

# **Assessment by Self-Organizing Maps of element-release from sediments in contact with acidified seawater in laboratory leaching test conditions**

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## **ABSTRACT**

Carbon capture and storage (CCS) is gaining interest as a significant global option to reduce emissions of CO<sub>2</sub>. CCS development requires an assessment of the potential risks associated with CO<sub>2</sub> leakages from storage sites. Laboratory leaching tests have proved to be a useful tool to study the potential mobilization of metals from contaminated sediment in a decreased-pH environment that mimics such a leakage event. This work employs a Self-Organizing Map (SOM) tool to interpret and analyze the release of Dissolved Organic Carbon (DOC), As, Cd, Cr, Cu, Ni, Pb and Zn from equilibrium, column and pH-dependent leaching tests. In these tests, acidified seawater is used for simulating different CO<sub>2</sub> leakage scenarios. Classification was carried out detailing the mobilization of contaminants for environments of varying pH, liquid-to-solid ratio and type of contact of the laboratory leaching tests. Component planes in the SOMs allow visualization of the results and the determination of the worst-case of element-release. The pH-dependent leaching test with initial addition of either base or acid was found to mobilize the highest concentrations of metals.

**KEY WORDS:** Metal-release assessment, Carbon capture and storage, Self-Organizing Maps, Leaching tests, Sediment acidification

## **INTRODUCTION**

Emissions of carbon dioxide (CO<sub>2</sub>) have been identified as the key factor responsible for climate change and effective measures and technologies need to be implemented to decrease these emissions (IPCC 2014). Carbon capture and storage (CCS) using geological sequestration in on- and offshore formations is a promising measure being considered worldwide to allow the continued use of fossil-fuels while preventing the associated emissions of CO<sub>2</sub> from reaching the atmosphere (Corsten et al. 2013; Koornneef et al. 2012).

The CCS process consists of the capture of CO<sub>2</sub> from an industrial emitter, its transportation to a storage site in gas or liquid phase and its storage or sequestration in stable geological formations. Although CO<sub>2</sub> is injected into deep storage formations, there is a risk of CO<sub>2</sub> leakage from storage sites to the near-surface

environment and the effects of such a leakage need to be properly addressed. For offshore storage sites, an impact assessment of such leakages on the surrounding environment should include the mobilization of substances from caprock formations, marshes and sediment by the resulting seawater acidification (Payán et al. 2012a). The European Union (EU) Directive on the geological storage of CO<sub>2</sub> (DOL 2009), that is based on the London Protocol and the OSPAR Convention (OSPAR 2007; RAMF 2006), establishes the framework to determine the risk assessment for and management of CO<sub>2</sub> storage. Mobilization of metals in an acidified environment is a subject of concern in the CCS Directive as well as in the Marine Strategy Framework Directive (DOL 2008), both of which are focused on the marine environment.

In recent years, several studies have assessed the risks and potential impacts of CCS technology using a range of approaches. A diverse set of tools has been applied to the various technology stages in the CCS process with life-cycle assessment (LCA) and a variety of modeling methods often used (Table 1). While current LCA studies on CCS focus on different technologies, timeframes and aspects treated (Corsten et al. 2013), most storage analyses do not account for potential CO<sub>2</sub> leakages; considering them to be negligible, unlikely to occur, or zero (Table 1). Where CO<sub>2</sub> leakages during the storage stage are considered, the assessment is carried out according to degradation in aquifer properties and/or leakage rates, but is not related to the metal mobilization.

Modeling techniques, such as those detailed in Table 1, can be used when predicting the spatial and temporal evolution of injected CO<sub>2</sub> and to identify changes in water quality that may ensue. The results from the modeling techniques may also help to develop possible mitigation strategies if leaks were to occur at storage sites. Predictive models have been used to estimate the risk of CO<sub>2</sub> leakages from storage sites, analyzing changes to the storage formation, the probability of leakage occurrence and the leakage ratio (Table 1). Birkholzer et al. (2008) show different possible geochemical reactions—such as mineral dissolution and metal mobilization— because of CO<sub>2</sub> leakage during storage. Despite the promise that modeling offers, field and laboratory studies are still required to decrease uncertainties in model assumptions and to validate model findings.

To complement LCA and modeling studies, analysis of natural and industrial analogues have been conducted both in-situ and in laboratory experiments to develop understanding of the risk posed by CO<sub>2</sub> leakages. Laboratory leaching tests have been widely used for studying the potential mobilization of elements in a decreased-pH environment because of ocean acidification and CO<sub>2</sub> leakages during the CCS

storage stage (Martín-Torre et al. 2014, 2015 a, b). Equilibrium, column, core flow, sequential, pH-dependent and multiphase leaching tests have been used, among others, to evaluate the mechanisms and the levels of metal mobilization from sediments exposed to acidified seawater (De Orte et al. 2014; Varadharajan et al. 2013; Payán et al. 2012 a, b; Ardelan et al. 2012, 2010, 2009; Ellis et al. 2011; Carey et al. 2009 ).

The use of an assortment of leaching tests allows for the assessment of metals' behavior under a wide range of variables, such as acidification, time of contact, and hydrological conditions. Thereby, the metal-release in different scenarios of sediment acidification can be tested. Equilibrium tests simulate the re-suspension of sediments in acidified seawater due to CO<sub>2</sub> gas bubbling or dredging operations; column leaching tests simulate advective flow of acidified seawater arising from rapid fracture deterioration in caprock; and pH-dependent leaching tests simulate scenarios of constant acidification (Payán et al. 2012 a, b; Martín-Torre et al., 2015 a).

Classical multivariate statistical techniques, such as Principal Component Analysis and Hierarchical Component Analysis, have been commonly used to assess and classify sediment quality according to their contamination and metal-release behavior under different conditions using a variety of physico-chemical data (Khosrovyan et al. 2015; Moukhchan et al. 2013; Choueri et al. 2009; Cesar et al. 2007; Morales-Caselles et al. 2007; Simeonov et al. 2007). Self-Organizing Maps (SOMs) and an artificial neural network with unsupervised learning have so far been used in a more limited way as an alternative to classical multivariate statistical techniques to assess sediment quality (see for example: Tsakovski et al. 2009; Álvarez-Guerra et al. 2008; Arias et al. 2008).

The main objective of this work is the use of a SOM tool to analyze element-release data from contaminated sediment under different laboratory leaching tests that simulate conditions of CO<sub>2</sub> leakages from a CCS storage site. The work is divided into equilibrium and column tests with CO<sub>2</sub> acidified seawater, and pH-dependent leaching tests with nitric acid (HNO<sub>3</sub>) acidified seawater. The proposed methodology permits the integration of element-release concentrations obtained during experiments of varying pH, liquid-to-solid ratios (L/S) and type of contact, which together simulate different CO<sub>2</sub> leakage scenarios.

## **MATERIALS AND METHODS**

### **Sampling site and data sets**

The data used in this study are originated from four different leaching tests carried out under different conditions. These leaching tests have been applied to sediment sampled in the Suances estuary (Northern Spain), a narrow and shallow mesotidal estuary, which has been identified as a potential CCS storage site. The sediment contains significant concentrations of metals and organic pollutants that are derived from different activities upstream of the estuary. A detailed description of the studied area and sediment characterization is shown in Martín-Torre et al. 2015 a.

The sediment used for experimental assays was sieved through a 2mm mesh to remove the gravel fraction, homogenized and frozen in 3 kg plastic bags until use. The used seawater ( $\text{pH}=8.02\pm 0.076$  and 35 ‰ salinity) was supplied by the Maritime Museum of Cantabria in Santander, filtered through 0.45  $\mu\text{m}$  and it is used within the next 24 hours. The seawater is chemically analyzed by the same procedure of the sample leachates of each leaching test. Concentrations of As, Cd and Zn of the used seawater, considered in all data analysis, are  $2.91\pm 0.858$ ;  $0.528\pm 0.653$  and  $13.788\pm 7.506$ , respectively. Concentrations of Cr, Cu, Ni and Pb are below the detection limit of the equipment (4, 2, 2 and 0.4  $\mu\text{g/l}$ , respectively).

Equilibrium leaching tests were performed at the liquid to solid ratio (L/S) of 2, 4, 10, 15, 20, 30 and 40 l/kg over a 24-hour period as the EN 12457 standard (EN 12457 1-2, 2002) provides. Leaching tests used seawater and  $\text{CO}_2$ -acidified seawater at pH values of 7, 6 and 5 as leaching agents (Payán et al 2012a).

Column leaching tests were carried out according to the CEN/TS 14405 standard (CEN/TS 14405 2004) using the same leaching agents than in equilibrium leaching tests. However, in these experiments, the L/S ratios of 0.1, 0.2, 0.5, 1, 2, 4, 5, and 10 were employed in experiments that lasted 56 h (Payán et al. 2012b).

The pH-dependent leaching test with initial acid/base addition was performed following the CEN/TS 14429 standard (CEN/TS 14429 2005) although three modifications were included: the use of seawater as leaching agent, the particle size of the solid (2 mm) and the pH range covered (Martín-Torre et al. 2015 a). The whole pH range (0–14) is studied for simulating different acidification and alkalisation situations, including seawater conditions, ocean acidification, leakages from  $\text{CO}_2$  storage sites and potential chemical spills. For this test, samples of L/S = 10 l/kg were used in experiments that lasted 48 h. The acidified state

was achieved by adding predetermined amounts of acid ( $\text{HNO}_3$ ) in three stages (at 0, 30 and 120 min), as explained in the standard. The quantity of added acid varied from 0 to 8 eq/kg whereas the quantity of added base was from 0 to 3.5 eq/kg; thus, the obtainment of the most extreme pH values was assured (Martín-Torre et al. 2015 a; 2014).

The pH-dependent leaching test with continuous pH-control standard (CEN/TS 14997, 2006) was conducted using seawater as leaching liquid. The seawater and the sediment were placed at L/S=10 l/kg. For reaching the pH objective (4, 5, 5.5, 6, 6.5 or 7) and keep it constant through the 96 hours of the assay, nitric acid ( $\text{HNO}_3$ ) was added by a pump connected to a pH control equipment when pH was higher than the established set point.

To detail the performed leaching tests and clarify the modifications compared with standardized leaching tests, more information about experimental procedure is presented in Supplementary Information.

pH of the final eluates from the different assays was measured using a Crison pHmeter GLP 22, with a suitable electrode for samples with suspended solids; the equipment was calibrated against standard solutions with an accurate to 0.01 pH units. Final eluates samples were filtered through a 0.45  $\mu\text{m}$  pore size nitrocellulose filtration membrane and divide in two subsamples: one for the measurement of Dissolved Organic Carbon (DOC) and the other one acidified for analysing the concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn. DOC analyses were performed by Analytical Services Unit of Sosprocan (University of Cantabria) following UNE-EN 1484 with a total organic carbon Shimadzu TOC-V Analyzer, applying the difference method Total Organic Carbon=Total Carbon–Total Inorganic Carbon (TOC=TC-TIC). Calibration was done using five dissolutions from 5 to 200 mg/l DOC. Accuracy was measured analysing patron dissolutions (50 and 100 mg/l TOC) each 15 samples and a blank solution each 5 samples. Element concentrations were determined by Metal Analysis Center of Scientific and Technological Center (University of Barcelona) using an Agilent 7500CE inductively coupled plasma-mass spectrometry (ICP-MS) equipment in helium-collision mode and by a Perkin Elmer Optima 3200 RL inductively coupled plasma-optical emission spectrometry (ICP-OES) equipment. Metal standards for ICP-MS analysis of 1000 mg/L were purchased from Merck (Darmstadt, Germany). The Certified Reference Material NASS-5 (Seawater Reference Material for Trace Metals) from NRCC (Ontario, Canada) was analyzed for quality control. Samples were diluted (1:20) with  $\text{HNO}_3$  1% prior to analysis and Rh was added as internal

standard to correct for eventual drift of signal during analysis. The metal concentrations were calculated using external calibration with internal standard correction. The NASS-5 CRM was spiked with the elements at two different concentration levels 1 and 10 ppb. The CRM and the two spiked levels of concentration were measured every 6 samples as quality control. The detection limits for the elements under study (As, Cd, Cr, Cu, Ni, Pb and Zn) were 2, 0.4, 4, 2, 2, 0.4 and 10 µg/l, respectively. All leaching tests were performed in duplicate and the results shown in next tables are the medium value of both data. Prior to the experiments, all sampling and laboratory material was pre-cleaned, acid washed (10 % HNO<sub>3</sub>) and rinsed with Milli-Q water (Direct-Q 5 UV, Merck Millipore).

The data used in this work includes 60 samples from leaching tests with CO<sub>2</sub> acidification (28 samples from the equilibrium leaching tests and 32 samples from column leaching tests) and 24 samples from pH-dependent leaching tests with HNO<sub>3</sub> acidification (18 samples from tests with initial addition and 6 samples from tests with continuous pH-control). Each set of data has been analyzed separately by the SOM methodology (Figure 1).

The data analysis included quantification of As, Cd, Cr, Cu, Ni, Pb, Zn as well as the mobilization and concentration of Dissolved Organic Carbon (DOC). These variables were chosen to evaluate the contaminants released into the seawater because of leaked CO<sub>2</sub> coming into contact with contaminated sediments. The complete dataset with the values of the eight variables obtained in the different leaching tests is provided in Table 2 and Table 3.

### **Self-Organizing Maps (SOMs)**

The SOM tool applied to the environmental classification of sediments has been previously used by the authors; in these works (Alvarez-Guerra, 2008, 2010), the SOM it is show as an effective tool for the integration of multiple physical, chemical and ecotoxicological variables in order to classify different sites under study according to their similar sediment quality. Details about the methodology background and use of the SOM are described in these previous articles. Briefly, a SOM is a statistical tool based on a neural network with the SOM considered a map that consists of units (neurons) organized on a regular grid, usually a 2-dimensional hexagonal grid. Each neuron is represented by a weighted vector (prototype vector or codebook vector) whose dimension is equal to the dimension of the input space. The SOM Toolbox for

Matlab (version 2) was used to carry out the analysis, which was based on unsupervised learning and was trained using the Kohonen algorithm (Vesanto et al. 1999; Kohonen 1998).

This methodology uses two distinct phases: the initialization, where the simple vectors of the input dataset are presented to the SOM as a whole, and the training steps that involves iterative calculating and comparing Euclidean distances between each vector and all the weigh vectors of the SOM (Vesanto et al., 1999). The neuron with the input vector at minimum distance to the weigh vector was chosen as the Best-Matching Unit (BMU) (Álvarez-Guerra et al. 2008). In each training step, the weight vectors were updated in such a way that the new weight vectors are weighted averages of the input data vectors. During this iterative training, the SOM behaves like a flexible net that folds onto the ‘cloud’ formed by the input data with BMUs of similar data samples being closely co-located on the final map grid (Vesanto et al. 1999; Álvarez-Guerra et al. 2008).

The SOM analysis displays the obtained results in a map. This map shows which unit is the BMU inside each element in the input data (in this work, the different leaching tests samples). As the iterations described above proceed, the samples that exhibit similar values of the evaluated variables are expected to be assigned to the same neuron, while the samples with differing values are expected to be distant from each other. The ‘Component planes’ are the tool to interpret the SOM results, emphasizing identical values of the weight vectors for each component (eight in this work) in each neuron. Simple inspection of a component plane provides an idea of the spread of values of that variable and comparison of component planes allows correlations between variables to be observed (Álvarez-Guerra et al. 2008).

Normalization of variables is of vital importance because of the SOM algorithm uses Euclidean metrics to measure distances between vectors (Vesanto et al. 1999). The Normalization removes the influence of the scalar of measurement of the variables, avoiding variables with high values dominating the maps on account of their greater influence on the Euclidean distances (Álvarez-Guerra et al. 2010). Three normalization methods available in the SOM Toolbox were considered: standardization, which normalizes the variance of each variable to unity and its mean to zero (‘var’); normalization, which scales the variable values in the range 0–1 with a linear transformation (‘range’); and normalization using a logarithmic transformation (‘log’) (Álvarez-Guerra et al. 2008).

The quantization error (QE) and the topographic error (TE) are two criteria used to evaluate the quality of SOMs obtained, permitting comparison between the suitability of the various normalization methods (Vesanto et al. 1999; Álvarez-Guerra et al. 2008). QE is the average distance between each data vector and its BMU and, thus, measures map resolution (Kohonen 2001; Álvarez-Guerra et al. 2010). TE is used as a measure of topology preservation; it represents the proportion of all data vectors for which the first and the second BMUs are not adjacent (Kiviluto 1996; Álvarez-Guerra et al. 2010).

The map size is important in SOMs in detecting any deviation in the data. If the map is too large, the SOM can be over-fitted, but if the map is too small, some differences cannot be shown (Álvarez-Guerra et al. 2010, 2008; Lee et al. 2006; Leflaive et al. 2005).

The algorithm proposed by Alhoniemi et al. (2002) was applied to decide the size of the SOM. In this algorithm, the optimum map size is estimated to be five times the square root of the number of the input data vectors, and then is further refined according to the ratio of the two largest eigenvalues of the input (Álvarez-Guerra et al. 2010). Therefore, each analysis was trained with different map sizes, and the optimum map size was determined on the basis of the minimum QE and minimum TE. The k-means cluster analysis method (MacQueen et al. 1967), which minimizes the sum of the distances between each data vector and the center of its cluster, was used to group neurons of the trained map into a smaller number of clusters that represent similar behaviors (Vesanto and Alhoniemi, 2000). Detailed information about SOM is included in the Supplementary Information.

## **RESULTS AND DISCUSSION**

### **Classification of equilibrium and column leaching tests with CO<sub>2</sub>-acidification**

The results of QE and TE for the three normalization methods applied and different map sizes are shown in Table 4.

'Range' was the normalization method that obtained the lowest values of QE and TE. A 49-unit map ( $7 \times 7$ ) was selected as the best compromise between a low QE and an acceptable number of neurons, similar to the size of the 34-unit map proposed by the Alhoniemi et al. (2002) algorithm. Interestingly, in this case TE was zero, so the map preserved the topology of the input data very well (Kohonen 2001). Figure 2 represents the SOM of  $7 \times 7$  units obtained. The application of the k-means algorithm to the

trained map classified the samples into five clusters (Clusters I–V). Figure 3 shows the component planes of the SOM for the eight solubilized constituents from the equilibrium and column leaching tests.

Cluster I grouped all of the column leaching tests (Ec) at the most acidic conditions (pH 5) for all the values of L/S evaluated in this test (0.1, 0.2, 0.5, 1, 2, 4, 5 and 10). The main characteristic of the leaching test of this cluster was that these samples showed the highest levels of mobilization of Cu, Pb and Zn (Figure 3).

Cluster II grouped the equilibrium leaching tests (Eq) at pH 5 at low L/S ratios (2, 4 and 10). This cluster was characterized by the highest release of Cd and Ni. Cu, Cd, Ni, Pb and Zn showed higher releases at pH 5 and values of the L/S ratio lower than 15 in both equilibrium and column leaching tests. A decreasing amount of metal-release with neutral and slightly alkaline pH values was observed for these metals. This is thought to be related to the higher adsorption of some pollutants to soil and sediments at higher pH values (Payán et al. 2012b; Voegelin et al. 2003).

Cluster III included samples from both leaching tests. This cluster contained all of the column leaching test samples at pH 6 and a number of those at pH 7 (L/S=0.2, 0.5, 1, 2, 4 and 10) and pH 8 (L/S=4 and 10). Furthermore, equilibrium leaching test samples for the highest values of the L/S ratio (30 and 40) at all pH values and equilibrium leaching test samples for the L/S ratio of 10 at pH values of 6 and 7 were placed in this cluster. Therefore, this cluster collected samples at pH values of 6 and 7 at L/S ratios lower than 10 in the column leaching test and samples at the same pH at L/S ratios higher than 10 in the equilibrium leaching test. This cluster was characterized by minimum values of solubilization for all variables evaluated (Figure 3). This could be because this cluster grouped the highest values of the L/S ratio for both leaching tests and when the exchangeable fraction has been depleted, the dilution of leachates is more accentuated as the L/S ratio increases (Payán et al. 2012a; Ndiba and Axe 2010).

Cluster IV showed a similar situation to Cluster III. Here, column leaching test samples at elevated pH (7 and 8) for low values of the L/S ratio (0.1 at pH 7 and 0.1, 0.2, 0.5, 1 and 2 at pH 8) were found. Also located here were equilibrium leaching test samples at circum-neutral to slightly alkaline pH (6, 7 and 8) at L/S ratios of 2 and 4, and L/S = 10 for pH 8. The cluster comprised the samples at pH values between 7 and 8 from the lowest values of the L/S (0.1 to 2) in the column leaching test, and samples at pH 8 from values of the L/S of 2 and above in the equilibrium leaching test. The results additionally show that these samples produced elevated concentration of DOC and As. DOC was mainly leached in alkaline (pH 8) conditions

with low values of the L/S ratio (0.1–1 l/kg in column tests and 2–4 l/kg in equilibrium tests), that approached typical pore water solutions. Solubilization of organic matter was responsible for the decreased releases at high values of the L/S that can be further attributed to the decreased availability of DOC after its initial dissolution (Payán et al. 2012b). Arsenic displayed a similar trend in leaching behavior, which was associated with organic matter with the highest releases at higher pH values (7 and 8) and lower values of the L/S (2–4). We highlight that As could also be mobilized after dissolution of oxides (Achard et al. 2012).

Cluster V contained samples of all pH values with L/S ratios of 15 and 20 in the equilibrium leaching test and samples that exhibited the maximum levels of Cr mobilization. The amphoteric character of Cr leads to it leaching in both acidic and alkaline conditions.

The maximum release of Ni and Cr were observed in equilibrium leaching tests whereas the Cu, Zn and Pb were found to mobilize more readily during column leaching tests. Cd, As and DOC presented similar release patterns in both of the included leaching tests.

Figure 4 shows a qualitative map where the three variables analyzed in this paper (leaching test, value of pH and L/S) are summarized for each cluster. Clusters I and III simulated advective flow of acidified seawater through the sediment column and the results highlight the release of Cu, Pb and Zn in acidic conditions at low L/S values. Clusters II, IV and V simulate CO<sub>2</sub> bubbling over contaminated sediment and show high releases of Cd, Ni, Cr and As at low-to-medium values of L/S across the entire pH range.

### **Classification of pH-dependent leaching tests with HNO<sub>3</sub>-acidification**

The results of QE and TE for the three normalization methods applied and the different map sizes are summarized in Table 5.

“Range” was again the normalization method that obtained the lowest values of QE and TE. A 24-unit map (6 × 4) was selected as the best compromise between a low QE and a number of neurons that matched the 24-unit map size proposed by the Alhoniemi et al. (2002) algorithm. TE was again zero, indicating that the map preserved the topology of the input data very well (Kohonen 2001). Figure 5 shows the SOM of 6 × 4 units that was obtained.

The application of the k-means algorithm to cluster the trained map classified the samples into five clusters (Clusters I-V) (Figure 5). Figure 6 shows the component planes of the SOM for the eight mobilized constituents from the pH-dependent leaching tests.

Cluster I grouped pH-dependent leaching test samples with pH in the range 4–11. Additionally, aside from the sample at pH 4, all of the pH-dependent tests with continuous pH-control (Edc) samples were located in this cluster. The main characteristic of the results of leaching tests in this cluster was that these samples showed intermediate values for solubilization of DOC, Cu and As and minimum solubilization of the rest of the metals. These results are explained by the neutral and alkaline conditions grouped in this cluster (Figure 6).

Cluster II collected the samples for pH-dependent tests with initial addition (Ed) where alkaline values of pH were simulated. This cluster was characterized by a high release of DOC and As. DOC is known to be released in alkaline solutions because of the higher negative charges on both organic matter and soil surfaces that cause the particles to repel each other (You et al. 1999). The release trend of As was similar to that of DOC, showing a maximum concentration and a high release of As in alkaline conditions. Again, this is due to the negatively charged surfaces above the point of zero charge; above this point, the sorption of anions is less favorable (Rigol et al. 2009).

Cluster III grouped the pH-dependent test with initial addition (Ed) samples for pH values between 3.97 and 4.42. Intermediate values of release for all variables evaluated were located in this cluster.

Cluster IV comprises only samples of pH dependence test with initial addition where pH was found between 0.6 and 2.49. The main characteristic of the leaching test of this cluster was that these samples showed the highest levels of leached Cr and Ni (Figure 6).

The samples which have the highest acid pH for both tests are grouped in cluster V (pH=4 for pH dependence test with continuous pH-control, and pH=0.27 for pH dependence test with initial addition). The maximum release of Cd, Cu, Pb, and Zn are located in this cluster.

The maximum leaching rates of Cd, Cr, Cu, Ni, Pb, and Zn were observed at pH ranged from 0 to 4 (clusters IV and V). The release of Cr, Ni, Pb and Zn at these conditions is consistent with the observation that in acidic conditions, the solid sediment surfaces are positively charged and metal-sorption is not

avored. Furthermore, dissolution of organo-metallic complexes is expected in these conditions leading to a higher metal-release than in alkaline conditions. In this work, Cu release is higher at acidic pH values due to the low sorption of this metal in these acidic conditions (Güngör and Bekbolet 2010; Impellitteri et al. 2002; Almås et al. 2000).

The maximum release of all variables evaluated (a worst-case scenario) took place in the pH-dependent test with initial addition (where the pH condition is fixed initially). The release under this testing regime was higher than that expected for a pH-dependent test with continuous pH-control.

Figure 7 shows the qualitative map for the pH-dependent leaching tests with the pH, the L/S ratio and the leaching test for each obtained cluster.

## CONCLUSIONS

This paper used a SOM-based methodology for interpreting and analyzing the information collected from the classification of 60 samples obtained from equilibrium and column leaching laboratory tests using CO<sub>2</sub>-acidified seawater. The combination of the leaching results with the statistical treatment of SOMs provides conclusions about the mobilization of elements from contaminated seabed sediments because of CO<sub>2</sub> leakages and, for example, illustrated that for Ni and Cr the mobilization is higher in equilibrium leaching tests at L/S = 10 and pH 5 for Ni, and at the L/S ratio of 20 at all values of pH for Cr.

For Cu, Zn and Pb, the highest risk of mobilization was originated in column leaching tests at pH 5 and at L/S ratios of 2, 4, 5 and 10. The risk of mobilization of Cd, As and DOC was present in both tests. However, while the maximum DOC mobilization was found in column leaching tests with a pH of seawater (pH=8) and a low L/S ratio, Cd and As presented a stronger leachability in equilibrium leaching tests. Acidic conditions (pH 5 at the ratio L/S of 10 and pH values of 6 and 7 at the ratio L/S of 2 and 4) were responsible for the highest levels of mobilization of other elements (Cd and As).

The analysis of 24 samples obtained from pH-dependent leaching tests using HNO<sub>3</sub>-acidified seawater at a constant L/S value of 10 showed that the maximum mobilization of DOC, As, Cd, Cr, Cu, Ni, Pb and Zn variables was produced in samples of pH-dependent leaching tests with initial addition. For all studied

elements except As, a more acidic sample led to a higher release of elements. Conversely, the release of DOC and As was higher in alkaline conditions.

The results described herein are useful for simulating element-release from contaminated sediment in contact with acidified seawater under different environmental conditions. This scenario could equally apply to marine acidification caused by CO<sub>2</sub> leakages from CCS technologies as well as arising from other accidental spills of acid.

Finally, the SOM-method has demonstrated its advantage as a powerful visualization tool that enables analysis of the impact on a number of variables.

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### **COMPLIANCE WITH ETHICAL STANDARDS**

The authors declare that they have no conflict of interest.

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## Figures

### Assessment by Self-Organizing Maps of element-release from sediments in contact with acidified seawater in laboratory leaching test conditions

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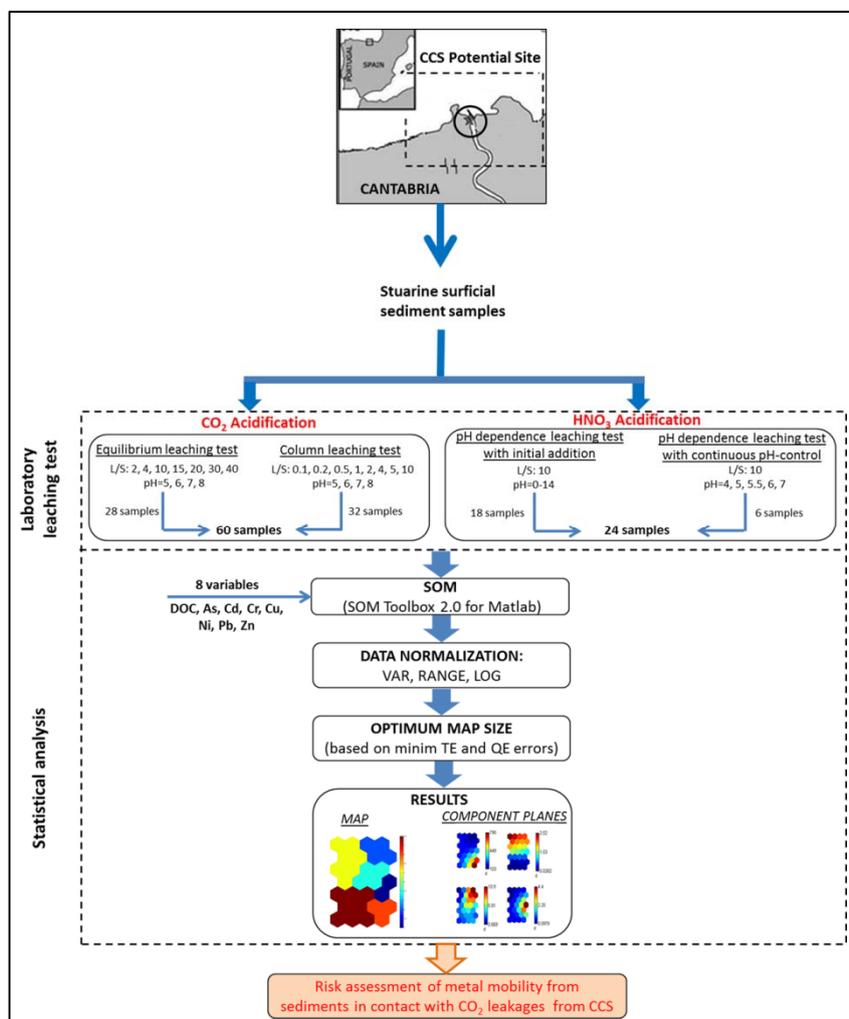


Fig1. Schematic representation of the methodology followed in this study.

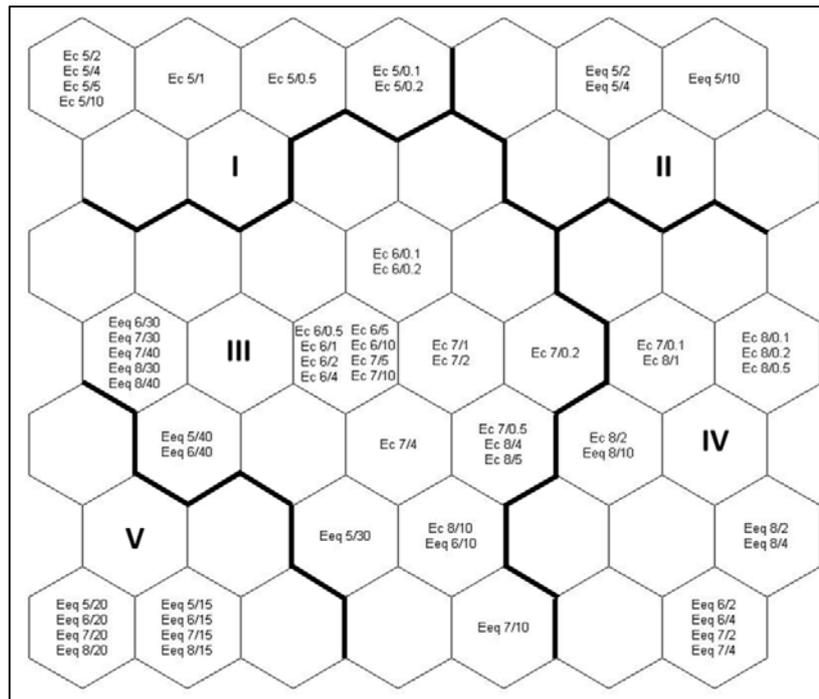


Fig2. Distribution of equilibrium and column leaching tests acidified with CO<sub>2</sub> samples. The 5 clusters (I-V) have been derived from the *k*-means algorithm applied to the trained SOM. The labels in the hexagons of the map show the BMU corresponding to each leaching test sample.

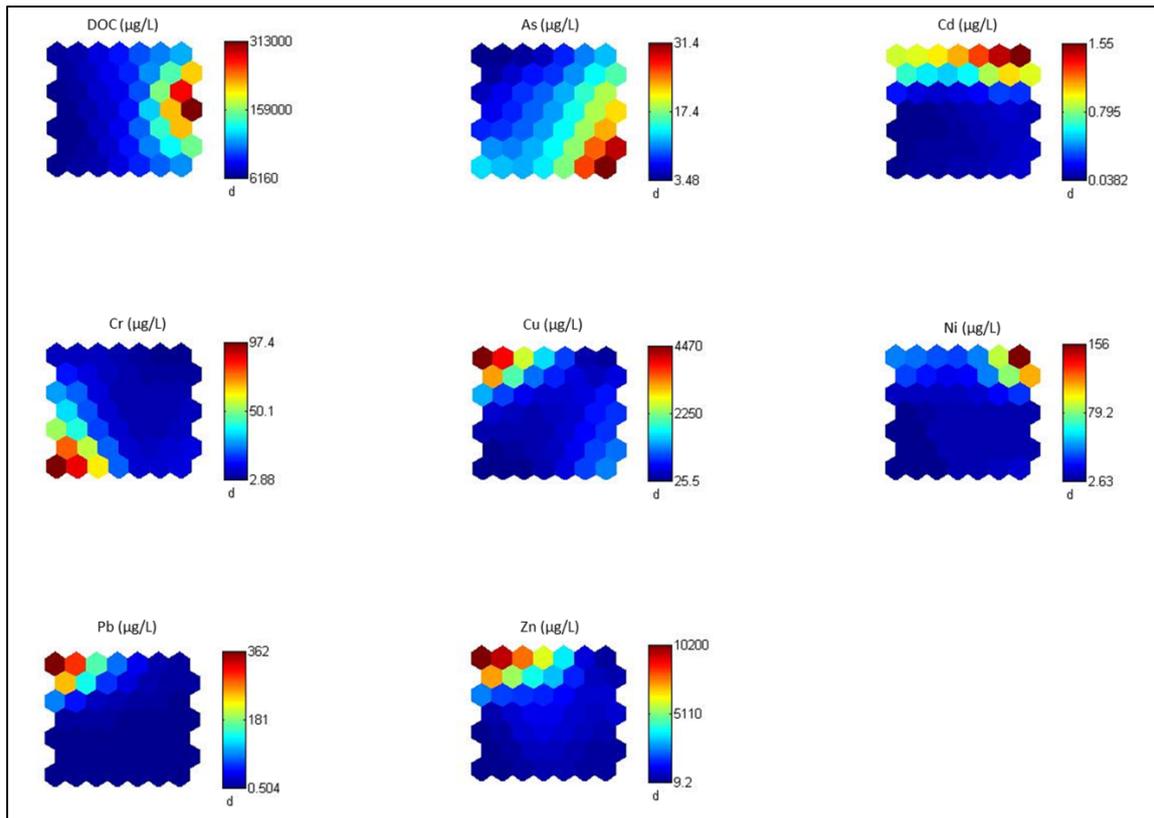


Fig3. Component planes of the SOM for the 8 input variables. Each map corresponding to one variable (component) should be compared to the map representing the distribution of the equilibrium and column leaching tests acidified with  $\text{CO}_2$  samples presented in Figure 2; hexagons in the same place on different component planes correspond to the same map unit. The colors indicate the value of the component in the weight vector of each unit of the map, according to the color bars on the right.

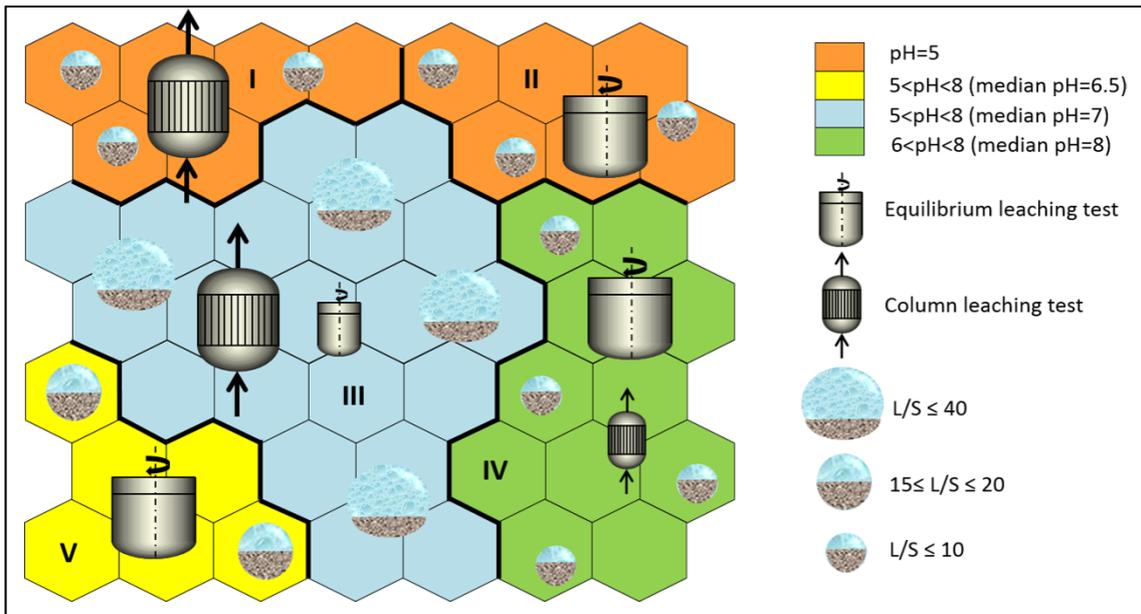


Fig4. Qualitative map for equilibrium and column leaching tests with CO<sub>2</sub> acidification. Clusters are characterized by the pH (color), by the liquid to solid (L/S) ratio with higher sizes of bubbles meaning higher L/S ratios and by the leaching contact, represented by reactors; in clusters with both of the reactors, their relative size is identified with the number of samples of each contact in the cluster.

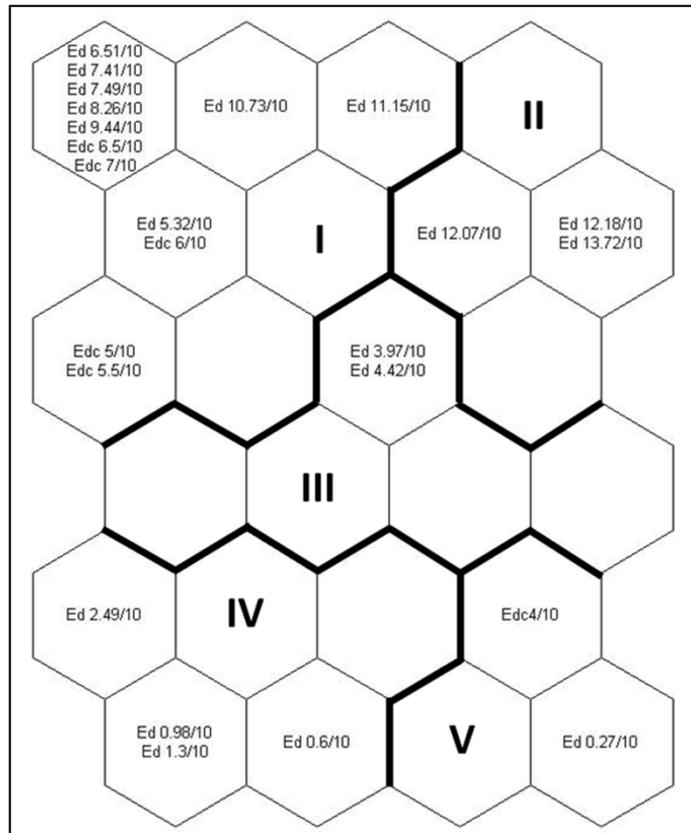


Fig5. Distribution of the pH dependence leaching test acidified with HNO<sub>3</sub> samples. The 5 clusters (I-V) have been derived from the *k*-means algorithm applied to the trained SOM. The labels added to the hexagons of the map indicate the BMU corresponding to each leaching test sample.

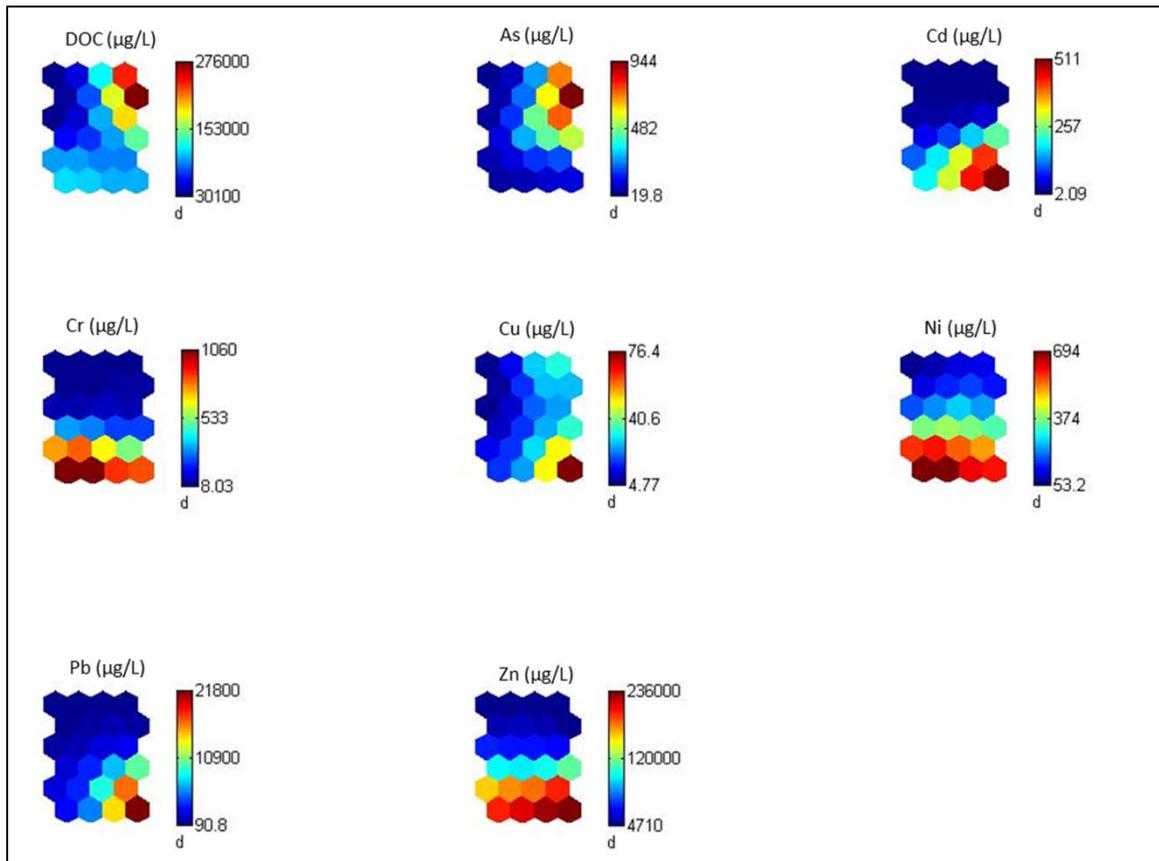


Fig6. Component planes of the SOM for the 8 input variables. Each map corresponding to one variable (component) should be compared to the map representing the distribution of the pH dependence leaching tests acidified with  $\text{HNO}_3$  samples presented in Figure 5; hexagons in the same place on different component planes correspond to the same map unit. The colors indicate the value of the component in the weight vector of each unit of the map according to the color bars on the right.

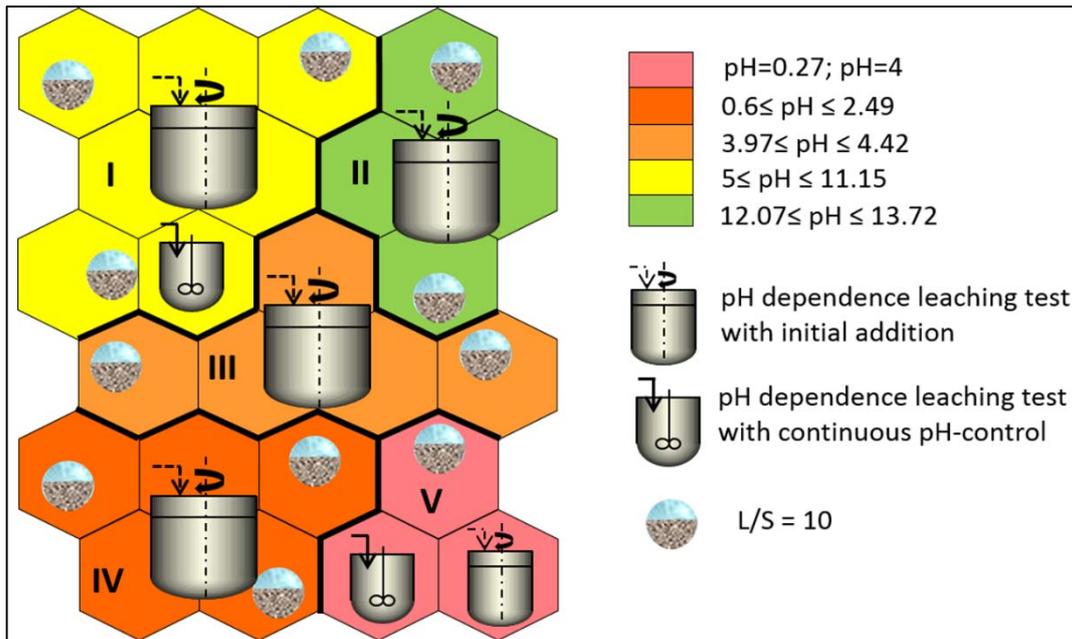


Fig7. Qualitative map for the pH dependence leaching tests with  $\text{HNO}_3$  acidification. Clusters are characterized by the pH (color), and by the leaching contact, represented by reactors; in clusters with both of the reactors, their relative size is identified with the number of samples of each contact in the cluster. The liquid to solid ratio is the same in all clusters ( $L/S=10$ ).

## Tables

### Assessment by Self-Organizing Maps of element-release from sediments in contact with acidified seawater in laboratory leaching test conditions

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TABLE 1. Main characteristics of the LCA and modelling risk assessment tools used for CCS evaluation.

Risk assessment tool applied	Phases of CCS analyzed	Leakages in storage phase taken into account	Parameters used for risk assessment as consequence of leakages	Reference
Life Cycle Analysis (LCA)	Capture, transport and storage	Yes	Leakage ratio	BMU (2008)
	Capture, transport and storage	No	-	Hertwich et al. (2008)
	Capture, transport and storage	No	-	Pehnt and Henkel (2009)
	Capture, transport and storage	No	-	Nie et al. (2011)
	Capture, transport and storage	No	-	Singh et al. (2011)
	Capture, transport and storage	Yes	Leakage ratio	Hussain et al. (2013)
	Capture, transport and storage	No	-	Iribarren et al. (2013)
	Capture & transport	No	-	Akai et al. (1997)
	Capture & transport	No	-	Nagashima et al. (2011)
	Capture & transport	No	-	Singh et al. (2012)
	Capture	No	-	Khoo et al. (2006)
	Capture	No	-	Viebahn et al. (2007)
	Storage	No	-	Chadwick et al. (2004)
	Storage	Yes	Degradation of aquifer properties	Korre et al. (2009)
	Storage	Yes	Leakage ratio	Hou et al. (2012)
Modelling	Storage	Yes	Alterations on groundwater	Birkholzer et al. (2008)
			Metals mobilization	
			pH variations	
	Transport & storage	Yes	Probability of leakage occurrence	Hill et al. (2011)
	Storage	Yes	Degradation of aquifer properties	Keating et al. (2011)
	Transportation	No	-	Mazzoldi et al. (2011)
Storage	No	-	Xiao et al. (2009)	
Modelling and Simulation	Storage	Yes	Leakage ratio	Meyer et al. (2009)
	Storage	Yes	Degradation of aquifer properties	Sakamoto et al. (2011)
Techno-economic Modelling	Capture, transport and storage	No	-	Van der Zwaan and Gerlagh (2009)

Table 2. Data set of values of the 8 variables in the 60 samples from equilibrium and column leaching tests with CO<sub>2</sub> acidified seawater.

SAMPLE	VARIABLES (µg/L)							
	Cr	Ni	Cu	Zn	As	Cd	Pb	DOC (10 <sup>-4</sup> )
<b>Ec5/0.1</b>	6.93	30.3	1370	6880	3.41	1.59	43.8	6.85
<b>Ec5/0.2</b>	7.26	35.1	1710	7890	3.20	1.31	86.8	4.70
<b>Ec5/0.5</b>	7.15	38.6	3170	9110	3.60	1.02	188	2.16
<b>Ec5/1</b>	7.21	38.6	3870	9690	3.61	0.92	258	1.63
<b>Ec5/2</b>	7.37	40.0	4210	10720	3.48	1.08	365	1.59
<b>Ec5/4</b>	7.66	43.6	4890	11500	3.38	0.89	424	1.42
<b>Ec5/5</b>	7.77	43.2	5100	11160	3.40	0.90	439	1.09
<b>Ec5/10</b>	7.98	39.0	5000	9670	3.26	0.90	376	1.79
<b>Ec6/0.1</b>	6.18	11.4	399	1710	9.81	0.09	24.7	5.76
<b>Ec6/0.2</b>	6.15	9.18	296	1870	9.39	0.07	14.8	3.30
<b>Ec6/0.5</b>	6.09	8.27	215	1620	8.64	0.05	8.18	2.10
<b>Ec6/1</b>	6.06	8.58	176	1430	8.43	0.05	7.34	4.58
<b>Ec6/2</b>	6.02	8.19	150.	1230	8.39	0.05	4.86	3.20
<b>Ec6/4</b>	5.95	8.88	138	1270	8.29	0.05	4.25	0.827
<b>Ec6/5</b>	5.90	9.18	135	1230	8.33	0.06	3.91	2.67
<b>Ec6/10</b>	5.78	10.6	134	792	8.20	0.06	4.08	1.00
<b>Ec7/0.1</b>	6.04	12.5	286	770	15.4	0.23	8.91	2.42
<b>Ec7/0.2</b>	6.37	10.8	241	752	14.3	0.22	6.25	1.10
<b>Ec7/0.5</b>	5.95	9.49	205	754	12.9	0.14	4.02	6.18
<b>Ec7/1</b>	5.77	9.73	185	890	12.0	0.13	3.30	4.10
<b>Ec7/2</b>	5.58	8.93	169	731	11.4	0.09	2.86	6.65
<b>Ec7/4</b>	5.47	9.32	160	792	10.4	0.08	2.29	1.69
<b>Ec7/5</b>	5.48	9.46	153	818	10.2	0.08	2.11	1.40
<b>Ec7/10</b>	5.43	9.27	139	611	9.28	0.06	2.23	1.73
<b>Ec8/0.1</b>	8.66	9.76	997	1100	24.6	0.12	4.68	55.9
<b>Ec8/0.2</b>	8.45	7.98	939	861	22.6	0.09	3.53	40.9
<b>Ec8/0.5</b>	7.82	6.62	840	640	20.5	0.06	2.81	32.3
<b>Ec8/1</b>	7.35	5.98	723	522	18.6	0.05	2.17	19.5
<b>Ec8/2</b>	6.79	5.97	582	466	16.7	0.05	1.85	13.6
<b>Ec8/4</b>	6.35	5.97	437	523	14.8	0.04	1.74	6.90
<b>Ec8/5</b>	6.23	5.97	395	546	14.2	0.04	1.62	6.46
<b>Ec8/10</b>	6.07	5.43	305	446	13.0	0.04	1.94	4.85

Ec a/b: samples from column leaching test (Ec) at pH=a, and L/S=b.

Eeq a/b: samples from equilibrium leaching test (Eeq) at pH=a, and L/S=b.

Table 2 (Cont.). Data set of values of the 8 variables in the 60 samples from equilibrium and column leaching tests with CO<sub>2</sub> acidified seawater.

SAMPLE	VARIABLES (µg/L)							
	Cr	Ni	Cu	Zn	As	Cd	Pb	DOC (10 <sup>-4</sup> )
Eeq5/2	1.84	13.5	64.7	355	6.92	1.45	8.30	8.90
Eeq5/4	4.74	42.1	25.0	124	13.4	1.50	9.38	6.58
Eeq5/10	1.48	339.6	121	69.5	13.0	1.90	8.35	7.78
Eeq5/15	83.7	4.11	13.8	9.72	15.0	0.06	0.44	1.38
Eeq5/20	104	4.09	15.0	9.86	18.0	0.01	0.33	0.740
Eeq5/30	34.0	8.27	67.8	257	12.0	0.04	2.10	0.810
Eeq5/40	40.0	6.14	85.7	17.4	11.0	0.06	5.00	0.310
Eeq6/2	11.2	18.4	1290	580	34.4	0.26	4.74	3.99
Eeq6/4	7.29	14.5	844	157	34.4	0.07	8.57	3.74
Eeq6/15	85.1	2.10	13.2	11.3	10.0	0.23	0.81	0.98
Eeq6/10	5.42	22.0	191	578	15.3	0.13	5.72	3.72
Eeq6/20	109	2.18	20.4	1.19	13.0	0.03	0.17	0.82
Eeq6/30	35.9	3.65	268	60.9	5.12	0.03	2.43	0.52
Eeq6/40	42.5	2.64	162	8.12	6.09	0.01	1.73	0.19
Eeq7/2	13.3	3.53	1180	31.7	32.0	0.15	1.99	6.47
Eeq7/4	9.39	28.7	1320	153	33.8	0.08	2.39	4.21
Eeq7/10	6.17	4.20	272.2	46.2	17.4	0.13	1.66	2.89
Eeq7/15	86.8	1.73	12.1	2.61	9.16	0.10	0.11	1.25
Eeq7/20	115.0	2.05	8.49	0.90	13.2	0.09	0.09	1.07
Eeq7/30	32.01	2.68	250	39.6	3.94	0.01	0.87	0.61
Eeq7/40	36.38	2.09	336	17.1	4.65	0.01	0.79	0.28
Eeq8/2	14.6	2.35	1000	23.8	31.7	0.22	0.88	23.3
Eeq8/4	11.2	2.38	1400	27.5	32.5	0.11	0.64	15.0
Eeq8/10	7.31	2.57	454	23.7	20.1	0.16	0.75	12.7
Eeq8/15	90.1	1.70	11.2	6.66	9.50	0.04	0.43	1.52
Eeq8/20	115.3	1.94	9.24	0.20	13.0	0.02	0.47	0.95
Eeq8/30	38.0	2.69	352	18.3	4.81	0.02	2.73	0.45
Eeq8/40	45.4	1.55	554	3.39	5.29	0.04	2.29	0.19

Ec a/b: samples from column leaching test (Ec) at pH=a, and L/S=b.

Eeq a/b: samples from equilibrium leaching test (Eeq) at pH=a, and L/S=b.

Table 3. Data set of values of the 8 variables in the 24 samples from pH dependence leaching tests with HNO<sub>3</sub> acidified seawater.

SAMPLE	VARIABLE (µg/L)							
	Cr	Ni	Cu	Zn	As	Cd	Pb(10 <sup>-4</sup> )	DOC(10 <sup>-4</sup> )
Ed0.27/10	1290	732	116	257450	51.9	547	2.66	13.7
Ed0.6/10	1280	720	24.2	243870	36.1	439	0.428	11.9
Ed0.98/10	1270	724	8.93	238520	37.8	242	0.224	12.2
Ed1.3/10	1140	809	24.5	188740	37.0	101	0.204	11.7
Ed2.49/10	536	506	6.62	127710	71.2	18.5	0.134	10.5
Ed3.97/10	130	426	23.0	48640	560	10.8	0.193	5.02
Ed4.42/10	13.4	388	15.9	36060	593	4.31	0.285	4.23
Ed5.32/10	2.68	170	2.45	7950	24.3	1.65	0.019	3.27
Ed6.51/10	1.52	47.7	1.89	506	14.9	0.33	0.001	3.08
Ed7.41/10	6.82	2.79	2.76	23.1	9.98	1.16	0.001	1.80
Ed7.49/10	20.3	6.01	11.7	111	8.76	0.82	0.000	1.62
Ed8.26/10	7.32	12.6	4.23	873	12.0	1.36	0.002	3.13
Ed9.44/10	1.62	8.33	1.52	30.1	15.5	0.34	0.000	3.59
Ed10.73/10	43.6	84.9	12.8	2278	55.6	3.72	0.004	10.9
Ed11.15/10	5.70	78.64	82.0	160	81.7	1.24	0.004	14.7
Ed12.07/10	12.0	58.3	16.2	54.5	469	0.44	0.001	20.5
Ed12.18/10	13.8	99.2	28.2	362	1260	0.31	0.006	38.9
Ed13.72/10	35.9	105	23.6	580	1360	1.35	0.008	36.0
Edc4/10	8.73	373	27.6	210180	148	506	1.95	4.01
Edc5/10	1.01	282	2.45	93220	14.7	43.8	0.155	2.27
Edc5.5/10	1.27	228	1.80	51450	15.0	14.4	0.040	1.74
Edc6/10	2.23	118	2.58	12230	4.39	3.02	0.011	0.999
Edc6.5/10	1.03	35.9	3.73	1370	3.31	0.24	0.002	1.56
Edc7/10	0.66	12.8	2.07	283	2.21	0.19	0.001	0.642

Ed a/b: samples from pH dependence leaching test with initial addition (Ed) at pH=a, and L/S=b.

Edc a/b: samples from pH dependence leaching test with continuous pH-control (Edc) at pH=a, and L/S=b.

TABLE 4. Quality measures (quantization error (QE) and topographic error (TE)) of the SOMs of different map sizes obtained with three normalizations of the data (n=60).

Map Size	Normalization LOG		Normalization RANGE		Normalization VAR	
	QE	TE	QE	TE	QE	TE
6X6=36	1.294	0	0.152	0.05	0.705	0.017
7X5=35	1.323	0.033	0.153	0.017	0.666	0.017
7X6=42	1.198	0.017	0.143	0	0.610	0.017
7x7=49	1.102	0.017	0.119	0	0.527	0.05
8x5=40	1.191	0.017	0.138	0	0.649	0
8X6=48	1.091	0.017	0.121	0.017	0.532	0.033
9x4=36	1.249	0.033	0.154	0	0.684	0.017
9X5=45	1.122	0.033	0.129	0.033	0.563	0.017

TABLE 5. Quality measures (quantization error (QE) and topographic error (TE)) of the SOMs of different map sizes obtained with three normalizations of the data (n=24).

Map Size	Normalization LOG		Normalization RANGE		Normalization VAR	
	<i>QE</i>	<i>TE</i>	<i>QE</i>	<i>TE</i>	<i>QE</i>	<i>TE</i>
5x4=20	2.556	0	0.257	0	0.915	0
5x5=25	2.342	0	0.231	0	0.865	0.042
6x4=24	2.331	0	0.225	0	0.796	0
6x5=30	2.103	0.042	0.204	0	0.691	0
7x3=21	2.444	0	0.231	0.042	0.79	0
7x4=28	2.148	0	0.196	0	0.697	0
8x3=24	2.181	0	0.223	0.083	0.771	0.083