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Have decades of abiotic studies in sediments been misinterpreted?

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Abstract

Sterilization techniques are largely employed to distinguish biotic and abiotic processes in biogeochemical studies as they inhibit microbial activity. Since one century, chemical sterilizers, supposed to preserve original environmental samples, have taken precedence over physical sterilization techniques considered too destructive. Sodium azide (NaN_3) is nowadays the most commonly used inorganic chemical sterilizer. It is sufficiently purified to study trace metals, as well. Nevertheless, its (in)activity in physico-chemical processes was never ascertained. Through the investigation of sediment resuspension in seawater, the present work unequivocally demonstrated that NaN_3 can impact carbon and trace metals' transfers by altering the redox balance and pH. Unlike decades of blind practice, NaN_3 should be used with great care to track abiotic processes from organic matter rich and reductive matrices.

Keywords

Sodium Azide; Sediment; Mixing; Impact; Organic Matter; Metals

1. Introduction

Since a century, more and more studies focused on the processes controlling the contaminants' mobility at the solid/liquid interface, spanning from the fate of contaminants linked to suspended matter along the salinity gradient (Cindrić et al., 2015; Gerringa et al., 1998; Liu et al., 1998) to the resuspension of contaminated sediment (Dang et al., 2020; Fanguiero et al., 2005). In addition, the diffusive flux of contaminants at the sediment-seawater interface (Dang et al., 2014a) also interest researchers. A particular interest targeted biotic or abiotic nature of such processes. In order to particularly address the questions, researchers used different methods to inhibit biological activity. Physical techniques such as autoclave and gamma irradiation were largely employed (Berns et al., 2008; Kelsey et al., 2010; McNamara et al., 2003). Nevertheless, both techniques were singled out as matrix destroyers, increasing surface area of clays as well as significantly altering the organic matter structure (Berns et al., 2008; Kelsey et al., 2010; McNamara et al., 2003).

The use of chemical sterilization techniques (such as sodium azide (Cabrol et al., 2017; Martin et al., 2018), mercury(II) chloride (Martin et al., 2018; Wang et al., 2011) and antibiotics (Thiele-Bruhn and Beck, 2005)) gradually overthrown physical ones, which was found advantageous in avoiding matrix modifications. Poisoning with sodium azide (NaN_3) is now the most common sterilization method used in the studies of biotic/abiotic processes: there are around 12000 published studies over the last 25 years, addressing NaN_3 use in the determination of such processes in soil or sediment.

The impact of NaN_3 onto remobilization of organic matter and trace metals from sediments was never studied. On the one hand, NaN_3 is known for long to interact with oxidoreductive reactions (Hartzell and Beinert, 1976) and, more recently to change the optical properties of the organic matter (Retelletti Brogi et al., 2019). On the other hand, trace metals in soil and sediment are mostly linked to organic matter (OM) and/or exist in their reductive

forms. Therefore, it would be expected that sterilisation by NaN_3 would potentially impact the transfer of trace metals due to their subsequent oxidation, thus biasing our perception of the biological contribution in non-sterilized (real) conditions.

2. Methods

2.1. Sampling and samples pre-treatment

This work is questioning the relevance of NaN_3 use in remobilization experiments due to its oxidizing power. The intrinsic effect of this poison onto remobilization of organic matter and trace metals during sediment resuspension in seawater was evaluated. To avoid cross-interactions with biotic interactions, sterilized seawater and sediment were mixed during 2 weeks with NaN_3 concentrations covering the range commonly encountered in the literature (1 to 50 mM). At the end of incubation period, dissolved trace metals as well as dissolved organic and inorganic carbon were quantified and compared to reference (initial seawater) and control (no azide) values. In order to avoid potential contamination by the probes, pH and Eh were monitored in the same mixtures prepared in separate set of bottles.

For the purpose of this work, the sediment was sampled in an enclosed area of Toulon Bay (harbour of La Seyne-sur-Mer, 43.1026; 5.8827), ensuring the use of fine and heavily contaminated sediment (Coclet et al., 2018; Dang et al., 2018, 2015b, 2015a, 2014b; Pougnet et al., 2014; Tessier et al., 2011). The seawater was sampled in a more open and less contaminated part of the bay (43.0948; 5.9276) in order to maximize our ability to quantify transfers.

All materials (sampling devices, bottles, tanks, filters and syringes) were previously acid-cleaned (10% v/v HCl, pro analysis, Fisher Scientific) and fully rinsed with Milli-Q water (18.2 M Ω , Millipore) in the laboratory to avoid contamination.

The sediment was collected with a grab sampler (Tall Ekman Grab, Wildco 5.3 L) and twenty-five liters of seawater were sampled on top of the water column (-0.5 m) using a 4.2 L horizontal van Dorn type water sampler (Wildco, model Beta). Collected water was stored into clean 25 L LDPE bottle (Nalgene) previously rinsed three times with water from the site. Subsamples of 24 mL of filtered seawater (0.2 μ m cellulose acetate syringe filter, Sartorius) were stored in pre-calcinated (4 h, 450 °C) glass tubes (equipped with Teflon / silicon septum, Wheaton), poisoned with NaN₃ (final concentration 1 mM, Sigma Aldrich) and stored at 4 °C, in order to analyse Dissolved Organic Carbon (DOC) and Dissolved Inorganic Carbon (DIC) concentrations. Similarly, subsamples of 8 mL of filtered seawater were stored into HDPE bottles and acidified with 0.2% HNO₃ s.p. (Merck) to determine dissolved metal concentrations.

2.2. Laboratory resuspension experiments

In order to evaluate the intrinsic effect of NaN₃ onto the behavior of trace metals as well as DOC and DIC when sediment is resuspended into seawater, the seawater was filtered under 0.2 μ m (bacterial cut-off pore size; Durapore filter 47 mm) and the sediment was autoclaved in order to avoid azide-dependent interactions with biotic or biota-related transfers.

The sediment was mixed with the seawater (with a ratio corresponding to 130 g of wet sediment for 1 L of seawater, *i.e.* to 50 g of dry sediment for 1 L of seawater) into 500 mL FEP bottles. Different conditions were tested: without addition of NaN₃ and with a range of concentrations of sodium azide added into the mixture (1, 5, 10 or 50 mM, final concentrations). All experiments were performed in triplicates. All the bottles were submitted to continuous overhead shaking (15 rpm; Heidolph Reax 20) in an opaque box to prevent sunlight alteration. Water-sediment mixture was sub-sampled after 2 weeks of contact time.

Samples were taken with syringes equipped with Teflon tubes. Each sub-sample was filtered and stored as described above for seawater prior to DOC, DIC and trace metals analysis.

In parallel, the same mixtures were reproduced in 1 L HDPE bottles in order to monitor pH and the redox potential (Eh) through the experiment using PHC101 and MTC101 multiparameter probes (Hach).

2.3. Chemical analyses

Trace metals concentrations were obtained by High Resolution Inductively Coupled Plasma Mass Spectrometer (Element 2, HR ICP-MS, Thermo). All samples were spiked with an Internal Standard (Indium). A certified reference material (CASS-5, Nearshore seawater reference material for trace metals, National Research Council Canada) was used as a quality control of HR ICP-MS measurements. For HR ICP-MS measurement, filtered seawater samples were diluted 10 times. Matrix matching calibration (CASS-5) was used for concentration quantification.

DOC and DIC concentrations were determined using a TOC-VCSH analyzer (Shimadzu). The measurement is based on a high temperature catalytic oxidation followed by an infrared detection. The analysis was validated using certified reference material (SUPER 05, Canada).

2.4. Statistical analyses

All statistical analyses and heatmap visualizations were performed using RStudio (R Core Team, 2015) and packages *agricolae*, *ggpubr*, *gridExtra*, *Hmisc*, *reshape2* and *stats*. The influence of sodium azide on trace metals and dissolved organic carbon remobilization were assessed through one-way ANOVA and Tukey post-hoc comparisons. Correlations between DOC and dissolved trace metal concentrations were assessed by Spearman's correlation tests.

3. Results and Discussions

3.1. Resuspension experiment without Sodium Azide

In resuspension experiment performed without NaN_3 , Eh and pH slightly decreased after 2 weeks (**Figure 1.A**) if compared to the initial seawater: from 259 to 221 mV and from 7.99 to 7.03, respectively. Similar variations were previously observed in biotic sediment/water mixing experiments (Cabrol et al., 2017; Dang et al., 2014a; Pía Di Nanno et al., 2007; Zouch et al., 2018), but our experimental design demonstrates the abiotic control of such processes.

Sterilized sediment and water mixing increased dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) concentrations from 2.4 to 30 mg.L^{-1} and from 27 to 73 mg.L^{-1} , respectively (**Figure 1.B**). Previous observations of DOC increase were reported for sediment resuspension in seawater with a sediment/seawater ratio ranging from 1 to 100 g.L^{-1} (Kieber et al., 2006; Komada and Reimers, 2001; Shipley et al., 2011). Particulate organic carbon (POC) pool was assumed to be converted in DOC (Koelmans and Prevo, 2003; Komada and Reimers, 2001), thus potentially explaining the observed DOC increase in our experiment. Observed DIC increase could be related to dissolution of particulate carbonates as a consequence of the pH drop. Indeed, the dissolution of particulate carbonates at pH higher than that recorded in our experiment have already been demonstrated (Comeau et al., 2017).

Through sediment resuspension in the water column, remobilization of trace metals comes out either as a removal (adsorption or co-precipitation onto particles) or as a desorption from particles (Calmano et al., 1993; Dang et al., 2020, 2015b; Xie et al., 2019). In our study, after 2 weeks of contact time without addition of NaN_3 , most of the analyzed elements (Li, Mo, Sb, Cs, Pb, U, V, Mn, Co, Ni, Cu, Zn, Sr, Ba and As) had undergone a desorption from the particles (representative examples are shown in **Figure 1.C and D**). Such desorption was probably due to the oxidation of the sediment particles. Indeed, the oxidation will impact the organic matter which will release metals previously bound to it. In addition, reduced inorganic metals (linked to sulfides) will also be oxidized and therefore released in the dissolved

phase. Other metals (Al, Fe and Ti) had been adsorbed onto the particles (representative examples are shown in **Figure 1.E and F**). This adsorption was probably related to Fe and Mn oxidation, which will generate oxy-hydroxide and become new carrier phases for metals (Dang et al., 2020).

3.2. Geochemical transfers are poisoned by the use of NaN_3

Along with increasing NaN_3 concentration, pH and Eh increased compared to the control condition (**Figure 1.A**), Eh even reaching above-reference values with the highest NaN_3 concentrations. This clearly shows the strong oxidant power of NaN_3 . Moreover, pH increase is probably due to the reaction between azoture ions (N_3^-) and H_2O molecules, forming HN_3 and OH^- . This can be easily demonstrated by adding 50 mM sodium azide into milli-Q whose pH increased from 5.8 to 7.4.

With NaN_3 addition, DOC concentration increased by a factor 1.8 when compared to the control condition (from 30.3 to 54 mg.L^{-1}) whereas DIC concentration decreased by a factor 2.6, returning to the reference value (27 mg.L^{-1}) (**Figure 1**). NaN_3 -related DOC increase had already been documented (Koelmans and Prevo, 2003; Pett, 1989; Shipley et al., 2011). Pett (1989) explained this observation either by an alteration of algae cell walls' permeability or a release of enzymes by azide-killed bacteria. However, in the present study, the sediment was autoclaved and the seawater was filtered so the hypothesis of Pett could only fit with our control condition. Moreover, considering an average of 5×10^8 bacterial cells in each g of humid sediment (Whitman et al., 1998) and an average of 20 fg C per cell (Pedler et al., 2014), the bacterial-decay-related DOC increase should not have risen the concentration above 2.6 mg.L^{-1} , which remains far from the 29 and 54 mg.L^{-1} recorded in the control condition and with the largest NaN_3 addition, respectively. Thus, we hypothesize that the increase in DOC concentration was related to POC alteration by NaN_3 . Considering the

oxidant power highlighted above, such alteration could consist in an oxidation of the originally reduced pool of sediment POC.

Phytoplankton usually uses DIC for the photosynthesis. Yet, in the present study, all experiments were performed with sterilized sediment and water samples and protected from light, therefore any contribution from photosynthesis to DIC decrease can be ruled out. The NaN₃-induced pH increase could have strongly contributed to modify the carbonate system and thus DIC concentrations. An acidification caused the transformation of CO₃²⁻ into HCO₃⁻, leading to the dissolution of CaCO₃ (Honisch et al., 2012; Pedler et al., 2014). Then, the addition of NaN₃ concentration above 10 mM promoted pH values similar to the seawater reference and appeared to inhibit this phenomenon. Thus, the use of azide clearly modified the carbonates system in our experiment by inducing pH increase.

When NaN₃ was used in remobilization experiment, dissolved concentrations of most of the trace metals studied were statistically related to NaN₃ concentration (some examples are shown on **Figure 1C, D, E and F**) indicating strong effect of NaN₃ on their behavior. Only As, Sb, and Ti were not affected by NaN₃ addition. The positive (Al, Co and V) or negative correlation (Ba, Co, Cs, Fe, Li, Mn, Ni, Pb, Sr, U and Zn) with NaN₃ is probably linked the carrier phases and their respective specific alterations. **Figure 2** gathers trace metals according to their behavior and their link with DOC concentration considering all experimental conditions. Three groups can be deciphered: (1) Al, Mo and V were strongly and positively linked to DOC concentration, (2) Ba, Co, Cs, Fe, Li, Mn, Ni, Pb, Sr, U and Zn were strongly negatively linked to DOC concentrations and (3) As, Cu, Sb and Ti were not related to DOC and tend to show singular behaviors. Nevertheless, this behavior might not be directly linked to organic carbon fate. Trace metals strongly negatively linked to DOC were removed onto particles with NaN₃ additions. This removal might be explained by the increase of Fe and Mn oxides, generated by the oxidant power of NaN₃, becoming new carrier phases

for trace metals. Thus, NaN_3 -related organic carbon transformations as well as higher Fe/Mn oxide precipitation were the main driving forces influencing transfers of trace metals during sediment resuspension and reveal the incompatibility of millimolars of NaN_3 with geochemical studies.

Conclusion

Sodium azide was largely employed during the last century to inhibit microbial activity in biogeochemical studies in order to identify the contribution of biotic processes affecting transfers of trace metals and/or carbon without considering the intrinsic effect of NaN_3 . The present study clearly demonstrated that the addition of NaN_3 at concentrations commonly used in sediment resuspension studies (1-50 mM) strongly impacted both pH and Eh, DOC/DIC and trace element behaviors. Oxidative power of NaN_3 caused increase of DOC, whereas increase of pH diminished solubility of carbonates, leading to a decrease in DIC concentrations. Furthermore, oxidative power of NaN_3 promoted formation of the various carrier phases (i.e. oxides and organic matter) which were having strong influence on the behavior of trace metals during such experiments. An increase of NaN_3 caused enhanced transfer of some trace metals from solid phase to the dissolved form, while for others a decrease in dissolved concentration was observed. As a conclusion, the authors want to highlight the potentially unexpected strong effects of azide on physico-chemical properties of environmental matrices and recommend banishing its use for biogeochemical studies in organic and reductive matrices.

Recapitulation of the occurring processes is schematized on **Figure 3**.

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Figures and tables captions

Figure 1. Variation of pH and Eh (A), DOC and DIC (B), Pb and Ni (C), Cu and Mo (D), Al (E) and Fe (F) as a function of azide concentration. Column plots represent the mean value of triplicated experiments after 2 weeks of sediment and seawater continuous mixing. Error bars represent standard deviation. Horizontal lines represent initial values in seawater. Letters on the plots represent the significant variability between conditions coming from Tukey post-hoc comparisons.

Figure 2. DIC concentration as a function of the recorded pH during the experiment. This representation includes the 5 experimental conditions after 2 weeks of sediment resuspension as well as the measurement in initial seawater.

Figure 3. Heatmap of correlation intensity between studied trace metals and DOC. Correlations were calculated from 15 values corresponding to 5 triplicated azide concentrations. The color scale corresponds to Spearman's correlation coefficients. 1, 2 and 3 stars represent a pvalue <0.05 , <0.01 and <0.001 respectively.

Figure 4. Schematic conclusion representing the different processes occurring during the experiments.

Figure1
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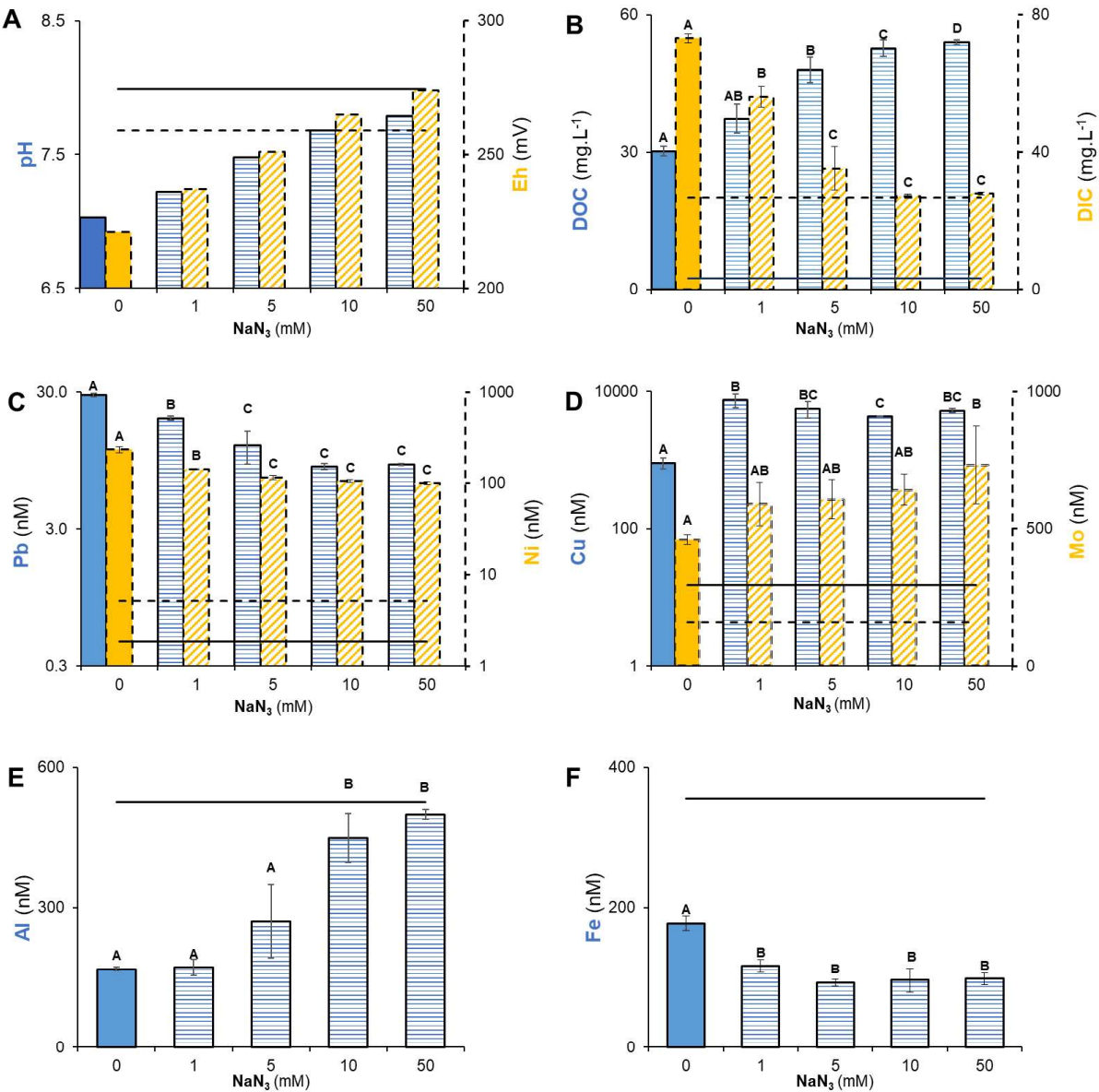


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Figure2
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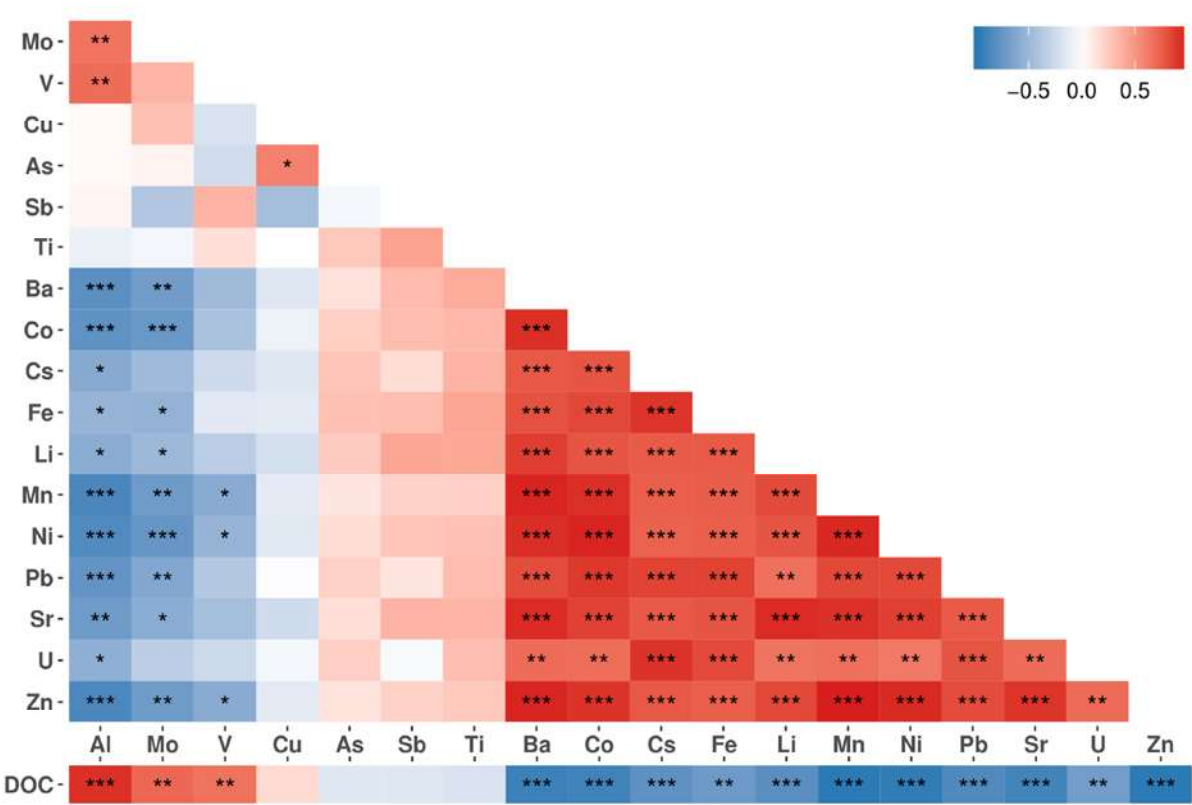


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Figure3

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