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Estimating iron and aluminum removal rates in the eastern equatorial Pacific Ocean using a box model approach

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ABSTRACT

Iron limitation plays an important role in maintaining the high-nitrate low-chlorophyll (HNLC) condition in the equatorial upwelling zone. The rate and depth of upwelling control Fe supply to the euphotic zone. This study constrains the transport fluxes and budget of two trace metals, Fe and Al, in the upper ocean. They are co-delivered to the eastern equatorial Pacific surface waters via the Equatorial Undercurrent and upwelling but show distinct biogeochemical cycling processes.

We combine the results of the *in situ* measurements of dissolved Fe and Al (dFe and dAl) with the modeled velocity fields to calculate the physical fluxes. The model calculations are evaluated with the conservation of heat, volume transport, NO_3 and $Si(OH)_4$ budgets for the equatorial Pacific. The vertical flux due to upwelling provides averaged dFe and dAl supply rates of 1.45 μmol m^{-2} d^{-1} and 11.51 μmol m^{-2} d^{-1}, respectively. The sum of the net physical fluxes in the eastern equatorial Pacific for dFe and dAl are 0.41 μmol m^{-2} d^{-1} and 2.77 μmol m^{-2} d^{-1}, respectively. These estimates are equal to the net biological and chemical removal rates of dFe and dAl. The calculated dFe:C net removal ratio is in the range of 3-9 μmol:mol, which agrees with most other estimates. This suggests that the majority of net dFe removal is due to biological uptake in the upper water column.

The results of this box model approach illustrate the usefulness of combining the modeled outputs and *in situ* measurements, which provide additional constraints on Fe transport and cycling in the equatorial Pacific and possibly other HNLC regions.

1. Introduction

The equatorial Pacific has become a subject of extensive field, laboratory and modeling studies during the last couple of decades in part due to two important characteristics and their link to the global carbon cycle. Firstly, a vast part of the eastern equatorial Pacific Ocean is considered as high-nitrate low-chlorophyll (HNLC) region (Barber and Chavez, 1991; Murray et al., 1994) and by Dugdale and Wilkerson (1998) as a high NO_3, low $Si(OH)_4$, low chlorophyll (HNLSiLC) waters; yet, it accounts for almost 10% of the global ocean productivity (Pennington et al., 2006). Secondly, the equatorial upwelling zone is the largest source of CO_2 flux from the ocean to the atmosphere, at about 0.7-1.0 $\times 10^{15}$ gC y^{-1} (Feely et al., 1999; Takahashi et al., 2003; Pennington et al., 2006). Observational and modeling studies have proposed that atmospheric CO_2 concentrations are partially regulated by nutrient and dissolved inorganic carbon (DIC) removal by phytoplankton during photosynthesis (Martin et al., 1990; Sarmiento and Orr, 1991), hence the interest in processes regulating the phytoplankton growth in the eastern equatorial Pacific (EEP). Martin et al. (1990) hypothesized that the supply of Fe must play an important role in controlling the primary production in this region. Several experiments carried out in this region (Martin and Fitzwater, 1988; Martin et al., 1991, 1994; Coale, 1991; Greene et al., 1994) have confirmed that low Fe concentrations are a physiological constraint on phytoplankton growth, especially for diatoms. Limited available concentration of $Si(OH)_4$ can also interact with the rate of diatom growth (Dugdale and Wilkerson, 1998; Dugdale et al., 2002a, 2007). The diatoms are responsible for up to 60% of NO_3 uptake in the EEP (Dugdale et al., 2007), thus low $Si(OH)_4$ also affects primary productivity in the equatorial Pacific. Based on growout experiments Brzezinski et al. (2008) reported that Si and Fe together controlled diatom uptake rates of $Si(OH)_4$ by almost a factor of 3, which suggests co-limitation by Fe and Si. However, no relationship between ambient Fe concentrations and $Si(OH)_4$ or NO_3 uptake could be found in the study area during the 2004 and 2005 Equatorial Biocomplexity (EB04 and EB05) cruises. The question of the relative dominance of Fe and Si limitation is discussed in several other manuscripts in this issue (Baines et al., 2011; Balch

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et al., 2011; Brzezinski et al., 2011; Demarest et al., 2011; Dugdale et al., 2011). Zooplankton grazing exerts strong pressure on the phytoplankton community and might additionally keep the total phytoplankton biomass below the level that could be supported by available nutrients (Cullen et al., 1992). It is likely that it is the combination of several factors that result in the persistent HNLC conditions in the EEP (Chavez et al., 1991; Frost, 1991; Price et al., 1991; Chai et al., 1996; Landry et al., 1997).

Fe supply is said to regulate a wide range of marine biogeochemical processes (Morel and Price, 2003). It affects the autotrophic community through algal physiology (Boyd, 2002) and phytoplankton species composition (Bruland et al., 2001), but also impacts the heterotrophic community through physiological aspects of microzooplankton (Chase and Price, 1997) and heterotrophic bacteria (Tortell et al., 1996). Nonetheless, our knowledge of the biogeochemical cycling of Fe remains insufficient to understand its role in regulating the biological productivity in the EEP. Fe chemistry in sea water is controlled both by complex inorganic and biologically mediated processes. In the open ocean, organic complexation mostly via biological uptake and particle scavenging maintains total dissolved Fe levels above those predicted by the solubility of the inorganic species (Rue and Bruland, 1995; Rue et al., 1997; Macrellis et al., 2001; Wu et al., 2001). Depending on the source of Fe, its solubility as well as bioavailability will differ considerably.

Although Johnson et al. (1997) concluded that high coastal Fe concentrations do not normally penetrate far into the open ocean, the Equatorial Undercurrent (EUC) is now believed to be the main source of Fe and Al to the EEP surface waters (Wells et al., 1999; Christian et al., 2002; Slemons et al., 2009; Gorgues et al., 2010). The EUC is an eastward flowing subsurface current, with a core depth of about 200 m that shoals upward from west to east, stretching over some 13,000 km along the equator (Stewart, 2007). While atmospheric deposition is considered to be the main source of Fe to surface waters globally (Duce and Tindale, 1991), it is the upwelling of nutrient-enriched EUC waters that controls the supply of dissolved Fe (dFe) to the euphotic zone in the EEP (Wells et al., 1995; Gordon et al., 1997; Kaupp et al., 2011). Continental shelf and fluvial fluxes of terrestrial material via surface and subsurface currents can deliver vast amounts of Fe and Al to the EUC at its origin around 150°E (Gordon et al., 1997; Wells et al., 1999; Mackey et al., 2002; Kaupp et al., 2011). The ratio of dFe to dAl in the EUC waters convinced Kaupp et al. (2011) that hydrothermal vents are an unlikely source of these elements for the EEP. Fluxes of dFe and dAl are expected to vary in strength at the EUC source, which will in turn be reflected in the magnitude of their upwelling flux and most likely in enhanced new production in the EEP (Slemons et al., 2009; Kaupp et al., 2011). The EB04 and EB05 cruises showed that the distribution of enhanced dFe and dAl coincides with the path of the EUC (Kaupp et al., 2011). It is speculated that this is even more pronounced in the western equatorial Pacific. West of 140°W, there is a significant reduction in dFe concentrations in surface waters (Kaupp et al., 2011). The different distributions of dFe and dAl in the EEP surface waters (Kaupp et al., 2011) could be attributed to preferential biological removal of dFe. Even though both dFe and dAl are scavenged onto particles, the differences in depth and rate of remineralization could explain the distinct vertical profiles of their concentrations.

Despite improvements in developing precise analytical methods for trace metal measurements, the limited spatial and temporal resolution of observations prevent the quantification of the physical transport of Fe. Studies of marine Fe biogeochemistry have therefore focused on either geochemical (Johnson et al., 1997; Martin et al., 1989; De Baar et al., 1995; Fung et al., 2000; Parekh et al., 2004) or biological aspects (Bowie et al., 2001; Tortell et al., 1999; Price and Morel, 1998). Constructing Fe budgets has been hindered by the lack of estimates of several flux terms (*e.g.* Fe remineralization dynamics, particle sinking) (Boyd et al., 2005; Wu and Boyle, 2002; Fung et al., 2000). Iron removal is a function of many factors such as: biological uptake, number and size distributions of colloidal and small particles, aggregation processes and Fe ligand dynamics (Moore and Braucher, 2007). Because Fe removal rates are highly non-linear, especially in areas of high input fluxes, surface Fe concentrations are not good indicators of input and removal processes (Moore and Braucher, 2007). This feature stresses the need to study the aspects of biogeochemical cycling of trace elements from a flux rather than a reservoir perspective. A detailed biogeochemical flux budget was constrained under unperturbed conditions in a small patch of HNLC waters south east of New Zealand by Boyd et al. (2005). A simple budget for dFe was made by Landry et al. (1997) for the equatorial Pacific but it was based on few data points and several key assumptions that require revision.

In this paper we use a box model approach to calculate physical transports of dFe and dAl and constrain their biogeochemical budgets. This approach combines high-resolution circulation model velocity fields with dFe and dAl concentration from the EB04 and EB05 cruises. Through the application of a box model we estimate the average supply and removal rates within the EEP, which can potentially complement scarce *in situ* measurements of rate processes.

2. Methods

A box model was created and designed to constrain the flux budget of a chosen oceanographic property within a given area. Fig. 1 shows the extent of two large domains within the equatorial Pacific region delineated for the purpose of this study. The 'Wyrtki Box' encompasses the area between 180°and 90°W, and 5°S and 5°N. The 'EEP Box' represents the area between 140°W and 110°W with different meridional extents ranging from 0.5° to 4° around the equator. Based on the results of volume transport balance analysis, the vertical extent is set at the depth of 75 m (see Section 3.1.).

Flux budget calculations are based on the advection conservation equation of the following form:

$$\frac{\partial(uC)}{\partial x}+\frac{\partial(vC)}{\partial y}+\frac{\partial(wC)}{\partial z}=SUM \quad (1)$$

The flux term is defined as the spatial gradient of the product of velocity (zonal - u, meridional - v, or vertical - w) and a property concentration (C). The box model evaluates the sum of physical advective fluxes in- and out- of each side of a three-dimensional box. The transport at each wall is a surface integral of all fluxes measured along that side of the box, and the difference between the opposite sides of the box gives the net flux in that

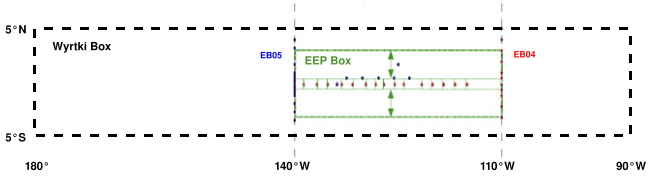

Fig. 1. The geographical extent of the two domains used in this study: the Wyrtki Box (black dotted) and the EEP Box (green dotted). Additionally, the EEP Box is divided into adjacent composite boxes. Their meridional extent is variable, as they stretch from 0.5° to 4° north and south of the equator (marked by green arrows). The sketch also displays the location of cruise stations from EB04 (red dots) and EB05 (blue dots), at which dFe and dAl concentration measurements were taken.