Sea bottom sediments of Elefsis Gulf: A potential secondary source of metals under simulated ocean acidification conditions

A.Tziava[1], E.Stathopoulou[1], N.Kapetanaki[1], E.Dassenakis[1], M.Scoullos[1]

[1] Laboratory of Environmental Chemistry, Department of Chemistry, University of Athens, aspatziava@gmail.com, estath@chem.uoa.gr, nataliekapetanaki@gmail.com, edasenak@chem.uoa.gr, scoullos@chem.uoa.gr

Abstract

Hypoxic coastal areas are considered as high-priority systems for Ocean Acidification (OA) research, because the co-occurrence and interaction of low oxygen with other environmental stressors, such as elevated pCO_2, warming and eutrophication, may put them at greater risk. In this work, an anoxic coastal phenomenon exhibiting relatively reduced pH at the near bottom water layer was studied. *In-situ* and microcosm experiment measurements, simulating OA conditions, were conducted in order to assess the fate of dissolved trace metals that could either sink towards the sediment or be released towards the water column. OA conditions seem to induce the release of Al, Ni, Cd, Fe, Mn and As from the sediment while, in combination with anoxia, a restriction in this dissolution mechanism was found. Cr, Zn and Pb seem to follow a sink type mechanism under more acidified conditions while, in addition to anoxia, a source type mechanism is revealed. Hg seems to follow a source type mechanism under OA in any case. Regarding Fe species, it becomes evident that Fe (II) is the dominant species, indicating an increased stability as a result of acidified conditions.

1. Introduction

Ocean uptake of anthropogenic CO_2 alters ocean chemistry, leading to more acidic conditions and lower chemical saturation states (Ω) for calcium carbonate ($CaCO_3$) minerals, a process commonly termed “ocean acidification” (OA). OA, especially when combined with hypoxic phenomena (Melzner, 2013), affects carbon and nutrient biogeochemistry, dissolved trace metal species and complexes’ stability and sediment mineral phases, causing changes in benthic fluxes in the sediment-water interface (Ardelan et al., 2009, Atkinson et al. 2007, Scoullos, 1983) . Therefore, experiments combining acidification and low oxygen conditions are essential to fully understand and correlate the aforementioned observations in coastal environments (Melzner, 2013).

The aim of this project was to study the impacts of ocean acidification on a coastal industrialised system (Elefsis Gulf), affected by intermittent anoxic conditions, in order to distinguish if sediments act like a source or a sink for trace metals. Furthermore, it was evaluated, whether these sediment processes are imposed to alterations, as a result of acidification combined with intermittent anoxia.

2. Materials and methods

Elefsis Gulf is a small sized coastal system characterized by shallow depths (68 km^2, maximum depth 33 m) and limited communication with the wider Saronic (Scoullos, 1978). Due to the increased organic load and physiographic region, the inflow and the water exchange is restricted, resulting in the development of hypoxic/anoxic conditions during summer (intermittently anoxic) (Scoullos, 1978, Scoullos, 1983). Two laboratory experiments (I concerning only ocean acidification impact and II combining anoxia with ocean acidification) were conducted using experiment microcosms (25L), containing water and sediment from the greater depth (33 m) of the Gulf (at a proportion 80% to 20%, respectively). In both experiments, the stability of pH was maintained using a continuous flow system (IKS Aquastar, IKS Computer Systeme GmbH), which automatically adjusted CO_2 gas addition to the systems; in experiment II, the anoxic field conditions were also maintained by Ar supply. During the exp. II, on the 25th day of the experiment, the Ar supply was ceased and the systems were left to re-oxygenate until day 33th in order to fully simulate the intermittent anoxic conditions of the study area. The pH values selected for the experiment conditions were (a) for the control conditions (C) the pH value measured during sampling (7.85 for exp. I – 7.75 for exp. II), and (b) for the ocean acidification conditions (OA) the pH value predicted for the year 2300 (6.80) for latitudes corresponding to Mediterranean (Caldeira and Wickett, 2005). Each one of the two conditions was applied in two replicate tanks. Water samples were collected daily during the four week period of the experiment; sediments were collected and treated according to EPA 3050 for final measurement with ICP-MS for As, Cr, Cu, Ni andPb using the Collision Cell Technology (CCT) mode of the instrument, FAAS for Al, Fe, Mn andZn, GFAAS for Cd and CVAAS for Hg. A colorimetric determination of Fe species was also applied for wet sediment samples (combined method of Bloom, 2004 and GEOMAR). All determinations were checked with Certified Reference Material treatment and analysis. Supplementary analyses included organic and inorganic carbon determinations (TOC and $CaCO_3$), nutrients' determinations (TP, TN) and mineral composition with XRF,XRD analyses.

3. Results

In exp. I, sedimentary Cr appears to decrease under OA conditions, whereas in exp. II, this process seemed to be restricted in OA along with anoxic conditions. This decrease in Cr particulate form, could be attributed to an increase in Cr solubility as a result of enhanced CO_2; in C conditions no such variation was observed indicating perhaps a restrictive mechanism in Cr solubilization.

Sedimentary Al appeared to slightly decrease in exp. I, under OA conditions, indicating perhaps release from the sediment but in the second experiment, a sharp increase was observed in both conditions. For Cr and Al, from previous experiments (Ardelan, 2009), it was found that under enhanced CO_2 concentrations, they are both effectively removed in dissolved forms as a result of increased solubility.

Ni also presented similar trend to Cr, with a decrease in sedimentary concentrations in exp. I, under OA conditions; in exp. II, in OA conditions combined with anoxia, particulate Ni seemed to sink on sediment surface. From previous experiments, Ni has been found to dissociate more rapidly from the sediment into more labile phases towards the pore water and the supernatant seawater, which was confirmed in this study. Thus, the minimum oxygen conditions, seem to restrain this solubilisation mechanism and preserving particulate Ni phases within the sediment. (Roberts et al., 2013)

In exp. I, Cu, Zn, Pb decrease in a lesser extent in OA conditions, in relation to C conditions; in exp. II, Cu decreased dramatically in both OA and C conditions. In anoxia, a direct extraction from the sediment with concomitant Cu dissolution from the suspended material became more effective within the first days of exp. II for both conditions, indicating that sediment acts as a source of Cu. From this study, sedimentary Zn and Cu, under OA conditions and OA combined with anoxia, seemed to act as a source for solubilised metals toward the water column, in contrast to previous results in the area (Prifti et al. 2015) that show that unaffected sediments act as a sink for these two metals under oxic conditions. A potential cause of this alteration could be the different redox conditions during our experiment, as acidified conditions were implemented along with minimum oxygen conditions, in contrast with oxic conditions implemented in Prifti et al. (2015) study.

Cd appeared to decrease in exp. I, in both conditions, while in exp. II, an increase of Cd concentration was observed for both conditions. For Pb and Cd during OA conditions along with anoxia, a sink type mechanism of particulate phases precipitating on sediment surface was found; this is in agreement with the mechanism reported under oxic conditions for Pb and Cd (Prifti et al. 2015) while, a source type mechanism from sediment toward the water column was observed for these two metals, when only acidified conditions prevail.

Hg presented a decrease in sediment concentration in both experiments; in exp. I, under OA conditions the decrease seems to be restricted in relation to C conditions. In exp. II, the Hg decrease was not affected by OA conditions, a distribution which seems to be affected only by the anoxia prevailing. Hg distribution, usually presents decreased surface values either because of its increased volatility or its precipitation in particulate phases. In stratified environments, an elevated content is found in the thermocline zone while it decreases below the thermocline. Hg is known to accumulate in deeper anoxic areas, removing dissolved Hg from the surface water. In reducing aquatic environments, Hg(0) is known to be the most stable Hg species, which is released as a gas towards the atmosphere. In this case, the sediment acts as a source but it is not clear to what extent Hg remains in the water column or it eludes in the atmosphere. (Colombo et al., 2013)

Fe seemed to slightly decrease during exp. I in OA conditions, while no changes were observed during C conditions; in exp. II a slight increase was observed for both conditions. Sedimentary Mn appeared to remain invariable in exp. I, during OA conditions, while in C conditions, a decrease was observed. In exp. II, both in OA and C conditions, an increase was observed. Under oxic conditions, it was previously found that, sedimentary Fe acts as a source while for Mn acts as a sink toward the sediment (Prifti et al. 2015). It has been shown (Ardelan et al., 2010) that CO_2 seepage is able to transform sedimentary Fe and Mn , leading to an enhanced release of these metals from the sediment to the overlying water, both as dissolved and suspended particulate forms.

As presented different trends during the two experiments. In exp. I, a decrease for both OA and C conditions was observed, leading to the assumption that sediment acts as a source of As towards the water column. In exp. II, an increase in As concentration was found, being more significant under acidified conditions; in this case, it appears that sediment act as a sink for As. From previous experiments, it was found that under anoxic conditions, As (III) being the major arsenic species, is mobilized from the upper sediment surface to the overlying water (Bennet, 2012). The mobility of As in sediments is known to be closely linked to Fe biochemistry. Fe(III) (hydr)oxide minerals strongly adsorb dissolved inorganic As via complexation. Reductive dissolution of these arsenic- bearing Fe(III) (hydr)oxides, under anoxic conditions, can release dissolved As into the porewater and result fluxes of As to the overlying water column. In this study, under OA conditions, a sharp decrease of sedimentary As was observed, while for Fe only slight alterations were detected. Moreover, in OA along with anoxia, although Fe remains invariable, Mn tends to precipitate in a larger extent leading to As accumulation (Bennet, 2012), a phenomenon that was verifed in the present study as a significant increase of As concentration in the sediment was observed.It has been previously demonstrated, that metal release from metal-contaminated sediments is influenced by Fe and Mn redox chemistry (Atkinson et al., 2007). From previous experiments, the rate of oxidative precipitation of released Fe and Mn increase, as pH decrease, and appear to greatly influence the sequestration rate of released Pb and Zn. Released metals were sequestered less rapidly in waters with lower dissolved oxygen concentrations (Atkinson et al., 2007).

Table 1. Trace metal concentrations for field and experimental samples under the different conditions (cond.) and during the experiment days (Exp. day) [As, Mn, Cr, Cu, Ni, Pb, Zn, Cd and Hg in mg/kg, Fe and Al in %]

Exp.	cond.	Exp. day	As	Fe	Mn	Cr	Cu	Ni	Pb	Zn	Cd	Al	Hg
	field	-1	12,6	2,04	330	117	63,2	130	108	414	0,37	3,50	0,29
I	OA	25	10,9	1,93	335	101	26,4	118	79,1	301	0,30	3,05	0,20
	C	25	9,79	2,05	302	124	8,3	156	54,0	206	0,26	3,30	0,16
	filed	-1	9,12	1,88	284	122	107	127	102	506	0,26	3,26	0,42
II	OA	18	12,6	1,95	324	112	33,0	130	106	411	0,42	3,48	0,22
		33	12,1	2,12	350	112	33,4	138	111	408	0,39	3,57	0,21
	C	18	11,4	2,03	327	120	38,9	141	108	386	0,41	3,60	0,21
		33	10,9	2,09	345	108	15,1	140	79,9	350	0,27	3,63	0,19

From the Fe ratio results (Fig. 1), it becomes obvious that, in both experiments Fe(II) is the dominant Fe species, even without anoxia prevailing. Under acidified conditions, Fe(II) is likely to show increased stability (Breitbarth et al., 2010), which is evident during the experiment, as Fe(II) remains high, even in ordinary oxic conditions. In exp. I, Fe(II) ratio seems to decrease in OA conditions, while Fe(III) ratio seems to increase. During the exp. II, Fe(II) ratio seems to increase slightly for OA conditions, whereas a significant decrease was observed for C conditions after the re-oxygenation phase. Fe (III) ratio presented the opposite trend, with a decrease in the OA conditions and an increase in C conditions. At the current pH of surface seawater, Fe(III) is at its minimum solubility and as pH decreases, solubility increases. A decrease in pH from 8.1 to 7.4 would increase the solubility of Fe (III) by approx. 40%, which could have a large impact on the biogeochemical cycles, because Fe is an important micronutrient (Millero et al., 2009). During this study, the increasing Fe(III) ratio in OA conditions in exp. I, indicate an increase in Fe oxidation rate that, may also increase Fe(III) solubility towards the water column. In exp. II, the Fe (III) ratio decrease, as a result of the anoxic conditions, which indicate a reduction mechanism of Fe(III) to Fe(II), with possible restrictive Fe(III) solubilization mechanisms.

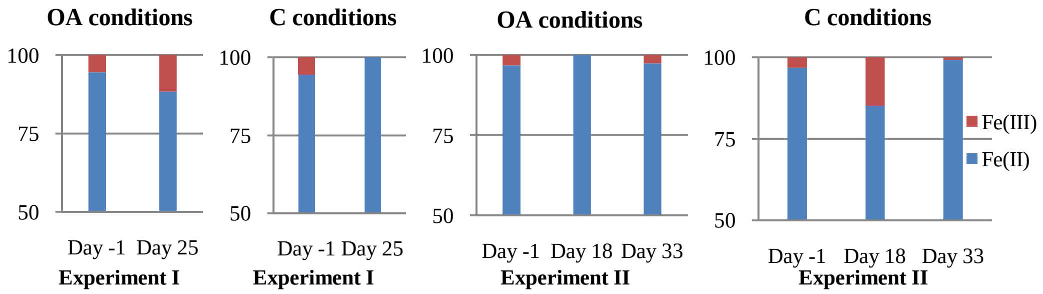

Figure 1 - Fe species ratios in % (Fe(II)/Fetotal and Fe(III)/Fetotal) variation during the two experiments

4. Conclusions

The results of this study revealed that under OA conditions, metals such as Al, Ni, Cd, Fe, Mn and As seem to follow a source type mechanism from sediment towards the water column. In contrast, OA along with anoxia conditions, a diverse sink type mechanism was observed for these metals. Cr, Zn and Pb, followed a sink-type mechanism under enhanced $CO_{2,}$ while in OA along with anoxic conditions, a source type mechanism from the sediment towards the water column was found. Hg seemed to act as a source type mechanism under acidification, regardless of the oxygen conditions but it remains unknown whether it is maintained in the dissolved form or it is released in the atmosphere. Regarding the Fe ratio, it became evident that in both experiments Fe(II) was the dominant Fe species, even without anoxic conditions prevailing, indicating the increased stability of Fe (II) as a result of increased CO_2.

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