (2016). Eddy-driven filaments may play a role in the extension of the shelf derived plume that extends towards the open ocean. However, the lateral extension of these features seems to be limited. Thomsen et al. (2016) observed filaments up to 79°W off Peru. Our high $^{228}$Ra concentrations in surface waters extend up to ~110°W. As a result, even though the eddy-driven filaments may play a role, this mechanism is likely minor relative to horizontal diffusion and general circulation. The general ocean circulation in the eastern South Pacific, also called the Humboldt Current System or the Peru-Chile Current System, is dominated by several currents flowing parallel to the coast: (1) the Peru Oceanic Current (POC) and the Peru Coastal Current (PCC) contribute to the South Equatorial Current (SEC) flowing equatorward at the surface following the coast before turning offshore at around 15°S, and (2) the subsurface Peru-Chile Undercurrent (PCUC), which flows southward near the shelf (Penven et al., 2005). Thus, assuming that the net shelf-ocean exchange over the 8000 km length-scale of our study is primarily driven by eddy diffusion, which we think it is satisfied due to the Meridional average circulation at 12°S (Penven et al., 2005), the shelf TEI flux can be estimated as follows:

$$F_{\text{TEI,shelf}} = F_{\text{Ra,shelf}} \times \text{TEI/}^{228}\text{Ra}$$

where $F_{\text{Ra,shelf}}$ is the total flux of $^{228}$Ra from all coastal sources in the first 200 m derived from a global inverse model as discussed above (Kwon et al., 2014) and TEI/$^{228}$Ra corresponds to the slope of the best fit relationship between the dissolved TEI concentrations and $^{228}$Ra observed in surface waters (Fig. 11). This approach allows us to estimate the flux of the dissolved TEI across the shelf-open ocean boundary, but may not equal the sum of all shelf inputs due to water column shelf processes such as biological uptake and scavenging removal of TEIs. The TEI/$^{228}$Ra gradients along the offshore transect integrate the seasonal variability on the shelf. This method can be applied to all TEIs, from highly particle reactive to non-particle reactive TEIs, assuming that the main sources of TEI and $^{228}$Ra are over the shelf. However, it is important to highlight that the calculated TEI flux represents the net dissolved shelf inputs, which do not necessarily reach the ocean interior due to varying degrees of TEI particle reactivity and biological cycling (Charette et al., 2016). In order to investigate the dissolved TEI/$^{228}$Ra relationships within the shelf plume, we focused on samples located between the surface and the 26 kg m$^{-3}$ isopycnal, where the highest $^{228}$Ra activities were observed (Fig. 6). Shelf data are shown individually, while at the offshore stations we reported the weighted average concentration of samples from depths above the 26 kg m$^{-3}$ density surface. The weighted average $^{228}$Ra concentration decreases from station 5 to station 17. Note that station 9 displays a high $^{228}$Ra, as well as DMn, DCo, and DFe concentrations relative to the surrounding stations, which could potentially be related to the presence of an eddy as discussed in Section 3.2.

The upper water column DMn and $^{228}$Ra fell along two linear trend lines, each with relatively high r$^2$ values (Fig. 11a). The shelf data had a slope of $6.0 \times 10^{-5}$ nmol atom$^{-1}$ ($r^2 = 0.73$) with a DMn intercept of 1.4 nM. The offshore samples also followed a straight line with a DMn/$^{228}$Ra slope of $2.17 \times 10^{-5}$ nmol atom$^{-1}$ ($r^2 = 0.70$) and an intercept close to zero. The former is the expected mixing relationship for shelf and upwelled water. The linearity is consistent with conservative mixing between nearshore and offshore waters, on timescales that are short compared to the 6-year half-life of $^{228}$Ra. It is possible that offshore data reflect the long term average shelf DMn and $^{228}$Ra.

---

Fig. 10. Distribution of oxygen (a), dissolved Mn (b), dissolved Co (c), and dissolved Fe (d) in the upper water column (> 500 m). The isocontours represent the distribution of $^{228}$Ra activities.
samples also followed a linear trend with $^{228}\text{Ra}$ (slope $\text{DCo}/^{228}\text{Ra} = 6.94 \times 10^{-6} \text{nmol atom}^{-1}$; $r^2 = 0.89$; Fig. 11b). However, only two samples collected over the shelf fell along this mixing curve, including the station 3 sample that displayed the highest $^{228}\text{Ra}$. Dissolved Co concentrations on the shelf relative to $^{228}\text{Ra}$ were higher than offshore, such that upwelling of high DCo/low $^{228}\text{Ra}$ waters could account for this pattern (Hawco et al., 2016). However, contrary to DMn, no specific trend was observed between DCo and $^{228}\text{Ra}$ on the shelf, suggesting that DCo has different sources and/or sinks than $^{228}\text{Ra}$. Biological uptake, export, and/or remineralization of Co, as suggested by the linear correlation between DCo and dissolved phosphate along GP16 (Hawco et al., 2016), may also account for decoupling DCo and $^{228}\text{Ra}$ over the shelf. The conservative mixing line for the offshore data suggests no significant Co inputs with relatively slow scavenging removal of during offshore transport (Noble et al., 2012).

The 13 m sample from station 3 is the only one that displays both higher Fe and $^{228}\text{Ra}$ concentrations relative to offshore samples. Further, no specific trend was observed between DFe and $^{228}\text{Ra}$ over the shelf. Although Fe concentrations were highly variable over the shelf, the consistently higher shelf DFe concentrations suggest that there must be a positive shelf-ocean exchange of DFe. The variability likely reflects the wide range of DFe sources combined with a short transport length scale due to its affinity for particles. We therefore use the station 3 sample as an upper limit anchor for computing the DFe/$^{228}\text{Ra}$ trend relative to DCo and DMn, suggesting that only a small fraction of the dissolved iron released from the shelf sediments is transported offshore, most likely due to scavenging processes.

### 3.4. Shelf TEI fluxes

The correlation between DMn and $^{228}\text{Ra}$ over the GP16 transect to 109°W (station 17) suggests that Mn was transported over significant length scales into the open ocean (Fig. 11a). From Eq. (4) and the DMn/$^{228}\text{Ra}$ slope observed in offshore waters, we derived a F-Mn$_{\text{shelf}}$ of 3300 $\mu$mol m$^{-2}$ y$^{-1}$ (Table 1). This F-Mn$_{\text{shelf}}$ is one order of magnitude higher than the Mn flux from the Western North Atlantic shelf (220 $\mu$mol m$^{-2}$ y$^{-1}$; Charette et al., 2016), but within the range of estimates of other shelf sedimentary Mn fluxes (140 $\mu$mol m$^{-2}$ y$^{-1}$; Landing and Bruland, 1987; 2900 ± 1800 $\mu$mol m$^{-2}$ y$^{-1}$, McManus et al., 2012). Scholz et al. (2011) estimated a benthic Mn flux of 400 $\mu$mol m$^{-2}$ y$^{-1}$ at 85 m on the Peru continental shelf for the same season as the GP16 transect (Nov–Dec 2008). The higher estimates reported here could be explained by spatial/temporal variability or the presence of other important shelf sources of Mn, such as river inputs and submarine groundwater discharge that are not accounted for in other estimates (e.g. Scholz et al., 2011).

### Table 1

<table>
<thead>
<tr>
<th>TEI/$^{228}\text{Ra}$ gradient</th>
<th>F-TEI$_{\text{shelf}}$</th>
<th>F-TEI$_{\text{shelf}}$</th>
<th>F-TEI$_{\text{out}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>$2.2 \times 10^{-4}$</td>
<td>3300</td>
<td>$3.6 \times 10^4$</td>
</tr>
<tr>
<td>Co</td>
<td>$6.9 \times 10^{-6}$</td>
<td>100</td>
<td>$1.1 \times 10^7$</td>
</tr>
<tr>
<td>Fe</td>
<td>$0.99 \times 10^{-4}$</td>
<td>1500</td>
<td>$1.6 \times 10^8$</td>
</tr>
</tbody>
</table>

* A continental shelf area of $1.1 \times 10^{11}$ m$^2$ is considered for the grid 0–20°S 70–90°W between 0–200 m depth (estimated from ETOP01 1-minute gridded elevation data).
* Dissolved aerosol flux to the South Pacific Ocean.
* F-Mn$_{\text{shelf}}$ is based on an abundance in the upper crust of $1.09 \times 10^{-8}$ mol g$^{-1}$ (Taylor and McLennan, 1985) and a 30% fractional solubility in dust (van Hulten et al., 2016).
* F-Co$_{\text{shelf}}$ is based on an abundance in the upper crust of $2.86 \times 10^{-8}$ mol g$^{-1}$ (McManus, 2001) and a 10% fractional solubility in dust (Shelley et al., 2012).
* F-Fe$_{\text{shelf}}$ is based on an abundance in the upper crust of $6.3 \times 10^{-8}$ mol g$^{-1}$ (Taylor and McLennan, 1985) and a 2% fractional solubility in dust (Jickells and Spokes, 2001).
The F-Co\textsubscript{shelf} determined using the same method was estimated at 100 \(\mu\)mol m\(^{-2}\) y\(^{-1}\), which is about twice as high as the broad Western North Atlantic margin input (Charette et al., 2016). Similar to Mn, DCo was transported well beyond the shelf into the open ocean (Fig. 11b). The high F-Co\textsubscript{shelf} is not particularly surprising given the presence of the OMZ, which serves to enhance the coastal DCo flux (Hawco et al., 2016). Assuming that most of the lithogenic sediments from the Peruvian shelf originate from rivers (Scheiderge and Krissek, 1982), Hawco et al. (2016) combined the particulate riverine flux with the difference between the crustal and buried sediment Co/Al ratios on the Peruvian margin (Böning et al., 2004) to calculate a total coastal DCo flux from the South American shelf of 110–200 \(\mu\)mol m\(^{-2}\) y\(^{-1}\).

We estimated the F-Fe\textsubscript{shelf} from the Peruvian shelf to be 1500 \(\mu\)mol m\(^{-2}\) y\(^{-1}\) (Table 1). However, we acknowledge that the uncertainty on this F-Fe\textsubscript{shelf} estimate is much higher than that for Mn and Co because of the single high DFe (and \(^{228}\)Ra) value over the shelf, which drives the DFe/\(^{228}\)Ra trend. Much higher Fe(II)\(^{+}\) fluxes have been previously reported for the OMZ of the Peruvian shelf (80–800 m); benthic chamber fluxes were up to 316 \(\times\) 10\(^{5}\) \(\mu\)mol m\(^{-2}\) y\(^{-1}\), while pore water diffusion models yielded values of 88.3 \(\times\) 10\(^{6}\) \(\mu\)mol m\(^{-2}\) y\(^{-1}\) (Noffke et al., 2012; Scholz et al., 2011). We note that the benthic diffusive Mn flux estimated by Scholz et al. (2011) was closer to our F-Mn\textsubscript{shelf} whereas their benthic diffusive Fe flux was much greater than our F-Fe\textsubscript{shelf} estimate, which is probably due to the fact that Mn(II) oxidizes more slowly than Fe(II) (Stumm and Morgan, 1996), and that a large fraction of DFe is oxidized near the sediment-water interface. Noffke et al. (2012) showed that the Fe flux was the greatest on the shelf at 85 m, moderate between 250 and 600 m, and negligible below this depth. Since the radium enrichment was the greatest on the shelf at 85 m, moderate between 250 and 600 m, and negligible below this depth. Since the radium enrichment was the greatest on the shelf at 85 m, moderate between 250 and 600 m, and negligible below this depth. Since the radium enrichment was the greatest on the shelf at 85 m, moderate between 250 and 600 m, and negligible below this depth. Since the radium enrichment was the greatest on the shelf at 85 m, moderate between 250 and 600 m, and negligible below this depth.

The total dust deposition to the oceans was estimated at 450 Tg y\(^{-1}\), which was limited in the upper ~200 m of the water column (depending on the 26 kg m\(^{-3}\) isopycnal depth; Fig. 6), there was no strong evidence of sedimentary Fe inputs between 200 m and 600 m during GP16. However, these other studies do not take into account water column removal processes, thus they are likely not representative of the actual input of shelf material from the shelf reaching the open ocean. When removal processes were taken into account, shelf-ocean Fe fluxes range from 160 \(\mu\)mol m\(^{-2}\) y\(^{-1}\) in the Western North Atlantic shelves (Charette et al., 2016) to 660 \(\mu\)mol m\(^{-2}\) y\(^{-1}\) near the Antarctic Peninsula shelf (Dulaiova et al., 2009) to 1570 \(\mu\)mol m\(^{-2}\) y\(^{-1}\) from the Crozet Island shelves (Charette et al., 2007). The F-Fe\textsubscript{shelf} estimated for our GP16 study region remains in the upper range of published shelf Fe flux estimates.

Because of the very specific features of the Peru coastal region such as the strong coastal upwelling, OMZ, and narrow shelf, the estimates of F-TEI\textsubscript{shelf} fluxes derived from this study may not be representative of F-TEI\textsubscript{shelf} fluxes from other continental margins. We thus decided to limit extrapolation of our F-TEI\textsubscript{shelf} flux estimates to the eastern subtropical South Pacific Ocean. Assuming a shelf area of 1.1 \(\times\) 10\(^{11}\) m\(^{2}\) between 0–20°S and 70–90°W (estimated from ETOPO1 1-minute gridded elevation data), we calculate a F-Mn\textsubscript{shelf} of 3.6 \(\times\) 10\(^{5}\) mol y\(^{-1}\), a F-Co\textsubscript{shelf} of 1.1 \(\times\) 10\(^{7}\) mol y\(^{-1}\), and a F-Fe\textsubscript{shelf} of 1.6 \(\times\) 10\(^{6}\) mol y\(^{-1}\) (Table 1). The total dust deposition to the ocean was estimated at 450 Tg y\(^{-1}\); 6% of this is deposited over the South Pacific Ocean, or 2.7 \(\times\) 10\(^{13}\) g y\(^{-1}\) (Jickells et al., 2005). The TEI fluxes from aerosol deposition (F-TEI\textsubscript{dust}) to the South Pacific Ocean is then estimated considering the abundance in the upper continental crust and the fractional solubility in dust of each element (Table 1). This results in a F-Mn\textsubscript{dust} of 8.8 \(\times\) 10\(^{6}\) mol y\(^{-1}\), F-Co\textsubscript{dust} of 7.7 \(\times\) 10\(^{7}\) mol y\(^{-1}\), and a F-Fe\textsubscript{dust} of 3.4 \(\times\) 10\(^{8}\) mol y\(^{-1}\). The input of Fe from the eastern South Pacific continental shelf between 0–20°S is thus about the same order of magnitude as the aerosol deposition over the entire South Pacific basin.

Furthermore, the inputs of Co and Mn from aerosol deposition represent only ~7% and ~24% of the fluxes from the eastern South Pacific continental shelf, respectively.

The shelf TEI flux gauge approach (Eq. (4)) relies on a model-based estimate of the shelf \(^{228}\)Ra input from the Peruvian margin, which was in good agreement with a simple box model-derived flux that drew on historical and new data presented herein. These estimates represent long-term averages, and are supported by recent work that has shown that terrestrial and shelf inputs of \(^{228}\)Ra to the upper Atlantic Ocean are at steady-state (Charette et al., 2015). On the other hand, the data collected during GP16 represent a ‘snapshot’ of shelf TEI and \(^{228}\)Ra distribution, and we know from limited historical data that \(^{228}\)Ra may vary seasonally over the shelf (Fig. 5). Differences in TEI concentrations in the Peruvian coastal upwelling region have also been highlighted between GP16 and previous studies at 5–10°S, which reported lower concentrations of DCo (Hawco et al., 2016; Saito et al., 2004) and DFe (Bruland et al., 2005; Resing et al., 2015). In addition to variability in terrestrial runoff, the Peruvian coastal upwelling is strongly seasonal, due in part to wind stress variations, with the strongest winds leading to the greatest thermocline depth amplitude in June and the lowest magnitude winds in January (Kessler, 2006). Spatial and temporal variations as a result of the mesoscale dynamics may also impact the TEI fluxes (Penven et al., 2005). Dissolved oxygen fluctuations due to ENSO have also been shown to play an important role on deposition and mobilization of Mn and Fe (Scholz et al., 2011). In addition, Scholz et al. (2014) discussed the relationship between oxygen concentration in both the water column and bottom water, and the export of Fe from the continental shelf over the past 140,000 years, and suggested that future deoxygenation of the Peru upwelling waters may lead to a decrease in Fe availability. However, these authors acknowledged that other upwelling areas associated with a less intense OMZ, such as the southeast Atlantic, may respond differently to deoxygenation. Hence, our application here of TEI\(^{228}\)Ra relationships based on GP16 data alone may not be representative of long-term averages, which introduces uncertainty with to the shelf flux estimates presented above. Additional process studies would be required to fully assess the seasonal variability in the TEI\(^{228}\)Ra relationship for the Peruvian shelf.

3.5 Slope TEI fluxes

Continental slopes receive substantial quantities of particulate material from the upper ocean as well as gravity-driven sediment flows from the shelf (e.g. Lamipp et al., 1995; Walsh and Nittouer, 1999). However, material inputs to the open ocean from slope sediments remain poorly constrained. Lam and Bishop (2008) reported substantial lateral advective inputs of labile particulate Fe and Mn from the upper continental slope to the high-nutrient low-chlorophyll (HNLC) North Pacific Ocean. Elevated Mn concentrations near the Mauritanian coast were well correlated with \(^{228}\)Ra, indicative of recent contact with shelf/slope sediments (Hatta et al., 2015). The breaking and dissipation of internal waves along the continental slope may generate sediment resuspension and maintain a mid-water nepheloid layer (Caccione and Drake, 1986). When internal waves break over a very steep slope, such as the Peruvian continental slope, the internal waves are very energetic and the energy is concentrated within a narrow band, causing intense sediment resuspension (Caccione and Wunsch, 1974). High concentrations of particulate aluminum (Al), titanium (Ti), Fe, and Mn were observed near the seafloor at station 5 located over the slope during GP16 (Lee et al. in this issue). The high dissolved TEI and \(^{228}\)Ra concentrations in the plume attached to the Peruvian continental slope might then be derived from reducing slope sediments. Strong zonal currents were observed in the Tropical Pacific Ocean at 1000 and 1500 m, however, they disappear east of 110°W (Cavanaugh et al., 2012), which suggests that the dissolved TEIs and \(^{228}\)Ra were likely transported away from the slope via turbulent diffusion rather than advection. Once released into the water column, dissolved TEIs, including radium, may then be transported along isopycnals towards the open ocean (Sarmiento and Rooth, 1980; Sarmiento et al., 1982). As a consequence, additional remineralization or dissolution of sinking particles, lateral transport of materials from the continental slope into the deep ocean should be considered in global TEI budgets. In addition,
vertical mixing and upwelling may deliver essential micronutrients from the continental margins to surface waters where they can sustain primary productivity (Lam and Bishop, 2008).

Along GP16, there was a broad mid-depth (~1000–2500 m) enrichment in DMn near the Peruvian margin, which matched the surface distribution of $^{228}$Ra (Fig. 7), suggesting a significant input of DMn from continental slope sediments. Dissolved Mn decreased monotonically from the Peru margin to 1800 km offshore, a pattern that suggests conservative mixing in the absence of a DMn inputs from sinking particle remineralization or dissolution along the GP16 transect (Fig. 12a). In contrast, DCo was relatively constant and homogeneous over this depth range (Fig. 12b). Thus, the input of DCo from the continental slope to intermediate and deep waters appears to be relatively minor, at least compared to water column sources and sinks. At the station closest to the Peru margin, high $^{228}$Ra activities below 1000 m were positively correlated with DFe concentrations, suggesting that the Fe distribution is influenced by slope sediment inputs (Fig. 12c). However, there was a sharp decrease in DFe between the margin and 100 km offshore (station 1), which indicates limited offshore transport due to rapid scavenging processes. However, there was still a discernible lateral gradient in mid water column DFe concentrations from 150–1800 km offshore that might be explained by a net lateral input of Fe from the slope sediments (Fig. 12c). This mid-depth Fe enrichment is also associated with a low $^{86}$Fe signature persistent over ~4000 km offshore (John et al., in this issue). This unexpected deep Fe feature led John et al., (in this issue) to employ a numerical model to try and reproduce the high DFe and low $^{86}$Fe plumes. They concluded that the DFe was the result of Fe released from the upper slope (100–1000 m) followed by scavenging onto sinking particles and remineralization deeper in the water column. However, the authors acknowledged that they could not rule out a slope sediment DFe source in a form more resistant to scavenging.

**Table 2**

| Sedimentary dissolved Manganese (Mn), dissolved Cobalt (Co) and dissolved Iron (Fe) fluxes from the Peruvian continental slope. |
|-----------------|-----------------|-----------------|
|                  | TEI gradient (nmol m$^{-2}$ m$^{-1}$) | F-TEI$_{slope}$ (μmol m$^{-2}$ y$^{-1}$) | $^{228}$F-TEI$_{slope}$ (μmol m$^{-2}$ y$^{-1}$) |
| Mn               | $1.3 \times 10^{-4}$ | 6.4             | $1.3 \times 10^{4}$ |
| Co               | $1.2 \times 10^{-2}$ | -              | -          |
| Fe$_{1}$ (0–100 km) | $4.7 \times 10^{-4}$ | 590            | $1.3 \times 10^{4}$ |
| Fe$_{2}$ (150–1800 km) | $4.7 \times 10^{-4}$ | 24             | $5.4 \times 10^{5}$ |

$^{A}$ A continental slope area of $2.2 \times 10^{11}$ m$^2$ is considered for the grid 0°–20°S 70–90°W between 1000–2500 m depth (estimated from ETOPO1 1-minute gridded elevation data).

The TEI fluxes (F-TEI$_{slope}$) from the Peruvian slope sediments can be derived from the horizontal TEI gradients ($d$TEI/$dx$; Fig. 12), the coefficient of eddy diffusivity ($K_θ$), and the inclination of the slope (θ) as follows:

$$F_{TEI_{slope}} = K_θ \sin θ \cdot dTEI/dx \quad (5)$$

This model assumes a constant TEI and $^{228}$Ra source from the slope and thus that TEI gradients and $K_θ$ are at steady state, assumptions we believe are likely satisfied due to lack of seasonal forcing mechanisms in the deep ocean. We neglect any loss due to vertical mixing, and assume no advection orthogonal to the margin.

There was no significant lateral gradient in DCo, hence the slope sediment DCo flux is negligible relative to other processes supplying DCo to the mid water column (Fig. 12b). The product of the D Mn gradients with the $^{228}$Ra-derived $K_θ$ resulted in a F-Mn$_{slope}$ of 6.4 μmol m$^{-2}$ y$^{-1}$, which represents ~0.2% of F-Mn$_{shelf}$. Fe fluxes can be estimated for within 100 km of the slope (F$_1$-Fe$_{slope}$ of 590 μmol m$^{-2}$ y$^{-1}$; between the slope and station 1) and further afield (F$_2$-Fe$_{slope}$ of 24 μmol m$^{-2}$ y$^{-1}$; stations 1–11; Table 2). The F$_2$-Fe$_{slope}$ (50–1800 km away from the slope) is likely to be more representative of the net Fe input to the interior Pacific Ocean basin; this flux is ~4.2% of F$_1$-Fe$_{slope}$ and 1.7% of F-Mn$_{shelf}$.

Once released into the deep ocean, ligands may stabilize dissolved Fe through complexation, thereby limiting its removal from the water column via oxidation or scavenging removal by sinking particles (Elrod et al., 2004). Complexation is also important for DMn (Madison et al., 2013). Higher organic ligand concentrations were generally observed along GP16 compared to the Atlantic Ocean; in particular, a plume of higher TEI$_{shelf}$ input at the continental margin and the presence of an intense OMZ over the upper slope and shelf area between 0°–90°W (estimated from ETOPO1 1-minute gridded elevation data).

The unique combination of the steepness of the Peruvian continental slope and the presence of an intense OMZ over the upper slope may lead to distinct TEI fluxes that may not be representative on a global scale; therefore, we extrapolated the F-TEI$_{slope}$ estimates to the slope area between 0–20°S 70–90°W (estimated from ETOPO1 1-min gridded elevation data). For the depth range of 1000–2500 m, the slope area is 2.2 × 10$^{11}$ m$^2$, which produces a scaled F-Mn$_{slope}$ of 5.4 × 10$^{5}$ mol y$^{-1}$, and a F$_2$-Fe$_{slope}$ of 5.4 × 10$^6$ mol y$^{-1}$. When comparing to the total shelf TEI fluxes for the same grid, the F-Mn$_{slope}$ represents < 1% of the F-Mn$_{shelf}$, while the F$_2$-Fe$_{slope}$ is about the same order of magnitude as the F-Fe$_{shelf}$. The higher TEI fluxes released by continental shelves could be in part due to the decrease in grain size sediment across the Peru margin, although an unusual pattern was observed at 13'S with anomalous fine-grained sediments found in the upper-slope (< 1000 m water depth) due to local influences (Krissek et al., 1980). The greater permeability of large grain-sized sediment deposited on the continental shelf would thus favor a pore-water exchange mechanism (Huettel et al., 2014). Further, it is possible that bio-irrigation is more pronounced at shallower depths.
V. Sanial et al. Peruvian continental slope plays a greater role in the release of TEIs play a significant role in lateral transport over basin-scale distances where they may be maintained in the dissolved phase by ligands and as colloids, thus facilitating the open ocean.

4. Conclusions

Radium isotopes were used to identify major water masses (226Ra) and quantify shelf and slope TEI fluxes (228Ra) in the eastern Tropical South Pacific Ocean. The 226Ra distribution below 2000 m was characterized by an east-west asymmetry, with high 226Ra activities in the east versus low 226Ra activities in the west, largely the result of northward (AABW) and southward (PDW) flowing source waters, respectively. Elevated 228Ra activities were measured in the upper 200 m over the entire transect, a distance of 8500 km, as a result of sedimentary inputs from the continental shelf. A deep 228Ra plume was observed at ~1000–2500 m as far as 600 km away from the margin, evidence for the important yet underappreciated role of continental slopes as sedimentary TEI sources to the deep ocean. To our knowledge, this study is one of the few to provide direct estimates of TEI fluxes from the continental slope.

Shelf sediments were likely the main source of DMn to the upper ocean off Peru as demonstrated by the linear DMn/226Ra relationship observed both in shelf and offshore surface waters. A linear DCo/226Ra relationship was also observed in surface waters off Peru; however, no specific DCo/228Ra trend was seen in shelf waters, suggesting that Co has multiple sources/sinks over the shelf (other than sedimentary). A sharp DFe/228Ra gradient was observed near the margin suggesting a rapid removal of Fe. The DMn/226Ra ratio was relatively constant whereas the DCo/226Ra and DFe/228Ra relationships over the shelf were more complex and variable. This variability, including that shown by the historical 226Ra data, highlights the need to investigate the sensitivity of margin TEI fluxes due to changes in regional environmental conditions. The variable 226Ra may also reflect the passage of transient eddies with variable fractions of offshore, upwelled, and coastal components.

Radium-228 was used as a sedimentary flux gauge to estimate the ocean input of dissolved TEIs from the continental margin. We estimated that the Peru continental shelf releases 3300 µmol m⁻² y⁻¹ of DMn, 100 µmol m⁻² y⁻¹ of DCo, and 1500 µmol m⁻² y⁻¹ of DFe to the ocean off Peru. When extrapolated to the eastern South Pacific, the DFe released by the sediments from the continental margin appeared on par with the South Pacific aerosol DFe inputs, while the shelf sediment derived DMn and DCo fluxes were ~4 and ~14 times higher than the DMn and DCo aerosol inputs, respectively. Corresponding estimates of the DFe flux rates from the continental slope are of the same order of magnitude as the input of DFe released by the shelf. Conversely, the Peru continental slope was not a significant source of DCo and seemed to be only a minor source of DMn (<1% of the shelf DMn flux). Nonetheless, once released into deep waters, Mn and Fe may be maintained in the dissolved phase by ligands and as colloids, thus facilitating lateral transport over basin-scale distances where they may play a significant role in open ocean biogeochemical cycles.

Our study provides evidence that lateral transport of sediment-derived TEIs from continental margins, including shelves and slopes, play an important role in open ocean TEI budgets and biogeochemistry. The Peruvian continental slope plays a greater role in the release of TEIs than other continental slopes such as in the western North Atlantic (Charette et al., 2015), which could be the result of intense primary production seaward of the shelf break (Jahnke, 2010; Pennington et al., 2006). Our findings agree with recent work from Letscher et al. (2016) that emphasizes that ocean biogeochemistry is not solely controlled by vertical processes, and that lateral transport from continental margins are an important source of nutrients to the subtropical oceanic gyres. In addition, there may be seasonal and interannual variability in TEI fluxes from the continental shelf, as evidenced by variability in 228Ra activities between our study and historical values from the Peruvian margin. Establishing the mechanisms driving this variability requires further investigation in order to better constrain the shelf TEI source to the open ocean.

Acknowledgements

The authors would like to thank the chief scientists of the GP16 cruise J. Moffet and C. German. The authors gratefully acknowledge the Captain and crew members of the R/V Thomas Thompson. We are especially thankful to the members of the in-situ pump team D. Ohnemus, E. Black, S. Nicholas and S. Pike. The authors are grateful to E.Y. Kwon for sharing her shelf-derived 228Ra flux from the inverse model. We thank Evelyne Garçon for technical assistance at the LSM underground laboratory. The authors would like to thank the anonymous reviewers for their comments. The WHOI postdoctoral scholar V. Sanial was supported by the Center for Marine and Environmental Radioactivity (CMER). This project was funded by the NSF Chemical Oceanography program under grant numbers OCE-1232669 to M.A.C., OCE-1231121 to W.S.M., OCE-1237011 to JAR, OCE-1237034 to PNS, and OCE-1235124 to DEH. This is JISAO Publication 2016-01-51 and PMEL publication #4589.

References


