ENVIRONMENTAL TRANSFER OF ZINC IN CALCAREOUS SOILS IN ZONES NEAR OLD MINING SITES WITH SEMI-ARIDIC CLIMATE.

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SUMMARY

A study on the speciation and bioavailability of zinc in calcareous soils near an old mining site in semi-aridic conditions (S.E. Spain) is presented. The mobility of both solid particles and soluble compounds of zinc are considered. The processes governing zinc transfer from the element-rich zone to the neighbouring soils are strongly influenced by the semi-aridic climate, while the presence of a high proportion of carbonates is also an important factor in the mobilization of the metal. Reactions which take place in the solid-liquid-gas interfaces are discussed.

Data were obtained using both conventional methods for element speciation and a recently reported method especially adapted to highly calcareous soils. The procedure allows to outline the main speciation forms of zinc in these soils. Data obtained by means of X-ray diffraction spectrometry and SEM-EDX analyzer are used to confirm the chemical results. © 1999 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The fate and transfer pathways of Zn in soils are complex, and depend on the soils' mineralogy and the physical transport process involved. Transformations and transport are strongly influenced by site-specific conditions and management practices, although climatic and weather conditions other than rainfall may also influence the fate.

There are large areas of calcareous soils in SE Spain and many of these coincide with places where Pb and Zn are mined. These soils often present very high levels of these metals with a strong spatial dispersion of values.
Figure 1.- Location of the studied Zone
The area around Mazarron (Murcia, SE Spain) presents ideal characteristics for a study of the kind we describe in this paper. There are many old mining installations while the soil is calcareous and often has a very high Zn content. The study area (Fig 1) has geomorphological, pedological and climatic characteristics similar to other mining areas in the Mediterranean area with a scant, degraded vegetation. Agriculture is intensive, both in the open air and in greenhouse, and is mainly dedicated to horticultural crops.

The soils studied are located in Las Moreras Rambla (wadi complex) and may occasionally be flooded when this gully fills with water after heavy rain. The soils of the area feeding the rambla are calcic and petrocalcic Xerosols, and calcareous Regosols [1]. Nearby there is a drainage channel which carries substantial quantities of materials from the mining area (Urbic Antrosols) in Cabezo de San Cristobal and Las Pedreras.

MATERIALS AND METHODS.

Twenty samples were obtained from a 5 Km² sampling zone. The general characteristics of the arable soil layer were determined by the methods used to draw up a soil map of the area in the LUCDEME project [1].

The total zinc content was determined by flame atomic absorption spectrometry (FAAS). For this purpose the samples were slurried in a dilute hydrofluoric acid solution and the suspensions were directly introduced into the flame by means of a simple flow injection manifold [2]. A Perkin-Elmer model 1100 B AAS spectrometer was used to obtain the measurements.

The selective extractants used were: water (1:10); 1 M ammonium acetate at pH 7.0 [3]; oxalic acid-oxalate [4]; 0.1 M sodium pyrophosphate, [4]; sodium dithionite + sodium citrate [5]; 0.5 M acetic acid [6]; 0.5 M ammonium acetate + 0.02M EDTA + acetic acid at pH 4.65 [7]; DTPA [8] and sodium bicarbonate 0.1N, pH 8.5 [9]. In addition, an accepted sequential extraction procedure [10] based on three successive extraction stages was also applied to the same samples and the results were compared with those found using the above quoted reagents. The zinc content in each fraction was analyzed by FAAS.

The mineralogical composition of the samples was determined by XRD analysis using Cu-Kα radiation with a PW-1212 Philips Diffractometer, equipped with a digital recorder. The experimental conditions were: velocity 2 °/min., automatic window, Ni filter. Using the diffraction intensities obtained and the values for the same phases given in the bibliography, a semiquantitative analysis was made of the treated and untreated samples. The samples were also examined using a JEOL 6100 scanning electron microscopy (SEM) instrument, equipped with an EDX analyzer, Link Isis Oxford, with Si-Li detector and working at 39 mm height and 20 KV voltage.
RESULTS and DISCUSSION

Environmental Conditions

Annual rainfall is 185-312 mm and the average temperature is 16.5 to 18.8 °C. Mean potential evapotranspiration is 869-935 mm and there is a very pronounced hydric deficit. Rainfall is scarce and tends to be torrential. Flash floods may occur with occasionally disastrous consequences.

In our climatic conditions, the high temperatures cause the water contained near the surface of the soil to evaporate rapidly. The fundamental alteration and mobilization processes occur at the unsaturated zone or aeration zone, where the water is in the form of vadose water. The water remains here for a longer time and there is greater root development.

The materials which participate in the formation of these soils are sediments from soils developed on carbonated rocks (limestones, dolomites, sandy marls and conglomerates), volcanic rocks and slags which are found in the areas around the gully (Fig. 1) and which have undergone a process of erosion, transport and sedimentation.

The materials which contribute Zn to the study area (Table 1) come from mine wastes, which are a mixture of materials including: unaltered parent material (dacites and riodacites), altered parent materials, primary mineralization products (metallic sulfides), secondary mineralization (hydrothermal alteration and products of the supergenic alteration of sulfides) and remains from the mechanical and metallurgical treatment of exploited ores. These materials therefore are of a very varied nature with a heterogeneous granulometry [11].

Table 1.- Zn content in some parent materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Min</th>
<th>Max</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent volcanic rock (ppm)</td>
<td>41</td>
<td>211</td>
<td>95</td>
</tr>
<tr>
<td>Weathered volcanic rock (ppm)</td>
<td>158</td>
<td>2673</td>
<td>625</td>
</tr>
<tr>
<td>Sulfate mining waste (%)</td>
<td>0.34</td>
<td>7.67</td>
<td>0.98</td>
</tr>
<tr>
<td>Soil (ppm)</td>
<td>200</td>
<td>5000</td>
<td>620</td>
</tr>
<tr>
<td>Acidic water (ppm)</td>
<td>1690</td>
<td>40755</td>
<td>12285</td>
</tr>
</tbody>
</table>
Transport of materials; dissolved load and particulate forms: suspended and bed loads.

Floods are particularly important in the transport of sediment in this zone. Thus, the sporadic torrential rains of the area transport large quantities of carbonated materials and materials from the slags. Excessive rates of water flow prevent infiltration, lead to flash floods and cause soil erosion.

Slowly flowing water creates dams on the slopes of the mining areas, leading to new alteration phenomena. This water flows for several days after the rains in the vadose zone. The soluble products contained in the waters which leach from the slags are very rich in sulphate, Fe, Al, Mg, Zn, Mn, (major elements, > 10 mmol/l) and Si, Cu, As, Sb, Ge, Cr, Sn, Cd, Pb (as minor elements, <10 mmol/l). The pH is between 1.5 and 2.2. The mineralogical composition of the precipitates from acid waters are shown in Table 2 [12]. The mineralogy of these compounds is closely related with the overall chemical composition of the samples, as found in Nova Scotia [13].

When a rapid flow of water occurs, soluble and particulated forms are dragged unchanged from their place of origin as far as the gully. The mineralized materials contribute and generate insoluble sulfates (anglesite, jarosite, alunite, ...), oxides and oxihydroxides and clay minerals such as kaolinite and chlorite, with a different Zn content, which are transported with the soluble materials.

Table 2. Mineralogical composition of the precipitates in acid waters.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Max</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copiapite</td>
<td>(Zn,Fe,Mg)(Al,Fe)₄(SO₄)₆(OH)₂·20H₂O</td>
<td>50</td>
<td>14</td>
</tr>
<tr>
<td>Halotrichite</td>
<td>FeAl₂(SO₄)₄·22H₂O</td>
<td>35</td>
<td>18</td>
</tr>
<tr>
<td>Alunogene</td>
<td>Al₂(SO₄)₃·17H₂O</td>
<td>15</td>
<td>8</td>
</tr>
<tr>
<td>Paracoquimbite</td>
<td>Fe₇(SO₄)₃·17H₂O</td>
<td>14</td>
<td>10</td>
</tr>
<tr>
<td>Bianchite</td>
<td>(Zn,Fe, Mg) SO₄·H₂O</td>
<td>40</td>
<td>15</td>
</tr>
</tbody>
</table>

Sedimentation processes and chemical interactions solid-liquid-gas.

The waters which run off and leach from calcareous materials have a high HCO₃⁻ content. When this solution reacts with the above mentioned acidic waters there is a coprecipitation of basic iron carbonates, and these retain different proportions of Zn. The Fe (SO₄) 7 H₂O (melanterite) and other Fe(II) sulphate phases are only stable at very acidic pH. The importance of these phases is that the Fe(II) sulfates are precursors of the genesis of Fe(OH)₃, which is a Zn adsorbent, although it carries other metals besides Zn.
The extent of Fe(OH)$_3$ precipitation depends on pH, while Fe$_2$ CO$_3$(OH)$_2$ is only formed at high pH values.

The free soluble Zn can react with HCO$_3^-$:

\[ \text{HCO}_3^- + \text{Zn}^{2+} \rightarrow \text{ZnCO}_3(s) + \text{H}^+ \] [1]

\[ \text{H}_2\text{O} + \text{Zn}^{2+} \rightarrow \text{Zn(OH)}_2(s) + 2\text{H}^+ \] [2]

a reaction which is favored as the acidity of the medium is reduced.

If, in addition to HCO$_3^-$, ligands such as Cl$, \text{SO}_4^{2-}, \text{CO}_3^{2-}, \text{OH}^-, \text{humic} \text{and fulvic acids}, \text{and CN}^- (\text{used in sulfide flotation processes}) \text{are also present}, \text{Zn complexation reactions may occur.}

The oxidation of sulfides arises from the instability of these phases when they occur in an oxidising and acidic medium. The most important oxidation reactions for the mobilization of Zn are those involving pyrite and sphalerite:

\[ 4 \text{FeS}_2(s) + 15 \text{O}_2(g) + (8+2x) \text{H}_2\text{O} \Rightarrow 2 \text{Fe}_2\text{O}_3.x \text{H}_2\text{O} + 8 \text{SO}_4^{2-}(\text{aq}) + 16\text{H}^+(\text{aq}) \] [3]

\[ \text{ZnS} (s) + 2 \text{Fe}^{3+} + 1.5 \text{O}_2 + 2\text{H}_2\text{O} \Rightarrow \text{ZnSO}_4 + 2 \text{Fe}^{2+} + 2\text{H}^+ \] [4]

The carbon dioxide acts in the oxidation process by carbonating the metal and supplying sulfate ions which catalyze subsequent oxidation reactions and by increasing the medium's acidity:

\[ \text{ZnS} + \text{CO}_2 + \text{H}_2\text{O} + 2\text{O}_2 \Rightarrow \text{ZnCO}_3 + \text{SO}_4^{2-} + 2\text{H}^+ \] [5]

Finally, Zn sorption/desorption reactions occur in the above interactions with those involving Al and Fe oxides/hydroxides being especially important. Although humic substances act as Zn adsorbents in soil, this effect is of little importance in our case because they are present in very small quantities (Table 3).

**Characteristics of the soils: chemical and mineralogical**

Table 3 shows the mean values of the analytical data of the soil samples studied. All the samples were collected from the top 30 cm (approximately, the A horizon). The scarce organic material accompanying these soils undergoes subsequent oxidation and mineralization, which are very important biological degradation processes in the soils of semiarid areas such as those studied [14].

All the soil samples studied had a slightly basic pH, reflecting their high calcium carbonate content. The texture was sandy loam to clay loam and the cationic exchange capacity values were low, as it was expected in soils with a low proportion of organic matter and illite type clay. In some cases, the concentration of soluble salts was very high for cultivated soils.

A mineralogical study of the fine earth fraction showed that all the samples were of a similar composition: calcite (30-40%), quartz (20-35%), illite (10-25%), feldspars (10-20%) and dolomite (0-15%). Representing less than 5% in all samples and therefore not easily observed by XRD, were the oxides and oxihydroxides of Fe and Mn, which are of low crystallinity or amorphous. Some samples contained
gypsum, and others sulphates like bianchite and jarosite. It must also be noted that total Zn levels (Table 1) were higher than those proposed as maximum acceptable concentrations (MAC) in agricultural soils (Tables 4 and 5) [15].

<table>
<thead>
<tr>
<th>O.M</th>
<th>C/N</th>
<th>CaCO3</th>
<th>T°</th>
<th>E.C°</th>
<th>H2O</th>
<th>KCl</th>
<th>%Sand</th>
<th>%Silt</th>
<th>%Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>7.6</td>
<td>7.7</td>
<td>11.0</td>
<td>3.4</td>
<td>7.9</td>
<td>7.7</td>
<td>23.1</td>
<td>11.0</td>
<td>12.1</td>
</tr>
<tr>
<td>max</td>
<td>6.0</td>
<td>16.0</td>
<td>55.0</td>
<td>21.5</td>
<td>49.4</td>
<td>21.5</td>
<td>42.5</td>
<td>24.5</td>
<td>16.4</td>
</tr>
<tr>
<td>average</td>
<td>1.3</td>
<td>4.4</td>
<td>39.2</td>
<td>11.0</td>
<td>3.4</td>
<td>7.9</td>
<td>7.7</td>
<td>42.5</td>
<td>24.5</td>
</tr>
</tbody>
</table>

*Cationic exchange capacity
*Electric conductivity obtained from saturation extract of soil.

The values also exceed some of the maximum values considered acceptable in agricultural soils by the EU [16] and in soils to which sewage sludge has been added.

Table 4. Reference Values in Netherland (Zn ppm)*

| A level | 200 |
| B level | 500 |
| C level | 3000 |

* from Reference [15]

Table 5.- Maximum acceptable concentrations (MAC) of Zn (ppm) for soils in different countries*.

<table>
<thead>
<tr>
<th>Country</th>
<th>MAC (Zn ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>300</td>
</tr>
<tr>
<td>Canada</td>
<td>400</td>
</tr>
<tr>
<td>Poland</td>
<td>300</td>
</tr>
<tr>
<td>Japan</td>
<td>250</td>
</tr>
</tbody>
</table>

* from Reference [15]
Examination of the samples using a scanning electron microscope equipped with EDS analyser revealed quartz, calcite, clays, plagioclase and feldspars in different particle sizes. Mapping of the chemical element distribution showed that the zinc was distributed widely but with no set morphology. Figure 2 shows mapping image obtained from a representative sample (sample 3).

Figure 2. - Mapping of the chemical element distribution of sample 3 obtained by SEM-EDS.
**Sequential extraction for Zn speciation**

Chemical extraction sequences were applied to differentiate between exchangeable, carbonated, reducible (hydrous Fe/Mn oxides), oxidizable (sulfides and organic phases) and residual Zn fractions. The advantage of this approach lies in the fact that the rearrangement of specific solid "phases" can be evaluated prior to the actual remobilization of certain proportions of the element into the dissolved phase [17].

![Graph showing Zn extraction percentages](image)

**Figure 3.- Results for Zn extraction (nine samples) using sequential extraction procedure [10]**

Figure 3 shows the fractions of Zn in the sequence of extracts obtained from nine representative samples. The literature [10] suggests that the first extract corresponds to the acid soluble fraction representing the metal bound in exchange positions, water soluble metal and carbonate-bound metal. The second extract contains the reducible Zn fraction (Zn bound to iron and manganese oxides) and the third fraction, which is oxidizable, corresponds to the organic matter and sulfide-bound metal. However other unidentified phases may also be extracted [10, 18, 19]. Reactions involving desorption, coprecipitation or neutralization may also occur during the extraction steps [20].

Our results with calcareous soils show that the fractions extracted from each sample at each step vary greatly. However a relation appears to exist between the total carbonate content and the mineralogical species in question (calcite, dolomite) [21]. In highly calcareous soils, during the first step, acetic acid can neutralize the calcite when it represents up to 20% of the total mineral content, whereas where the calcite and dolomite contents are above this level they remain in the residue (Figure 4). These results are in agreement with electron microscopy observations. Figure 5 shows the distribution mappings of zinc, which may be partly related with elements such as S, O and Fe, possibly as jarosite crystal.
In the second step, nitric acid neutralizes the residual calcite fraction in large particle size and part of the dolomite (Figure 4). Data obtained by SEM reveal that zinc may be associated with dolomite crystals, sulfur compounds and silicates.

According to the mineral composition of the residue (Figure 4), acetic acid may also be involved in the third step where it neutralizes the rest of the calcite and dolomite present. The distribution mapping of zinc (Figure 5) suggests its association with sulfate and silicate crystals, which represent the least mobile residual zinc phase.

![X-ray diffractograms](image)

Figure 4.- X-ray diffractograms obtained from the remainders after the first, second and third extraction steps in sequential extraction procedure for sample number 3. I = illite; Q = quartz; C = calcite; F = feldspars; D = dolomite.

When the sequential extraction method proposed by the “Community Bureau of Reference” (BCR) is applied to highly calcareous soils, it is not possible to relate the zinc content to the different speciation forms described in the bibliography, since carbonates are present in the different extraction steps.

To summarize, the first step corresponds to the most soluble zinc, the exchangeable Zn forms and Zn bound to part of carbonates in the form of calcite.

Our experiments suggest that the carbonate-bound zinc is not totally extracted during the first step, and it remains unquantified in the following extraction stages. Consequently, the zinc bound to reducible forms (second extraction stage) also includes part of the metal still bound to calcite and dolomite. Further zinc bound to organic matter and sulfides (third step) also results higher than the true value. This, because it also includes the metal remaining in the carbonates which have not been neutralized in the previous steps. Our data agree with previous reports on calcareous soils [22] and show that significant and
substantial errors may occur in zinc speciation when using BCR methodology in soils with a high carbonate content.

Figure 5.- Mapping of the chemical element distribution obtained by SEM-EDS after the extraction step (acetic acid, sample number 3).
Other extractants for Zn speciation.

Because of the problems encountered in using the BCR speciation scheme involving sequential extractions, other schemes using different reagents to mimic environmental conditions were used to study Zn speciation in calcareous soils. For comparison purposes, nine soils samples were analysed which were the same as those studied by the conventional speciation procedure based on sequential extraction. Results obtained are shown in Figs 6 and 7.

The water soluble Zn content is extremely low (0.05-0.5%) (Figure 6) in good agreement with the mineralogy and pH of the soils studied. The exchangeable fraction, as determined by ammonium acetate (pH = 7) [3], is also low (Figure 6) but higher than that of the water soluble phase. It varies with the mineralogy and texture of clays, that is, with the exchange capacity of these soils.

The amount of zinc bound to the amorphous forms of iron oxides and extracted with oxalic acid-sodium oxalate at pH 3 [4] is considerable (Figure 7), even if soluble and exchangeable Zn forms, and part of the zinc arising from the mobilization of carbonates, are included. This extractant also partially dissolves active calcium carbonate, leading to a partial precipitation of Ca and Zn oxalates. Further, mobilization of metals from the crystalline structure of this carbonate is revealed by the XRD diagrams of treated samples, in which several peaks can be assigned to various phases of calcium oxalate in different states of hydration (Figure 8). Citrate-dithionite is a reducing reagent with a pH near to neutrality which
solubilizes amorphous minerals of low crystallinity [5], such as Fe and Mn oxides and oxihydroxides and metals associated to them. The values of Zn extracted with this reagent are up to 70% higher than those obtained using other selective extractants (Figure 7). Several carbonates are also solubilized by citrate-dithionite mixture, as it appears from the quartz/calcite ratio (Figure 8). Differently from the oxalic acid-sodium oxalate extraction, no precipitation reactions occurs in this case, and dolomite is hardly affected. The water soluble fractions are also included in this fraction [23].

Finally, sodium pyrophosphate is able to extract Zn bound to humic substances. Also this reagent dissolves part of the calcium carbonate and dolomite, precipitating the calcium as phosphate. Other metals contained in the carbonate structure are also extracted by complexation. However, because of the low humic matter content of the soils studied, this reagent mostly dissolves Zn in carbonates.

![Figure 7.- Zn availability (selective extractions).](image-url)

Figure 7.- Zn availability (selective extractions).
Zinc availability to plants

It is generally accepted that the amounts of Zn in soil extracts obtained using either 0.5 M acetic acid [6], or EDTA-ammonium acetate-acetic acid (pH 4.6) [7], or DTPA [8] correspond to the metal taken up by plants. The results obtained for our soil extracts (Figure 9) apparently differ considerably from one extractant to another, this suggesting that the above assumption is not valid when dealing with calcareous soils.
EDTA-ammonium acetate-acetic acid (pH 4.6) is known to complex metals that are associated to inorganic forms of Fe and Mn with a low crystallinity and fine granulometry. In our experiments this reagent appears also to solubilize carbonates (Figure 10). A decrease in calcite reflection and background noise is apparent, which can be ascribed to the presence of amorphous substances. For this reason, the values for plant-available Zn which are obtained by this procedure are low. Both soluble Zn and Zn associated to the exchange complex and to finely divided forms are affected by complexation with DTPA. The amounts of Zn extracted by this reagent are also variable and relatively low (Figure 9). The X-ray diagrams obtained after DTPA treatment show a decreased background noise, as for EDTA residues, an increase in illite crystallinity and a constant calcite content.

Acetic acid causes most problems when evaluating plant-available Zn in carbonated soils, since calcite dissolves totally in this reagent and dolomite does so when it is finely divided. Therefore, this method of extraction cannot be considered suitable for the determination of plant-available Zn.

In order to ascertain the extractant that best simulates the plant availability of Zn, the Zn content of tomato plants cultivated in the studied soils was analysed. The best correlation between the amount of Zn extracted from the soil and the zinc content in the plant material was obtained when using DTPA (Figure 11). The low availability of Zn to tomato plants grown in calcareous soils may be reflected by the low levels of Zn found in the root, leaves and fruit.

Figure 10 - X-ray diffractograms obtained from the remainders after bioavailability extractions (sample 3).
Zn mobility was also assayed by using a bicarbonate extractant of pH 8.5, which is considered [10] to be similar to the bicarbonate environment of soil solution in the rhizosphere. In general, the amounts of Zn dissolved in this extractant (Figure 8) can be considered acceptable for carbonated soils.

CONCLUSION

Because of the high amounts of carbonated materials which are supplied by the Moreras Rambla (wadi complex) in the area under study, the Zn leached from the slags is tendentially immobilized. Two immobilizing mechanisms can be supposed to act in these conditions, the one involving the formation of carbonates and the other the formation of sulfates. The first of these may lead to new solubilization reactions in which CO₂ and H₂O play an important role. In addition, during the solid particle - CO₂ - H₂O interaction, new stable phases can be formed, which are insoluble and can fix Zn in the lattice crystal.

The kinetics of these processes is strongly influenced by the peculiar climatic conditions. Low rainfall implies soluble Zn compounds (hydrated Zn polysulfates) to remain on the surface of slag heap for long periods of time. On the contrary, torrential rainfall transports all materials and the acidity of leachates is neutralized by carbonates. The slow process of Zn fixation can, however, be accelerated by water infiltration.
Apparently, the maximum Zn immobilization can be achieved at the acid water-carbonated material interface (bordering the ramblas) in periods of light rain, with formation of Zn (OH)₂ and Zn CO₃.

Another important factor that affects Zn speciation and bioavailability in calcareous soils is the low amount of organic matter in these soils. This condition, which is common to all semiaridic soils, explains why the organic matter plays no relevant part in Zn transport. However, the role played by the organic matter would become more important in the case of agricultural soils that are added with organic fertilizers.

Finally, the zinc speeiation methodology based on the use of conventional sequential extractions which is recommended for other soils seems to be unreliable for highly calcareous soils. A different approach, which takes into account the particular physico-chemical characteristics and mineralogy of these soils, appears to be necessary.

REFERENCES


