



Phosphorus dynamics in and below the redoxcline in the Black Sea and implications for phosphorus burial

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Abstract

Marine basins with oxygen-depleted deep waters provide a natural laboratory to investigate the consequences of anoxic and sulfidic (i.e. euxinic) conditions for biogeochemical processes in seawater and sediments. In this study, we investigate the dynamics of the key nutrient phosphorus (P) and associated elements such as manganese (Mn), iron (Fe) and calcium (Ca) in the euxinic deep basin of the Black Sea. By examining water column particles with scanning electron microscope – energy dispersive spectroscopy and synchrotron-based X-ray absorption spectroscopy, we show that Mn(III/IV)-P is the key form of particulate P in the redoxcline. Other forms of particulate P include organic P, Fe(III)-P, and inorganic polyphosphates. Most inorganic P particles that are formed in the redoxcline subsequently dissolve in the underlying sulfidic waters, with the exception of some particulate Fe(III)-P that accounts for <1% of all P settling onto the seafloor. Organic P is the dominant source of P to the sediment. Most of this organic P is degraded in the upper 2 cm of the sediment. Results of sequential extractions and a ³³P radiotracer experiment point towards the formation of labile Ca-P and P adsorbed onto calcium-carbonate and clays and a role of these phases as a major sink of P in the sediment. The total P burial efficiency in the sediments is ~27%, which is relatively high when compared to estimates for sediments in other euxinic basins such as the Baltic Sea (<12%). We suggest that the abundant presence of calcium carbonate may contribute to the more efficient sequestration of P in Black Sea sediments.

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1. INTRODUCTION

Oxygen concentrations in many coastal waters have been decreasing since the 1960s, resulting in an expansion of so-called dead zones where oxygen concentrations in bottom waters are below 2 mg/L (Diaz and Rosenberg,

2008; Rabalais et al., 2014). One of the primary causes for expansion of dead zones is the enhanced riverine input of nutrients from fertilizers, which stimulates primary productivity in coastal surface waters and increases the oxygen demand in deep waters linked to remineralization of the excess organic matter (Diaz and Rosenberg, 2008; Rabalais et al., 2014). An example of such a coastal human-induced dead zone is the Baltic Sea (Conley et al., 2009; Carstensen et al., 2014), where more than 60.000

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km² of bottom waters are seasonally or even permanently hypoxic, anoxic or euxinic (i.e. <2 mg O₂/L, no oxygen or free dissolved sulfide (referred to as HS⁻) in bottom waters, respectively).

Bottom water euxinia in restricted basins such as the Cariaco Basin and the Black Sea occurs naturally due to stable water column stratification that limits vertical mixing in the water column and thereby decreases the supply of oxygen to the deep waters (Degens and Ross, 1974; Wilkin et al., 1997; Arthur and Dean, 1998; Scranton et al., 2001). These euxinic basins provide a natural laboratory to investigate the consequences of low oxygen conditions on biogeochemical cycling in the water column and sediments. While many studies have investigated the carbon (C), manganese (Mn), iron (Fe) and sulfur (S) dynamics in these basins (Fry et al., 1991; Calvert et al., 1996; Wijsman et al., 2001; Trouwborst et al., 2006), the dynamics of the key nutrient phosphorus (P) in the water column and surface sediments are less well understood.

The potential carriers of P towards the seafloor in euxinic basins consist of both organic and inorganic particles (Benitez-Nelson et al., 2007; McParland et al., 2015). Euxinic basins are particularly enriched in inorganic P in or close to the redoxcline (i.e. the water layer that separates oxic surface waters from sulfidic deep waters). This is, in part, caused by a close coupling between the dynamics of particulate Mn, Fe and P (Dellwig et al., 2010). The redoxcline is typically enriched in Mn(IV) oxides such as birnessite (δ-MnO₂), which undergo reductive dissolution when sinking into deeper sulfidic waters (Tebo, 1991; Tebo et al., 2004). A portion of the released Mn²⁺ diffuses upwards into the redoxcline and is again oxidized to form Mn oxides, thereby driving a Mn pump in the water column. The cycling of Fe in the water column is also driven by redox reactions but, in contrast to Mn, a distinct maximum in particulate Fe(III) (oxyhydr)oxide (Fe oxide) is not always present in the redoxcline (Lewis and Landing, 1991; Pakhomova et al., 2009). Phosphate (henceforth termed PO₄) can bind to Mn and Fe particles, resulting in the presence of Mn-Fe-P phases within the redoxcline (Dellwig et al., 2010). In addition to these mixed particles, colloidal complexes containing Mn(III) and pyrophosphate (simplified as Mn(III)-P) can contribute to the particulate P pool in the redoxcline of the Black Sea (Yakushev et al., 2007, 2009). The formation and dissolution of Mn-Fe-P particles is assumed to be responsible for the classical structure in PO₄ depth profiles in euxinic basins with a minimum in PO₄ where oxygen becomes depleted and a PO₄ maximum at the depth where HS⁻ starts to accumulate (Shaffer, 1986; Dellwig et al., 2010; Yakushev et al., 2009). Particulate Fe(III) and Mn(III/IV) are highly susceptible to HS⁻-induced dissolution. Half-life times for reactive Fe oxides (except magnetite) in sulfidic waters are less than 30 days (Canfield et al., 1992) and Mn(IV) oxides quickly dissolve in the presence of HS⁻ (<10 min.; Burdige and Nealson, 1986). In addition, Mn(III)-P complexes dissolve within seconds in sulfidic waters (Kostka et al., 1995). In euxinic basins where particles experience long HS⁻ exposure times, most particulate Mn-Fe-P is thus assumed to undergo reductive dissolution before reaching the seafloor

(Dellwig et al., 2010). Recent studies in deep euxinic basins in the Baltic Sea and Black Sea (water depth > 170 m below sea surface (mbss)) suggest, however, that some Mn oxides and Fe oxides can survive transport through a euxinic water column and may act as a carrier of P towards the seafloor (Jilbert and Slomp, 2013; Dijkstra et al., 2014, 2016).

In addition to Mn-Fe-P phases, redoxclines can be enriched in inorganic polyphosphates (i.e. linear polymers of three to several hundred PO₄ groups; Kornberg, 1995), as has recently been shown for Effingham Inlet, a restricted anoxic fjord off the west coast of Vancouver Island (Diaz et al., 2012). These inorganic polyphosphates do, however, dissolve when entering deeper anoxic waters, presumably due to anoxic remineralization (Diaz et al., 2012). This is in line with other studies that show a release of PO₄ from polyphosphates under reducing conditions (Sannigrahi and Ingall, 2005; Schulz and Schulz, 2005; Brock and Schulz-Vogt, 2011).

Other forms of particulate P phases are less sensitive to dissolution in sulfidic waters than Mn-Fe-P and inorganic polyphosphates. These are, for instance, biogenic hydroxypapatites (Schenau and De Lange, 2000; Slomp et al., 2002) and detrital apatites (Ruttenberg, 2003). Sediments below sulfidic waters can also contain carbonate fluorapatite (e.g. Mort et al., 2010). These apatites may form in the water column in micro-environments in large sinking particles (Faul et al., 2005) and can precipitate *in-situ* in the sediment as suggested for the deep Black Sea (Dijkstra et al., 2014; Kraal et al., 2017). In sulfidic calcium-carbonate (CaCO₃)-rich sediments, P associated with CaCO₃ can be an additional important P burial phase besides organic P (Kraal et al., 2017). The formation of CaCO₃-P may already occur in the overlying water column via adsorption of PO₄ onto biogenic CaCO₃, as has been proposed for the oxic Ems estuary (De Jonge and Villerius, 1989). In addition to carbonates, PO₄ can also be adsorbed to clays (Krom and Berner, 1980) but their role as a carrier of P towards the seafloor in sulfidic basins has not yet been investigated.

While the dynamics of P in and around the redoxcline in euxinic basins have been intensively studied (e.g. Dellwig et al., 2010; Yakushev et al., 2009), the carriers of P towards the seafloor in such basins are still undetermined. The susceptibility to reaction with HS⁻ differs between P phases and with it the extent to which the various P phases survive transport through sulfidic waters. Thus, the nature of the P particles in the water column can determine the rate of P deposition and, ultimately, the burial of P in the sediment.

In this study, we investigate the dynamics of Fe, Mn, Ca and P in the water column and in the surface sediment at a site in the euxinic deep basin of the Black Sea using bulk geochemical analyses, ³³P radiotracer experiments with surface sediments and detailed analysis of particles with scanning electron microscope – energy dispersive spectroscopy (SEM-EDS) and synchrotron-based X-ray absorption spectroscopy (XAS). We demonstrate that organic P is likely the major carrier of P to the seafloor. Most of the incoming organic P is degraded in the surface sediment. We further find evidence for an important role for CaCO₃ in P sequestration in the deep

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