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INFLUENCE OF A CO₂ LONG TERM EXPOSURE ON THE MOBILISATION AND SPECIATION OF METALS IN SOILS

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ABSTRACT

This study investigates the potential risks associated with high levels and long term exposure of carbon dioxide (CO₂) on the mobility and speciation of exchangeable metals in soils. CO₂ incubation batch experiments at high pressure and temperature coupled with geochemical modelling were carried out to elucidate the behavior and mobilisation of metals and the response of soil chemical parameters as a result of long term CO₂ exposure. A t-Student analysis was performed to ascertain whether differences in the mean concentration of exchangeable metals in soils before and after CO₂-incubations are attributable to increase of metal mobilisation because of the long term CO₂ exposure. The t-Student revealed the CO₂ long term incubation was statistically significant (p<0.05) for the exchangeable concentration of Ni, Zn, and Pb. The CO₂-soil incubation induces the acidification of the pore water of soils via CO₂ hydrolysis and as a consequence, it increases the exchangeable concentration of Ni, Zn, and Pb in the soils. As, Al, Cr, Cu, and Fe show a different mobilisation pattern depending on the moisture content in soils. Al³⁺, Fe²⁺, Cr³⁺, and Cu²⁺ as free cations, As as HAsO₂, Pb²⁺ and PbHCO₃⁻, Zn²⁺ and ZnHCO₃⁻, are predicted to be the predominant aqueous complexes in the pore water of the incubated soils.

Keywords: CO₂ exposure; t-Student; acidification; exchangeable metals; soil pore water; CO₂ hydrolysis.
1. INTRODUCTION

Carbon dioxide capture and storage (CCS) is increasingly gaining attention as a strategy for the abatement of greenhouse gas emissions (Van der Zwaan et al, 2009). CCS involves capturing CO$_2$ at coal- or gas-fired power plants and industrial facilities (steel mills, cement plants, refineries, etc), transporting it by pipeline or ship to a storage location, and injecting into a suitable geological formation for long-term storage.

Potential CO$_2$ leakages across the CCS chain, particularly transportation and storage, need to be addressed prior to deployment (Damen et al., 2003; Gale and Davison, 2004; Steeneveldt et al., 2006). A major risk related to CO$_2$ transportation is a pipeline failure, which could be caused by third party interference, acidic gas corrosion, and/or construction or material defects (Gale and Davison, 2004; Koornneef et al., 2009), whereas potential CO$_2$ leakage from a geological storage reservoir could be produced by a diffuse leakage through caprock formations, by a concentrated CO$_2$ leakage through natural or induced faults and fractures, and/or by a poorly plugged old abandoned wells (Celia et al., 2005; Damen et al., 2003; Oldenburg and Lewicki, 2005).

Whilst most of the CO$_2$ leakage studies are focused on the impacts on human health and animals (Stenhouse et al., 2009), much less attention has been paid to the influence of CO$_2$, either to a high level exposure or a short-term or small continuous release of CO$_2$ in the surface and subsurface, on soil chemistry. It is acknowledged that high levels of soil CO$_2$ are likely to affect the pH of soil water and have adverse impacts on the chemistry of nutrients (Stenhouse et al., 2009). However, the mobility and speciation of exchangeable metals in the pore (interstitial) water of soils and variations of chemical properties e.g. solubility of metal complexes in the pore water of soils as a consequence of CO$_2$ exposure have not been investigated. The magnitude of determining the effects of CO$_2$ on the speciation of exchangeable metals in soils assumes even greater relevance when considering the toxicity of metals to the environment, e.g. plant growth is highly dependent on their speciation.
Therefore, an understanding of the occurrence, speciation and availability of exchangeable metals in soils is of paramount importance to environmental health, crop production, food and water quality, and ecotoxicology.

In this work, incubation batch experiments were conducted to assess the potential risks associated to high level and long term exposure of CO₂ in soil chemistry parameters and assess the potential impacts of CO₂ in soils. An aqueous and solid speciation model was used to investigate the influence of CO₂ on the pH and on the aqueous and solid speciation of exchangeable metals, namely Al, As, Cr, Cu, Fe, Ni, Pb, and Zn.

2. MATERIALS AND METHODS
2.1. Soil sampling and treatment
The soil sampling was carried out at the Artificial Soil Gassing and Response Detection (ASGARD) field. The ASGARD field (18m×16m) is an artificial soil gassing facility located in a field of permanent pasture at the University of Nottingham’s Sutton Bonington Campus. This facility was designed to observe and monitor the effects of different adjustable CO₂ concentrations on crops and plants and soil geochemistry (Al-Traboulsi et al., 2012). Geologically, the study area is characterised by up to 1.5 m of head deposit overlying mudstones of the Mercia Mudstone. Mineralogical analyses in 2006 showed that quartz was the dominant mineral (>90% of the total dry weight) followed by K-feldspar and albite as minor along with trace amounts of mica, kaolinite, chlorite and hematite (West et al., 2009) with no mineralogical difference between the A horizon (0.15-0.30 m depth) and B horizon (0.45-0.50 m depth) (West et al., 2009). The soil type lies within the Worcester Series and comprises 0.3 m deep sandy clay loam over 0.7 m clay and marl horizon. The top soil layer (~ 0.1 m) contains 8.91% clay, 22.89% silt and 68.2% sand (West et al., 2009).

The ASGARD is a field divided into 12 experimental plots (CO₂ injection), each 2.5 x 2.5 m, to be compared with six untreated reference plots (no CO₂ injection). Because the objective of this study is
to examine the effects of CO$_2$ leakages on soil chemistry, soils were collected from the untreated plots (no CO$_2$ injection) within the top 30 cm soil from the ASGARD site (Figure 1).

Soil samples were oven-dried at 40°C for 7 days and subsequently sieved to < 2 mm. The sieved soils were ground in an IKA Heavy-Duty Analytical Mill, 115 VAC/60 Hz for 3 minutes to obtain homogenous soil matrixes. After this procedure, all the soils were mixed by using a raffle splitter.

The influence of the gravimetric water content ($\theta_m$) of soils in the adsorption of CO$_2$ was also tested. Based on the measured $\theta_m$ (mass basis) of ASGARD soil, soils were saturated with Milli-Q water to obtain ground soils with 20% and 30% $\theta_m$. Three replicates per % $\theta_m$ were performed for each ground soil, amounting into the 20% and 30% $\theta_m$ ground soil sets, respectively. A third soil set consisted of oven-dried ground soil subsamples (no gravimetric water content). An oven-dried soil sample and additional soil samples with the 20% and 30% $\theta_m$, respectively, were not incubated in order to be used as control. The soil $\theta_m$ was determined by heating the soil samples in an oven model Sanyo Gallenkamp OMT at 105°C for 24 h. Soil $\theta_m$ was calculated by weight loss during the process (Heiri et al., 2001) by the following equation:

$$\theta_m = \frac{w_f - w_j}{w} \times 100 \quad \text{(Eq.1)}$$

where, $w_f$ is the weight of the crucible with sample after the 105°C oven heating, $w_j$ is the weight of the crucible with sample before oven drying and $w$ is the weight of the collected soil. Soil samples were then kept in the oven at 550°C for 24 h and subsequently at 950°C for 2h to determine the organic content (OC) and the Carbonate Content (CC) of soils by loss on ignition (LOI$_{550}$ and LOI$_{950}$), respectively according to the following equation (Heiri et al., 2001):

$$LOI_{550} = \left( \frac{d_{w_{550}} - d_{w_{550}}}{d_{w_{550}}} \right) \times 100 \quad \text{(Eq.2)}$$
\[ \text{LOI}_{550} = \left( \frac{dW_{105} - dW_{550}}{dW_{550}} \right) \times 100 \]  
(Eq.3)

where, LOI\(_{550}\) and LOI\(_{950}\) represents LOI at 550ºC and 950ºC, respectively, \(dW_{105}\) represents the dry weight of the sample before combustion, and \(dW_{550}\) and \(dW_{950}\) are the dry weight of the sample after heating to 550ºC and 950ºC, respectively.

2.2. Experimental procedure

CO\(_2\) incubation batch experiments were designed to investigate the soil response at high level and long term exposure of CO\(_2\). In these experiments, CO\(_2\) was introduced as 100% CO\(_2\) into a high pressure/ high temperature Parr reactor model 4843, which constitutes the CO\(_2\)-soil incubation unit. 100 g of soil was placed in each CO\(_2\)-soil incubation.

Because these experiments were aimed at enhance CO\(_2\)-soil uptake, CO\(_2\)-soil interaction was speeded up by increasing the CO\(_2\) partial pressure (\(p_{CO_2}\)) and temperature of soils. To accomplish this, two factors were considered: i) the CO\(_2\) critical point based on the CO\(_2\) gas phase diagram; and ii) the temperature and pressure range to prevent any CO\(_2\) phase-changing. As a result, 3 incubation days under 25.10\(^5\) Pa and 25°C were chosen as no obvious pressure drop was observed during a number of trial incubations under these operational conditions.

2.3. Soil analysis

X-Ray powder Diffraction (XRD) analysis was carried out to define the mineralogical composition of ground soil subsamples to identify changes of the mineralogy as a consequence of CO\(_2\) exposure. The analysis was carried out by using a HILTONBROOKS diffractometer with monochromatic Cu K\(\alpha\)\(_1,2\) radiation operated at 40KV and 20mA, from 4-60° 2\(\theta\), at a step size of 0.05°, and scan rate of 3s/step. The classification of ground soil particles was carried out by a Coulter Laser Scattering analyser employing Fraunhofer diffraction (LS 200, Variable-Speed Fluid Module Plus (VSM+)).
The pH of soils (before and after CO₂ incubation) was measured by using a soil test kit from Palintest Ltd., in aqueous solution at a 1:2 (w/w) soil-to-water ratio followed by equilibration (Stephens, 2002). The accuracy for pH measurement was set at ±0.01, while the accuracy for measuring temperature was ±0.4°C.

The exchangeable fraction of metals in pore water soils was evaluated to determine the role of CO₂ incubation on the exchangeable metal rate. The exchangeable fraction of metals from soils was extracted by adding 25 mL of CaCl₂ (0.01 M) to 5.0 g of soil (Feng et al., 2005). Soil samples with the extractant were placed into centrifuge tubes and shaken overnight at 200r/min. The solutions were centrifuged at 3700 rev/min for 10 min by a Beckman Allegra X-12 Benchtop Centrifuge equipped with an ARIES Smart Balance Swinging Bucket Rotor. After this procedure, the solutions were filtered by glass-fibre filters of 0.2µm pore size and acidified with 50% HNO₃ (100µL) to prevent oxidation of ions and stabilize the metal concentration. Soil solutions were then analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) by the X-SERIES II device from Thermo Fisher SCIENTIFIC. The quantitative analyses were performed with an external calibration, using an external standard of similar matrix to the samples, which covered concentrations range expected forming the calibration lines. The internal correction was carried out by means of an internal standard (In 10 ppb).

The effect of CO₂ exposure was evaluated on i) the mineralogical composition of the ground soils by using XRD and on ii) pH and mobility and speciation of exchangeable metals in the pore water of soils, as determined from the ICP-MS studies. The mobility patterns of exchangeable metals in the pore water of soils as a result of CO₂ incubation were determined by the ratio between the concentrations of elements in the incubated/non-incubated of soils. This ratio is defined as concentration factor (r).
The oven-dried and % θm non-incubated ground soils were used as control in order to ascertain the CO₂ incubation effect on soil chemistry. The results of CO₂ incubation tests and the analyses of soils are presented as average values.

2.4. Statistical analysis

A t-Student statistical test was performed to determine the accuracy of the results and to ascertain statistically whether the mean concentration of exchangeable metals in soils after CO₂-incubations is significant (p≤0.05). The t-Student test was also performed to determine whether the differences in the mean concentration of exchangeable metals in soils before and after CO₂-incubations are attributable to increase of metal molibilisation because of the long term CO₂ exposure. The t-Student was applied to mean concentration (µg/L) from 3 subsamples of the soil, for each element.

2.5. Geochemical modeling

The long term CO₂-incubation process was modelled during the 3 days in order to 1) compare model and experimental results; 2) determine the immediate and gradual response of pH in the water pore of soils during the CO₂ incubation work (3 days) of the oven-dried, 20% θm, and 30% θm ground soils; and to 3) estimate the aqueous speciation of elements in the water pore of soils and the saturation index (SI) with respect to selected minerals and solid phases after the CO₂ incubation.

The PHREEQC code (version 2.0) and the coupled thermodynamic database Lawrence Livermore National Laboratory (LLNL) (Parkhurst and Appelo, 1999) were used to model the long term CO₂-incubations by using the measured concentration of exchangeable metals and the pH value prevalent in the pore water of soils previously to the CO₂ incubation as input data. The CO₂-incubation experimental conditions were also used as input data.

3. RESULTS AND DISCUSSION

3.1 CO₂-soil incubations
The comparison of the pressure control tests with the CO₂ incubations (Figure 2) reveals a high pressure drop in the incubated soils, which is indicative that CO₂ was absorbed in the soil pore water and/or through filling in voids between soil particles along the incubation. These trends were especially pronounced in the CO₂ incubated ground soils with the highest % θm as a result of CO₂ absorption into the pore water of soils. CO₂ produces the acidification of the pore water of soils via CO₂ hydrolysis reaction:

\[
\text{CO}_2 (g) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 (aq) \leftrightarrow \text{HCO}_3^- (aq) + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} (aq) + \text{H}^+ \quad (R1)
\]

CO₂ diffuses through the gas to the pore water of soils where it dissolves. In this mass transfer, CO₂ reacts with H₂O and changes into H₂CO₃, and subsequently it dissociates in HCO₃⁻ + H⁺ and CO₃²⁻ + H⁺ acidifying the pore water of soils.

3.2 Effect of CO₂ exposure on the soil properties

The oven-dried non incubated unground soil, used as control, contains 51% sand, 36% silt, and 13% clay, and has high contents of quartz with feldspar, albite, dolomite, kaolinite, illite, and montmorillonite being the main crystalline phases (Figure 3a). The XRD patterns of the oven-dried ground soil and that of an oven-dried unground soil (Figure 3b) match each other, which indicate that, as expected, the grinding did not significantly modify the mineralogy of the ground soils.

The mineralogical composition of the CO₂ incubated and non-incubated ground soils match each other (Figure 3c). Quartz, the predominant mineral phase of these soil matrixes, as expected, is not sensitive to CO₂ incubation. Similar results were observed in the ASGARD field by West et al. (2009) showing no significant alteration of the mineralogical assemblages from gassed and non-gassed plots. However, it should be noted that this does not rule out minor changes in the mineralogy that may not be detected by XRD. The dissolution of certain soil mineral phases as a consequence of high CO₂ exposure may cause a potential transfer of a given element from the mineral to the soil solution phase reducing the minimum concentration required to be detected by XRD.
The OC and CC content in soils show no significant differences among the incubated and non-incubated ground soil samples, and no trends are observed based on the results (Table 1). This indicates that although CO2 diffuses through the gas to the pore water of soils (Figure 2) and changes into H2CO3, carbonate aqueous complexes remain in solution and do not precipitate.

3.3 Effect of CO2 exposure on the pH of soils

The experimental pH values of soils before and after CO2-incubations are depicted in Table 2. Oven-dried soils show initial pH of the 5.86 whereas 20% θm and 30% θm soils reach pH values of 5.36 and 6.33, respectively.

An important factor should be considered when discussing the experimental pH values after CO2-incubations. As stated in R1, CO2 once diffuses through the gas to the pore water of soils reacts with H2O and changes into H2CO3, and subsequently it dissociates in HCO3⁻ + H⁺ and CO3²⁻ + H⁺ acidifying the pore water of soils. However, the pH of the oven-dried, 20% θm, and the 30% θm incubated soils reached values of 6.45, 7.33, and 8.09 respectively, after CO2-incubations (Table 2). This could be explained as a sharp increase of the pH of pore water of soils when opening the incubation unit to compensate the release of CO2(g) from the reactor, which would lead to a shift of the CO2 hydrolysis equilibrium (R1) as the experiments were carried out under high pressure (25.10⁵ Pa). However, a consumption of H⁺ by mineral dissolution could also lead to an increase of the pH in the batch reactor. A similar trend in the pH change was also observed in by Fu et al (2009). Such a statement was evaluated by comparing the experimental and model pH pattern during the CO2 incubation work (3 days).

Long term CO2-incubation modelling reveals that CO2 causes the acidification of the pore water of soils via CO2 hydrolysis. As can be observed in the pH modelling (Figure 3), the initial pH of the oven-dried (5.86), 20% θm (5.36), and the neutral 30% θm (6.33) non-incubated soils experiences a sharp drop with increasing CO2 even with a small input of gas. The highest drop of the pH occurs during the first hours of the incubation with a gradual decrease along the 2nd incubation day. The
modelled pH variation of the oven-dried, 20% θm, and 30% θm incubated ground soils reaches stability with the soil solution at 2.67, 2.68, and 2.83 values, respectively, along the 3rd incubation day. Therefore, it can be stated that CO₂ causes the acidification of the pore water of soils via CO₂ hydrolysis.

3.4 Effect of CO₂ exposure on the mobility of metals

The concentration of exchangeable metals in soils before and after CO₂-incubations, the concentration factor (r) and Student t-test are shown in Table 3. Based on the concentration factor results, elements can be classified as follows:

Elements with high mobilisation potential in the pore water of soils (r >1.4): Ni, Zn, and Pb

Elements with moderate mobilisation potential pattern (1.0≤r ≤1.4): As, Al, Cr, Cu, and Fe

The concentration of CaCl₂-exchangeable metals in the pore water of soils increases with CO₂ incubation (p<0.05, Table 3). The pore water of the 30% θm incubated ground soil also shows an increase of concentration of CaCl₂-exchangeable metals Zn and Pb (r >1.4) with respect to the 30% θm non-incubated control soil. These patterns are also revealed when comparing the concentration of Ni. Nickel is enriched by a factor of > 8.0 and 6.2 in the 30% and 20% θm incubated soils, respectively, compared to the 30% and 20% θm non-incubated control soils (Table 3), which is supported by the statistically significant difference (p<0.05). The dissolution of the soil crystalline matrix may account for the increase in the concentration of CaCl₂-exchangeable Zn, Ni and Pb in the incubated ground soils.

No mobilisation pattern is shown by As, Al, Cr, Cu and Fe. Arsenic and Cu show high mobilisation potential 30% θm (r >1.4) incubated ground soil and a moderate mobilisation in the 20% θm and oven-dried soils (1.0≤r ≤1.4) after CO₂-incubations. Comparison of the oven-dried soil before and after CO₂ incubation supported by the statistically significant difference (p<0.05), suggests a high mobilisation of Al, Cr, and Fe in the oven-dried incubated soil (r >1.4).
When comparing the concentration of exchangeable metals in the pore water of soils among the incubated soils (Table 2), it can be noticed that the concentration of exchangeable Al, Fe and Pb are relatively higher in the ground soils with 0m treatment than in oven-dried ground soil. Al, Fe and Pb are enriched in the pore water of the 30% and 20% 0m incubated ground soils by factors \( r \) of 1.5 and 1.6 for Al and Fe, and by factors of 7.6 and 5.8 for Pb, respectively with respect to the oven-dried incubated control soil (Table 3). Cr, Cu, and As present similar concentrations in the ground soils despite the 0m, whereas Zn and Ni present a relatively higher concentration in the oven-dried ground soil than those with the 20% and 30% 0m. This indicates that the 0m in soils affects the response of soils under CO\(_2\) exposure conditions. A high % 0m enhances the CO\(_2\) uptake by pore water and leads to a higher mobilisation rate of the aforementioned elements in moister soils.

3.5 Geochemical modelling: Speciation of exchangeable metals in the pore water of soils

Four important factors should be considered when discussing the aqueous speciation of exchangeable metals in the pore water of these soils: i) the long term CO\(_2\)-incubation modelling was carried out to evaluate the effect of CO\(_2\) incubation in the speciation of exchangeable metals before, during, and after CO\(_2\) incubation; ii) the long term CO\(_2\)-incubation modelling before CO\(_2\) incubation was calculated at the pH of soils before incubation and provides the aqueous speciation of exchangeable metals for the studied soil; iii) the long term CO\(_2\)-incubation modelling during the CO\(_2\) incubation was calculated according to the modelled pH. This model represents the immediate response of soils to CO\(_2\) hydrolysis and allows us to elucidate the behaviour and aqueous speciation of the exchangeable metals after CO\(_2\) incubation; and iv) the long term CO\(_2\)-incubation modelling after CO\(_2\) incubation was calculated considering the modelled pH value (after 3 days) because of the unexpected pH increase in the pore water of soils by the CO\(_2\) release from the reactor.

The following discussion follows the grouping of metals according to the \( r \) value trends presented in the above section.
Elements with high mobilisation potential in the pore water of soils ($r > 1.4$): Ni, Zn, and Pb

Long term CO$_2$-incubation modelling reveals that the speciation of Ni would not be affected by the CO$_2$ incubation. Nickel as Ni$^{2+}$ free cation shows the highest activity in soils before and after CO$_2$ incubations (Table 3).

A similar pattern in the incubated and non-incubated ground soils is shown by Zn and Pb, showing their highest activity as Zn$^{2+}$ and Pb$^{2+}$ free cations, respectively. However, after CO$_2$ incubation, the long term CO$_2$-incubation modelling indicates that Zn and Pb could also occur in the pore water of soils as ZnHCO$_3^+$ and PbHCO$_3^+$, respectively, which suggests that Zn and Pb would be quite sensitive to CO$_2$ incubation in soils with $\theta m$ treatment. This would be in agreement with the under-saturation of all carbonate solid species ($SI = \log Q/K < 0$) in the acidic pore water of soils.

Elements with moderate mobilisation in the pore water of soils ($1.0 \leq r \leq 1.4$): Fe, Cr, Al, As, Cu, and

Long term CO$_2$-incubation modelling before and after CO$_2$ incubation indicates that Fe$^{2+}$ followed by Fe(OH)$_2^+$ would be the predominant aqueous complexes of exchangeable Fe in the oven-dried, 20% $\theta m$, and 30% $\theta m$ pore water of ground soils (Table 3). The model also indicates that all soils would be oversaturated before CO$_2$ incubation with respect to FeOOH and Fe$_2$O$_3$, and under-saturated with respect to the same mineral phases after CO$_2$ incubation (Table 4). The decrease of SI for FeOOH and Fe$_2$O$_3$ along CO$_2$ incubation would be consistent with a dissolution potentially transferring Fe as Fe$^{3+}$ from mineral phases to the pore water of soils. During anaerobic conditions, e.g. high occurrence of CO$_2$ in soil or relatively low pH of soil pore water, Fe$^{3+}$ is reduced to Fe$^{2+}$, such as it could occur in these soils.

Before CO$_2$ incubation, Cr(OH)$_2^+$ and CrOH$_2^+$ aqueous complexes are predicted to be the predominant aqueous complexes in the pore water of the oven-dried, 20% $\theta m$ and 30% $\theta m$ non-incubated ground soils. However after the CO$_2$ incubation, Cr$^{3+}$ as free cation would be the predominant in the pore water of all CO$_2$ incubated soils (Figure 3). The dissociation of Cr(OH)$_2^+$ and CrOH$_2^+$ under acidic conditions would account for the release of Cr as Cr$^{3+}$ in the soil solution. Geochemical modelling
predicts the saturation of the pore water of these soils with respect to CuCr₂O₄ and ZnCr₂O₄ before CO₂ incubation; and the under-saturation with respect to the same solid phases after CO₂ incubation. The decrease of their SI along CO₂ incubation (Table 4) indicates that the increase of the exchangeable Cr as Cr³⁺ in the pore water of soils after CO₂ incubation could also be the result of CuCr₂O₄ and ZnCr₂O₄ dissolution.

Long term CO₂-incubation modelling reveals that in the pore water of the oven-dried and 20% θm non-incubated ground soils Al(OH)₂⁺ followed by AlOH₂⁺ would be the predominant Al-aqueous complexes, whereas Al(OH)₄⁻ would be the predominant in the 30% θm non-incubated ground soil (Table 3). After CO₂-incubation, Al³⁺ followed, in decreasing order, by AlOH⁻ and Al(OH)₂⁺ are predicted to be the aqueous complexes with the highest activities of Al in the soil pore water of the oven-dried (2.67 pH), 20% θm (2.68 pH), and 30% θm (2.83 pH) incubated ground soils.

According to the long term CO₂-incubation modelling, before CO₂ incubation (5.8-6.3 pH), the pore water of these soils would be saturated with respect to K-feldspar (KAISi₃O₈) and kaolinite (Al₂Si₂O₅(OH)₄), which is in agreement with the mineral phases detected by XRD. However, after CO₂ incubation, these soils would be under-saturated (2.6-2.8 pH) with respect to the aforementioned mineral phases. The decrease of their SI along CO₂ incubation (Table 4) indicates that the increase of the exchangeable Al in the pore water of soils would be controlled by the dissolution of KAISi₃O₈ and Al₂Si₂O₅(OH)₄ as a result of CO₂ hydrolysis. As can be observed in the modelling diagrams of stability of exchangeable Al complexes as pH function (Figure 4), the CO₂ incubation would contribute to the release of Al³⁺ into the pore water of soils.

Long term CO₂-incubation modelling before CO₂ incubation (5.6-6.3 pH) reveals that H₂AsO₄⁻ and Cu²⁺ followed by HAsO₄²⁻ and Cu⁺, respectively, would be the predominant aqueous complexes in the pore water of soils. However, after CO₂ incubation (2.6-2.8 pH), HAsO₂ and Cu²⁺ would be the predominant aqueous complexes, respectively (Table 3). The variation of the aqueous speciation of
As during the CO₂ incubation would indicate a reduction of As species by the $\text{H}_2\text{AsO}_4^- + \text{H}^+ \leftrightarrow \text{HAsO}_2^{(aq)} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O}$ aqueous complexation reaction promoted by the CO₂ incubation.

The comparison of the concentration of exchangeable metals with the minimum safety limit and/or concentration tolerance range in these soils reveals that in general the concentrations of exchangeable the metals are below the established safety limit and/or tolerance range.

4. CONCLUSIONS
Long-term CO₂ exposure in soils results in the acidification of the pore water of soils via CO₂ hydrolysis. The pH drop induced by the exposure to CO₂ produces the dissolution of the mineral matrix and solid phases of soils giving rise to an increase of exchangeable metals in the pore water of soils.

The t-Student revealed that the CO₂ long term incubation was statistically significant (p<0.05) for the exchangeable concentration of Ni, Zn, and Pb. The CO₂-soil incubation induces the acidification of the pore water of soils via CO₂ hydrolysis and as a consequence, it increases the exchangeable concentration of Ni, Zn, and Pb in the soils. As, Al, Cr, Cu, and Fe show a different mobilisation pattern depending on the moisture content in soils.

The Long term CO₂-incubation modelling indicates that CO₂ exposure would modify the mobility and aqueous speciation of metals in the pore water of soils. Aluminium as Al³⁺, Fe²⁺, Cr³⁺, and Cu²⁺ as free cations, As as HAsO₂, Pb²⁺ and PbHCO₃⁻, Zn²⁺ and ZnHCO₃⁻ are predicted to be the predominant aqueous complexes in the pore water of the incubated soils.

The moisture content in soils is one of the most significant parameters affecting the response of soils under CO₂ exposure conditions. A high % ŧm boosts the CO₂ uptake by pore water and leads to a higher mobilisation rate of the metals in moister soils.
Further research will be focused on the potential environmental consequences (on soil and plants) of leaks of impure CO₂, focusing on the effects of controlled exposure to different concentrations of CO₂/SO₂ mixtures.

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