HOW WOULD THE CO_2 LEAKAGE INFLUENCE THE CHEMICAL DIFFUSION PROCESSES AT SEDIMENT-WATER INTERFACE?

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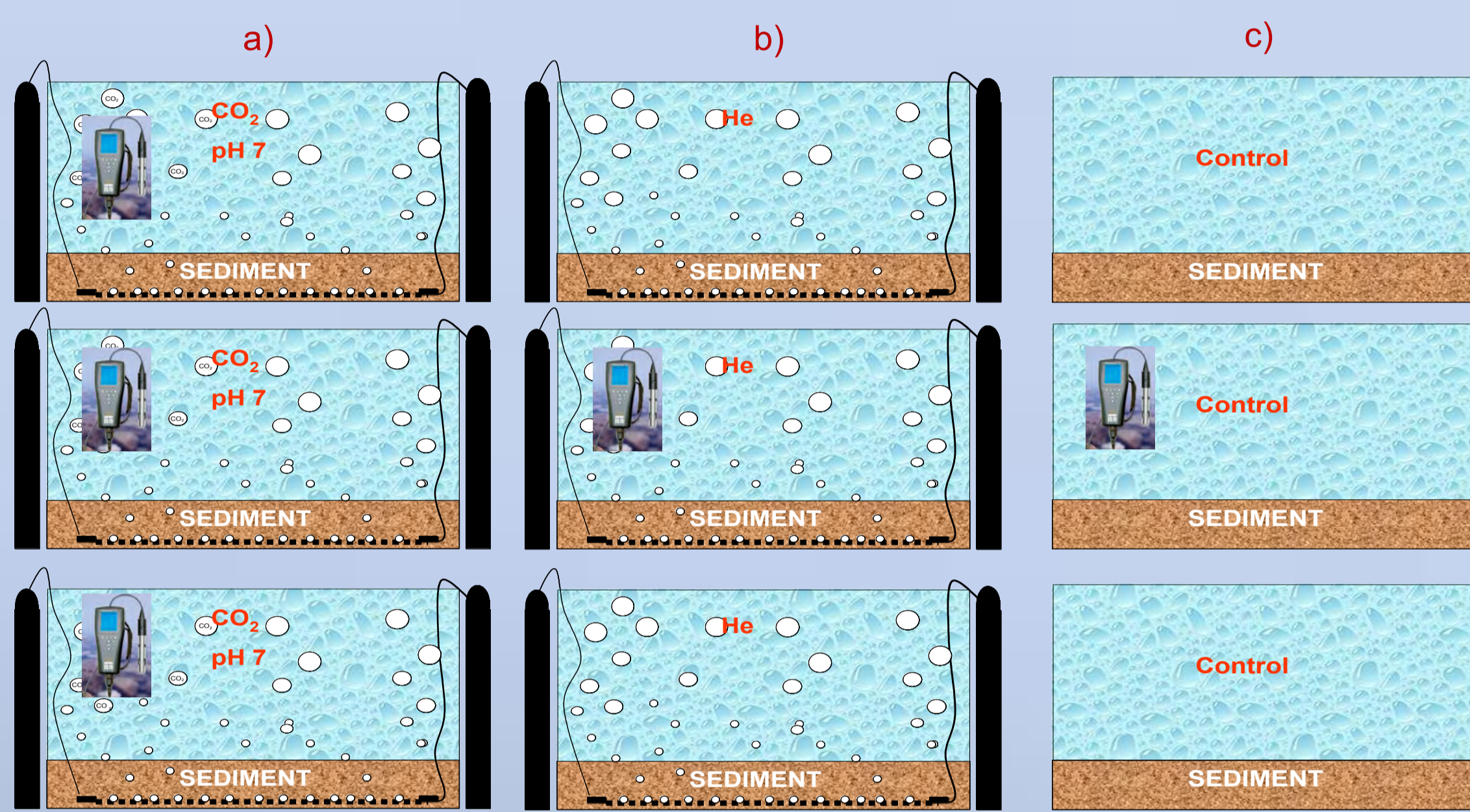
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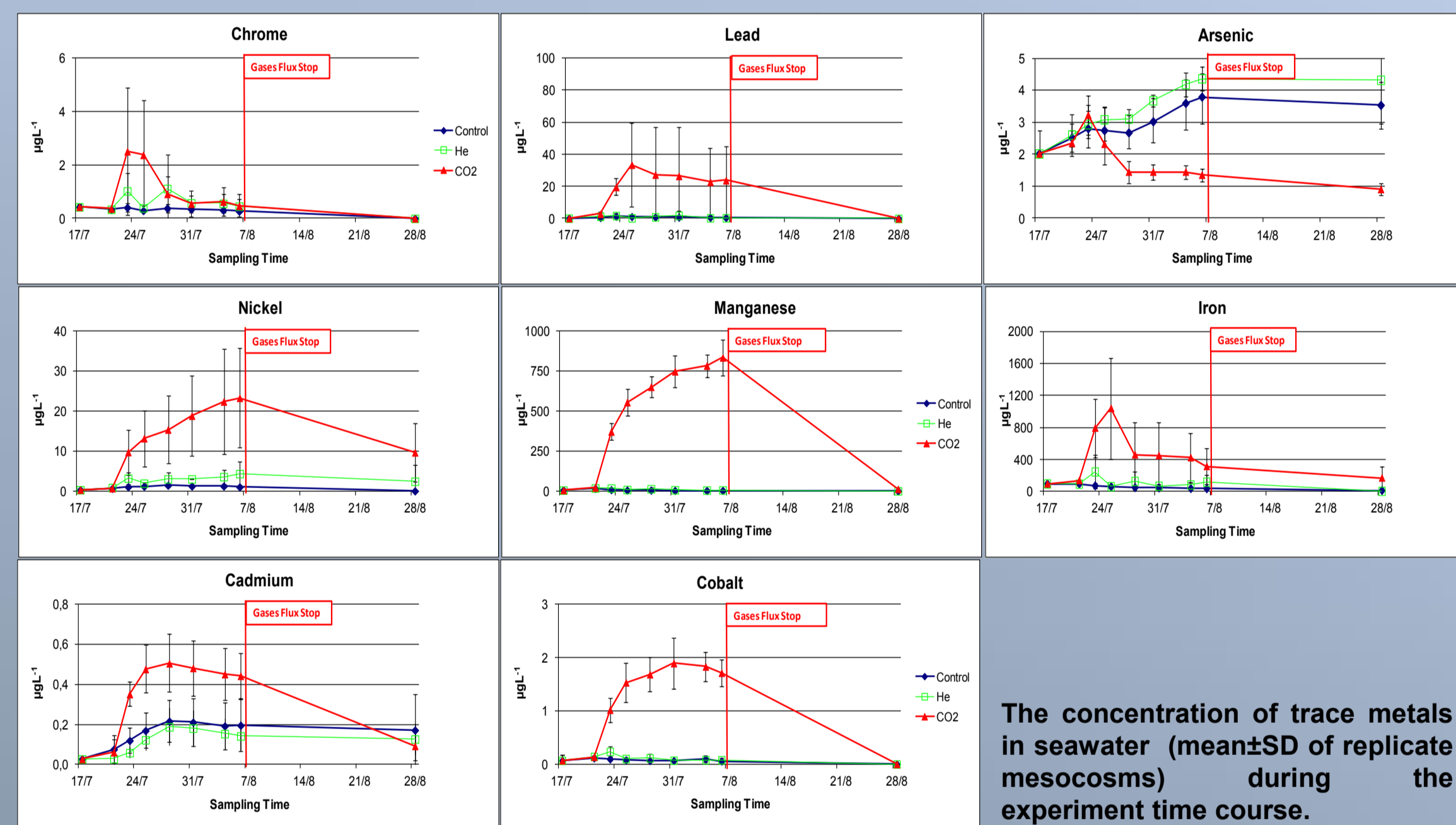
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Marine sediments act as a sink for pollution, since many contaminants, like metals, get trapped in the sediments resulting therefore not bioavailable. The **availability and mobility of metals** from sediments to water column depends on their association with the solid phases (*de Orte et al. 2014a*) and are mainly driven by the **redox conditions and pH** (*de Orte et al. 2014b*).
Previous studies have demonstrated that seawater acidification caused by an **increase of CO_2 levels** in the marine environment may increase the **toxicity** of metal-contaminated sediments due to the metals mobilization (*Rodríguez-Romero et al. 2014*). According to *Millero and coll. (2009)* pH decrease would significantly affect the **inorganic solubility of several trace metals**, particularly those forming strong complexes with hydroxide and carbonate ions.
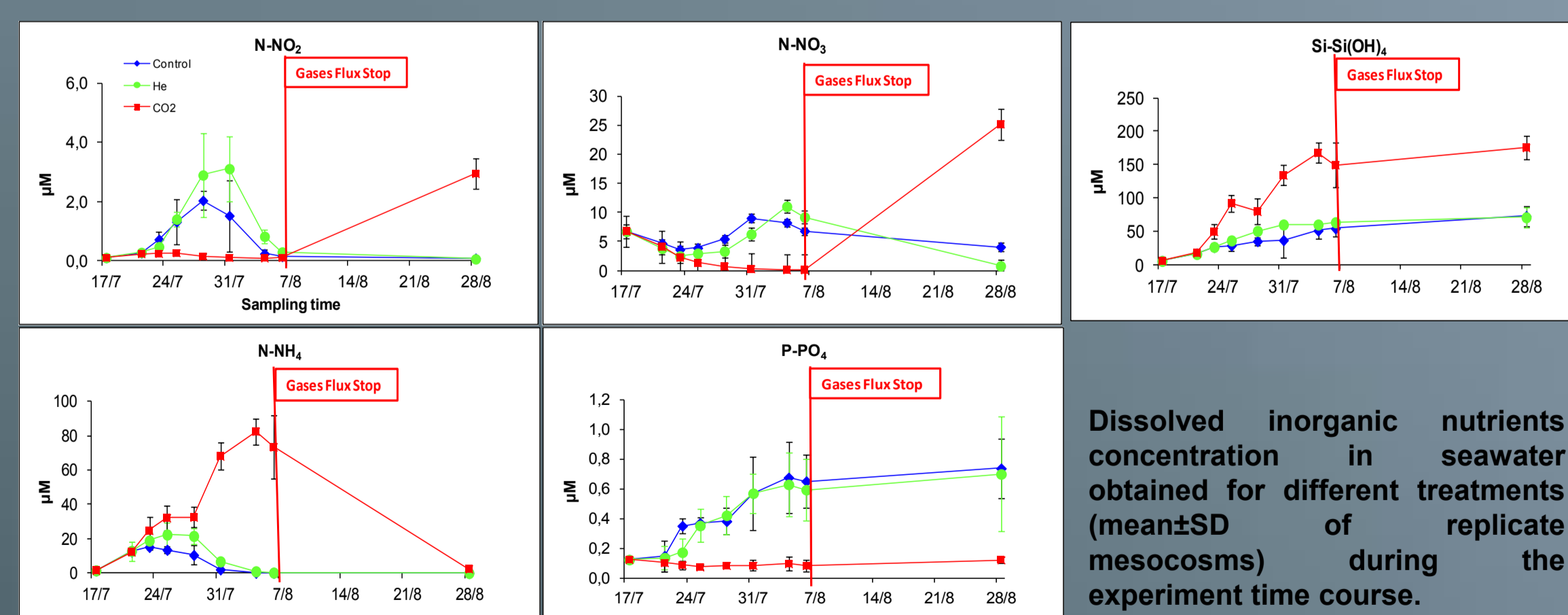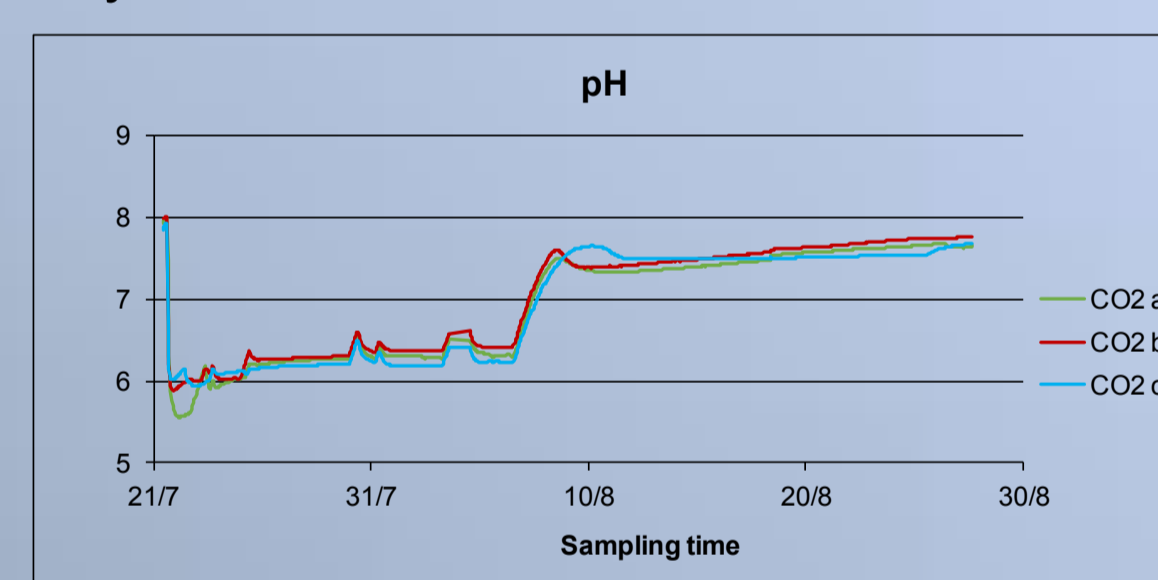
Carbon capture and storage (CCS) technology is considered as one of promising options in the portfolio of **mitigation measures** to face against climate changes effects (*IPCC 2005*). EU 2030 climate and energy policy framework make reference to the important role that CCS could play for the long-term CO_2 concentrations reduction measure due to the industrial production and stabilization of atmospheric greenhouse gas concentrations. Potential CO_2 leakage from Carbon Capture and Storage (CCS) plants in a seabed could very likely lead to a **considerable decrease of pH** in the sediments, sediment porewater and in the water column (*de Orte et al. 2014b*).
Here we investigated the possible **CO_2-leakage effects on release of metals at sediment-water interface**, over a relatively short-time period (3 weeks).

Experimental set up

The simulation of CO_2 leakage (a), inert gas (He) bubbling (b) and the control (c) in triplicate mesocosms containing contaminated sediment and seawater. The presence of multiparametric probes (YSI QUATTRO) are indicated.

The concentration of trace metals in seawater (mean±SD of replicate mesocosms) during the experiment time course.

Laboratory experiment consists of 9 mesocosms of ≅200 L volume containing two sections, a **lower sediment section** and an **upper water section** (1:4 v/v). Surface sediments (upper 10 cm) were collected from the nearby harbour (Trieste, Italy). because the area is **heavily contaminated by metals**. Various different sources of contamination affect this area, including industrial residues from chemical industry plants located in areas close to the port and the urban sewage from the city of Trieste and Muggia.
The mesocosms were treated in triplicate: **a) with CO_2** to assess the effect of CO_2 leakage; **b) with He** as an inert gas to assess the physical effect of the bubbling and **c) without treatment as a control**. The experiments were conducted over a **3 weeks** with 12:12 light : dark cycle with the gas flux of 0.2 NL/min. After then, gas flux was stopped and the mesocosms were maintained for other 22 days. Water circulation was assured by a submersible water pump.
Samples were collected initially (17th July 2014) and about once every three days.

Disposal of contaminated sediments into the containers.

The results of continuously monitored pH outtlined extremely good reproducibility of triplicate CO_2-mesocosms.

After the start of CO_2 bubbling the sharp **pH drop** and **DIC increase** were detected after the second sampling at July 21st, in accordance to our expectations. The chemical species monitored during the experiment reacted in different ways to the CO_2 addition due, primarily, to the influence of acidity on species form and mineral solubility. In terms of nutrients, silica rose during the entire injection phase due to the mineral dissolution, in agreement with the Panarea field results within RISCS and ECO2 projects. In contrast, phosphate concentrations decreased and remained quite low likely due to the adsorption or the lower solubility levels of mineral phases like variscite and strengite under acidic, oxidizing conditions. Both major and trace elements can be divided into two main groups. The first group shows an initial increase after the start of injection followed a few days later by a decrease to values that are higher than the starting concentration (e.g. Fe, Cr and Pb) or lower (e.g. As).

Analytical methods
pH was determined according to the potentiometric method (*Dickson et al. 2007*). The concentration of dissolved inorganic nutrients was analysed colorimetrically according to *Grasshoff et al. (1999)* using a Bran+Luebbe Autoanalyzer 3. For DOC analyses the HTCO method was applied using a commercial unit, the Shimadzu TOC-V CSH, according to *Cauwet (1994)*, as well as for DIC analyses. The concentration of metals was determined according to EPA 3050B/1996, EPA 3052/1996 and EPA 6010C/2000 methods.

pH (a), dissolved inorganic and organic carbon (b and c respectively) concentrations in seawater obtained for different treatments (mean±SD of replicate mesocosms) over the experiment time course.

Dissolved inorganic nutrients concentration in seawater obtained for different treatments (mean±SD of replicate mesocosms) during the experiment time course.

Iron mineral phases like hematite may be initially dissolved, then re-precipitated as oxy-hydroxides that scavenge the various trace metals that showed a similar behaviour. The second group instead shows a relative steady increase during the entire CO_2 injection period. The increase of Mn is particularly strong, likely due to the solubilisation of phases like manganite and rhodochrosite to Mn^{2+} under acidic conditions followed by re-precipitation and return to low background dissolved concentrations 3 weeks after injection was stopped. Other trace elements that showed similar behaviour are Co, Ni and Cd.
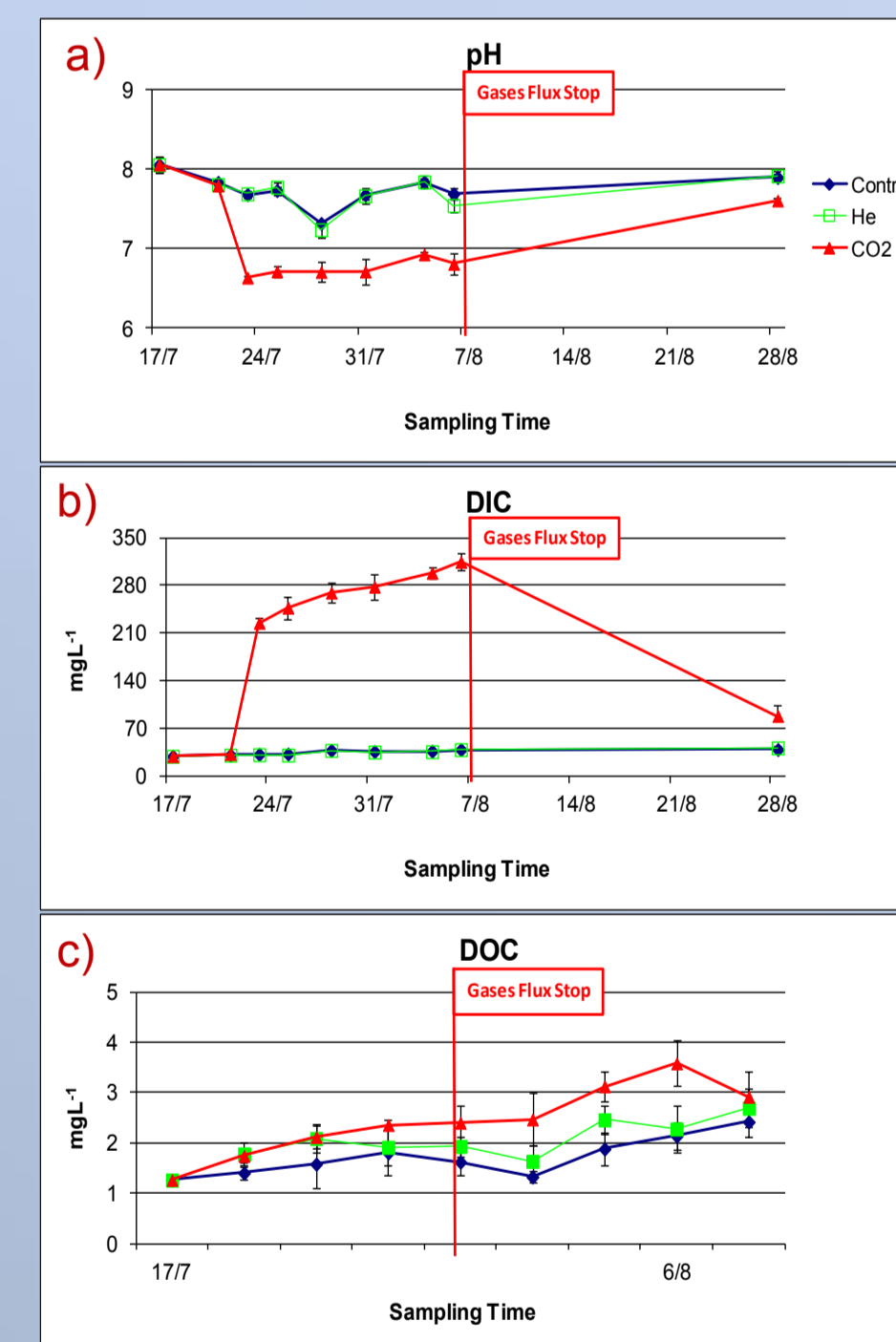These results clearly illustrate that any potential change in water chemistry induced by CO_2 leakage will be controlled by the pH and redox conditions, the related behaviour of the single species under those conditions, and the mineralogy of the sediments themselves.

Conclusions

The experiment clearly showed the **impact of the leaking CO_2 gas** on the chemistry of the overlying seawater in comparison to the similar behaviour of the inert gas (He) bubbling and the control. The lack of difference between these latter two indicates that the mechanical mixing or oxygen stripping induced by **bubbling had little or no influence on the results**, and that changes observed in the CO_2 tanks are strictly due to the **acidification** and the related changes in carbonate system.
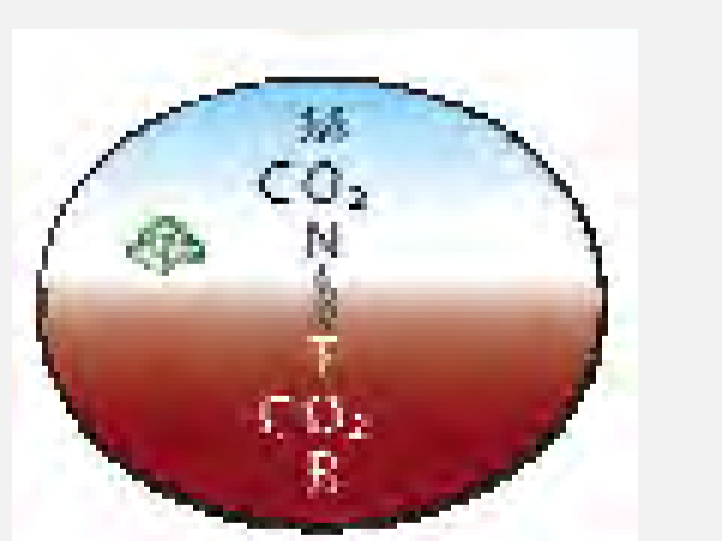
References
Cauwet, G., 1994. HTCO method for dissolved organic carbon analysis in influence of catalyst on blank estimation. Mar. Chem. 47, 55-64.
de Orte, M.R., Sarmiento, A.M., Basallote, M.D., Rodríguez-Romero, A., Riba, I., delValls, T.A., 2014a. Effects on the mobility of metals from acidification caused by possible CO_2 leakage from sub-seabed geological formations. Science of the Total Environment 470–471, 356–363.
de Orte, M.R., Sarmiento, A.M., delValls, T.A., Riba, I., 2014b. Simulation of the potential effects of CO2 leakage from carbon capture and storage activities on the mobilization and speciation of metals. Marine Pollution Bulletin (2014),
http://dx.doi.org/10.1016/j.marpolbul.2014.07.042
Dickson, A.G., Sabine, C.L., Christian, J.R., 2007. Guide to best practices for ocean CO_2 measurements. PICES Special Publication 3, 191 pp.
Grasshoff, K., Kremling, K., Ehrhardt, M., 1999. Methods of Seawater Analysis, 3rd Edition, Wiley-VCH, Weinheim, 600 pp.
Millero, F.J., Woosley, R., Ditrolio, B., Waters, J., 2009. Effects of ocean acidification on the speciation of metals in seawater. Oceanography 22, 72–84.
Rodríguez-Romero, A., Jiménez-Tenorio, N., Basallote, M.D., de Orte, M.R., Blasco, J., Riba, I., 2014. Predicting the Impacts of CO2 Leakage from Subseabed Storage: Effects of Metal Accumulation and Toxicity on the Model Benthic Organism Ruditapes philippinarum. dx.doi.org/10.1021/es501939c | Environ. Sci. Technol.