



The relationship between cadmium and phosphate in the Atlantic Ocean unravelled

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ARTICLE INFO

Article history:

Received 9 June 2017

Received in revised form 22 March 2018

Accepted 23 March 2018

Available online xxxx

Editor: D. Vance

Keywords:

GEOTRACES

cadmium

phosphate

Atlantic

extended optimum multiparameter analysis

ABSTRACT

Cadmium (Cd) is not generally considered a nutrient element, but behaves like a nutrient in the oceans and might play an important role in ocean biology after all. The relationship between Cd and the nutrient phosphate (PO_4) has been studied for over 40 yrs, but the debate on the driving mechanism and reason behind the 'kink', a change in the steepness of the slope is ongoing. Using new data of high accuracy and spatial resolution covering the West-Atlantic Ocean from north to south, in combination with a robust extended optimum multiparameter (eOMP) water mass model, we show that mixing between different water masses is the dominant factor explaining the observed correlation and its kink. Regeneration of Cd via remineralisation explains the smaller scale variability, notably in the surface ocean. Observations imply the availability of Cd in surface waters determines the Cd-uptake and thus the Cd: PO_4 remineralisation ratio. This ratio is variable between different ocean regions, notably between the northern and southern high latitude oceans. Due to their role in deep water formation, both the northern and southern high latitude oceans are a driving factor in the Atlantic and global Cd and PO_4 relation. Outside the Atlantic Ocean, the classical kink is not expected, but the relationship is by no means linear. Most likely, this is due to the interaction between low latitude surface waters and subsurface waters from high latitude origin, but more data are required to assess this in detail.

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1. Introduction

Dissolved trace metals in the oceans occur at low concentrations, yet many are essential for life as trace nutrients while others are valuable tracers of ocean processes (Bruland et al., 2014). The concentration of Cd in the ocean varies between $<1 \text{ pmol kg}^{-1}$ in surface waters and up to $\sim 1 \text{ nmol kg}^{-1}$ in old deep waters (Fig. 1). Since the first accurate oceanic measurements of dissolved Cd (Boyle et al., 1976; Bruland et al., 1978; Martin et al., 1976), marine scientists have been intrigued by the nutrient-type distribution of Cd as Cd was deemed to be a non-essential trace metal element for biota.

The mechanism of Cd-removal from surface waters is subject of debate but is clearly coupled to biological processes (e.g. Horner et al., 2013; Morel, 2013). A biological role for Cd as a co-factor

in a Cd-specific carbonic anhydrase enzyme has been identified in some phytoplankton species, notably diatoms (Lane and Morel, 2000). Other species that do not possess this Cd-enzyme have been shown to be able to substitute Zn or Co with Cd in the carbonic anhydrase enzyme (Morel, 2013; Xu et al., 2007). This plasticity via metal substitution has likely evolved in the open ocean due to the sparing availability of bio-essential trace metal elements, and Cd addition can stimulate plankton growth (e.g. Price and Morel, 1990; Sunda and Huntsman, 2000). In contrast, Horner et al. (2013) argued that Cd uptake is non-specific, i.e. 'mistaken identity' were phytoplankton are unable to differentiate between Cd and bio-essential divalent metals. The Cd is subsequently bound and stored inside the cell to avoid toxicity, coupling the cycling of Cd to the biological cycle of nutrients. Regardless of the actual underlying mechanism, it is clear that in the surface ocean there is net removal of Cd by phytoplankton that is returned into solution in the subsurface waters via remineralisation, leading to the coupling of the distributions of Cd and PO_4 .

The relationship between Cd and PO_4 is distinctly bi-linear (Fig. 1) and has often been described as having a 'kink', a change in the steepness of the slope, at a PO_4 concentration of

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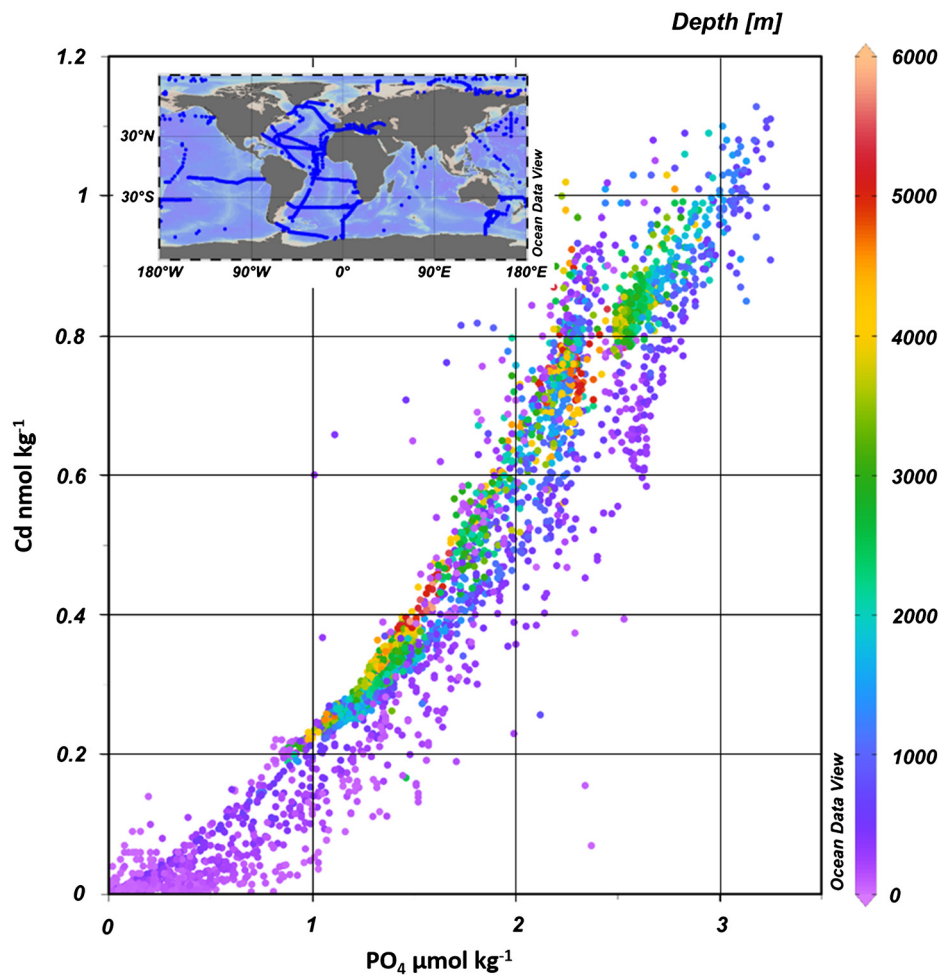


Fig. 1. Dissolved concentrations of Cd versus PO_4 from the GEOTRACES 2017 Intermediate Data product. The concentrations of dissolved Cd (pmol kg^{-1}) versus dissolved PO_4 ($\mu\text{mol kg}^{-1}$). This is all data that was included in the 2017 GEOTRACES Intermediate Data Product. We opted to show this data, as the accuracy has been verified for these data (Mawji et al., 2015; Schlitzer, 2016). (For interpretation of the colours in the figure(s), the reader is referred to the web version of this article.)

$\sim 1.3 \mu\text{mol kg}^{-1}$ (Cullen, 2006; De Baar et al., 1994). The origin of this kink in the Cd- PO_4 relations is, akin to the uptake of Cd, subject to scientific debate. The data to the left of the kink (i.e. $\text{PO}_4 < 1.3 \mu\text{mol kg}^{-1}$) is generally from surface waters and relatively young deep North Atlantic waters and the Cd- PO_4 linear regression tends to go through the origin of the graph (Fig. 1). Data to the right of the kink (i.e. $\text{PO}_4 > 1.3 \mu\text{mol kg}^{-1}$) is from the deep (deeper than 1000 m) waters from the Indian, Pacific and Southern oceans (De Baar et al., 1994), but the current GEOTRACES data shows this division is an oversimplification (Fig. 1). The regression to the right of the kink has a non-zero intercept i.e. there is 'left-over' PO_4 at zero Cd. This non-zero intercept leads to an increasing dissolved Cd/ PO_4 ratio with increasing concentrations of these elements. Since the concentrations of these nutrient elements increase with water mass age, older water masses will have a higher Cd/ PO_4 ratio. The latter ratio is referred to as the dissolved ratio or "spot ratio" and should not be mistaken with the apparent uptake or remineralisation ratio that can be deduced from the slope of the regression $\Delta\text{Cd}/\Delta\text{PO}_4$ in the surface and deep ocean, respectively (e.g. Abe et al., 2006; Baars et al., 2014). In this paper Cd/ PO_4 will be used to indicate a spot ratio, Cd: PO_4 to denote either a ratio of particles, and/or an uptake or remineralisation ratio. The slope of the regression should fit data over the entire water column and ideally be equivalent to the ratio in the particles. This only holds if both elements are taken up and remineralised in perfect harmony without influence of other processes, such as mixing of water masses with a

different spot ratio and/or different remineralisation ratio. For Cd, this idealised concept is clearly not the case given the kinked relationship. Preferential remineralisation of PO_4 over Cd has been suggested as the cause of the kink in the Cd- PO_4 relationship (Boyle, 1988), as has the influence of Sub-Antarctic waters depleted in Cd (Frew and Hunter, 1992; Xie et al., 2015) and relatively Cd-rich Antarctic Bottom Water (AABW) (Frew, 1995). Additionally, increased Cd uptake under limitation of bio-essential trace metal elements (notably Fe, Zn, Mn) (Cullen, 2006; Quay et al., 2015; Sunda and Huntsman, 2000 and references therein), as well as the influence of CO_2 concentrations (Cullen et al., 1999) have been suggested to explain the higher Cd/ PO_4 ratios in Antarctic origin water. The driving role of the Southern Ocean for the macronutrient distribution of the Atlantic Ocean is well established (Sarmiento et al., 2004) and recent studies show the importance of Antarctic origin water and water mass mixing for trace elements and isotopes as well (e.g. Vance et al., 2017; Wyatt et al., 2014; Xie et al., 2015).

Thus far most work on the Cd- PO_4 relationship has relied on regional studies or data compilations. The campaign of four consecutive GEOTRACES cruises (2010–2012) in the West Atlantic Ocean offered the opportunity to unravel and elucidate the remarkable coupling of Cd and PO_4 along the conduit of the southward travelling deep North Atlantic water and the northward travelling waters of Antarctic origin. The Cd measurements were all performed by the same analyst and the shipboard PO_4 measurements were done by members from the NIOZ nutrient laboratory that

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