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This is an **author produced version** of a paper published in:

Journal of Environmental Management 92.8 (2011): 2069-2075

**DOI:** <http://dx.doi.org/10.1016/j.jenvman.2011.03.030>

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# Natural attenuation of residual heavy metal contamination in soils affected by the Aznalcóllar mine spill

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## Abstract

Non-amended soils affected by pyritic sludge residues were monitored for 7 years to assess the long-term natural attenuation ability of these soils. The decrease in both the total concentration of elements (particularly As) and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable fractions of Mn, Cu, Zn, and Cd below maximum permissible levels indicate a successful natural ability to attenuate soil pollution. Soil acidification by pyrite oxidation and rainfall-enhanced leaching were the largest contributors to the reduction of high (Mn, Cu, Zn and Cd) and low (Fe, Al, and As) availability metals. Periodic use of correlation and spatial distribution analysis was useful in monitoring elemental dispersion and soil property/element relationships.

**Keywords:** Spatial-temporal variation, availability, heavy metals, arsenic, acidified soils, pyritic sludge

## Introduction

A serious arsenic and heavy metal contamination incident occurred after the widely-publicized pyrite mine reservoir accident in Aznalcóllar, Spain in 1998 (Aguilar et al. 2007). National and regional environmental authorities initiated a clean-up program by first mechanically removing toxic sludge and surface soil, then applying soil amendments to prevent dispersion of the contaminants. Despite the clean-up effort, the affected area remained contaminated with an irregular distribution of pollutants resulting from residual surface sludge being inadvertently buried during removal (Álvarez-Ayuso et al., 2008). Aerobically-enhanced pyrite oxidation in the sludge-contaminated soil mobilized metallic and metalloid elements through acidification. Both the level and availability of soil trace elements increased, incurring a risk of further contamination.

Reports describing the evolution of contamination from the Aznalcóllar spill have examined leaching across the soil profile (Kraus and Wiegand, 2006; Aguilar et al., 2007; Álvarez-Ayuso et al., 2008), temporal and spatial variations in the pollutant concentrations (Burgos et al., 2006; Vanderlinden et al., 2006; Ordoñez et al., 2007), the effects of soil amendments (Walker et al., 2004), and phytoremediation techniques (Clemente et al., 2005; Vázquez et al., 2006).

The dynamic behavior of trace elements in soil is complex, being influenced by factors such as pH, organic matter, texture, redox potential, and temperature (Alloway, 1995). Natural attenuation is a term used to describe a collection of *in-situ* physical, chemical, and biological processes that, under favourable conditions,

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act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater (EPA 1999). To our knowledge, the effect of two years of natural attenuation on the Aznalcóllar soil contamination has only been discussed in Clemente et al. (2006). In this study we sought to assess the long-term natural attenuation ability of non-amended soils affected by residual contamination from the Aznalcóllar spill. Correlations between soil properties and element concentrations, correlations between the concentrations of different elements, and spatial evolution of elemental profiles were also examined.

## Material and methods

### *Experimental site and design*

The study was carried out at the 1000 m<sup>2</sup> B2 experimental plot in the “El Vicario” area (37°26’21’’N 06°13’00’’W) located in Sanlúcar la Mayor, Spain. The soil physico-chemical properties were highly heterogeneous due to the residual sludge content, so the research area was divided into 32 (4x8) subplots of 25 m<sup>2</sup> each. The *Typic Xerofluvent* soil was previously characterized (Vázquez et al., 2006). Soil monitoring consisted of extracting five surface soil (<20 cm depth) samples (in 2000, 2001, 2003, 2005, and 2006) from each of the 32 subplots. The pH, electrical conductivity (EC), organic matter content (OM), iron oxide content, and total, available, and soluble concentrations of Fe, Mn, Cu, Zn, Al, As, and Cd were determined.

### *Analytical determinations*

The soil samples were air-dried and sieved to 2 mm. Quantitative paper-filtered (Filter-Lab, S.A) 1:5 soil/water extracts made by mixing air-dried soil and deionized water, shaking at 180 rpm for one hour and waiting for 30 minutes prior to using a digital pH meter (Model 8155SC; ORION Research Inc., Boston, USA) and a conductivity meter (Crisol CM 2200) (MAPA, 1994). The organic matter content (OM) was analyzed using wet oxidation with dichromate and titration with ferrous ammonium sulphate (Walkey and Black, 1934). Total OM was calculated using the 1.724 Waskmann coefficient (Spanish official methods of analysis, MAPA, 1994). The Fe oxide content was obtained from the citrate-bicarbonate-dithionite (CBD)-extractable Fe fraction (Mehra and Jackson, 1960). *Soluble fractions* were extracted from 2g samples with 20 mL of 0.1M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (Wenzel et al., 2001); and *available soil fractions* were extracted using 20 mL of 0.02M EDTA in 0.5M acetic acid/ammonium acetate buffer, pH 4.5 (Lakanen and Erviö, 1971). The extractions were performed in 60-mL plastic flasks shaken at 180 rpm for 4 h at room temperature. The total concentration of elements (pseudo-total) was assessed using hydrochloric-nitric acid (3:1) microwave-assisted digestion (Vázquez et al., 2008). The samples were filtered through quantitative filter paper (Filter-Lab, S.A.) and the filtrates were analyzed for metal and As content using atomic absorption (Perkin-Elmer Analyst 800) and atomic fluorescence spectrometry (PS Analytical 10.055 Millennium Excalibur system).

### *Statistical analysis*

The dataset contained 32 samples per year ( $n=32$ ), corresponding to the 32 subplots. Despite the subdivision of the plot, the data were highly disperse and produced a non-Gaussian distribution. Because of this, non-

parametric statistics were used as follows: box diagrams representing the median (line), percentiles (boxes and bars), and outliers (circles) were used to report values in place of the usual mean and standard error. Wilcoxon's test was used instead of Duncan's test to identify significant differences ( $\alpha = 0.05$ ) between years (represented by different letters in Figs. 1, 2, and 3). The Pearson coefficient was used to determine correlations between variables (Table 1). The spatial distribution of the variables is depicted using diagrams resembling level curves (Fig. 5), in which relative values are plotted to facilitate comparison between years and variables. The statistical analyses were performed using the SPSS v15.0 software package.

## Results

### *Temporal variation*

The pH remained quite constant (4.2-5.1), with the lowest values of 4.2 and 4.5 occurring in the years 2003 and 2005 (Fig. 1a). The electrical conductivity (EC) decreased significantly with time, reaching 50% of 2000 levels by 2005 and 2006 (Fig. 1b). Organic matter content (OM) did not display a clear trend with time; but seemed to increase toward the end of the experiment with a significant increase in 2005 (Fig. 1c). The iron oxide content increased significantly over time and was 1.2-fold higher during the last two years than in the first year (Fig. 1d).

All iron fractions (total, EDTA-extractable, and  $(\text{NH}_4)_2\text{SO}_4$ -extractable) decreased with time, particularly toward the end of the experiment (Figs. 2a-c). Manganese (Figs. 2d-f), Cu (Figs. 2g-i), Zn (Figs. 2j-l), and As (Figs. 3s-u) followed a more obvious trend than Fe, with all fractions decreasing with time and the highest reductions occurring in total concentration (35% for Mn, 27% for Cu, 53% for Zn, and 47% for As). In contrast, the total Cd concentration increased significantly with time, though the behavior was different for the EDTA-extractable and  $(\text{NH}_4)_2\text{SO}_4$ -extractable fractions (Figs. 3p-r). The Al concentration did not display any clear trend with time for any fractions (Figs. 3m-o).

### *Availability of elements in the soil*

The availability of the elements in the soil is indicated in Fig. 4 as the percentage of  $(\text{NH}_4)_2\text{SO}_4$ -extractable and EDTA-extractable concentrations with respect to the total concentration for that element. The elements may be sorted into two groups based on their availability, with Mn, Cu, Zn, and Cd classified as high available elements and Fe, Al, and As as low available elements. The concentrations of high availability elements ( $(\text{NH}_4)_2\text{SO}_4$ -extractable) decreased with time, with the highest reductions occurring in 2006 with respect to the 2000 concentrations (50% Mn, 70% Cu, 32% Zn, and 34% Cd).

### *Correlation analysis*

Relationships between soil properties and elemental soil concentrations and relationships between the concentrations of various elements are listed in table 1. Soil pH and EC were the variables most strongly correlated to the total concentrations of soil elements, particularly Fe, and to the  $(\text{NH}_4)_2\text{SO}_4$ -extractable concentrations of the other elements. The correlation between soil elemental composition and pH was

negative, while the correlation between EC and composition was positive. Moderate to low correlations were observed between the elemental composition and both Fe oxide content and OM. The Fe concentration was strongly and positively correlated to As and Al, with Pearson coefficients of 0.909 for Fe-As and 0.888 for Fe-Al. High correlation values were also observed between Fe and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable Cu and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable Zn. A remarkable positive correlation was observed between Mn and Zn concentrations, particularly for the EDTA and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable fractions.

#### *Spatial variation*

The most highly correlated variables (pH and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable Zn and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable fractions of Fe, Al, and As) were plotted to compare their spatial distribution in the soil and their evolution with time (Fig. 5). The same pattern of spatial distribution was observed for all of the correlated variables, being more similar between pH and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable Zn and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable fractions of Fe, Al, and As. The evolution of soil pH values suggests that an increase in soil acidity took place over time. Likewise, a dispersion of zones containing high levels of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable Zn seems to have simultaneously occurred. For (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable fractions of Fe, Al, and As this pattern of evolution with time was not as well-defined.

#### **Discussion**

The soil pH changed only slightly with time (Fig. 1a), whereas spatially the soil pH decreased with time (Fig. 5). This behavior could be explained by the effect of seasonal rainfalls on soil pyrite oxidation. Under field conditions, oxidation of pyrites preferably occurs in dry seasons (samples obtained in the summers of 2000 and 2001) whereas during wet seasons (2003, 2005, and 2006 autumn and winter samples) pyrite oxidation is hindered due to a lower concentration of oxygen in the soil (Vanderlinden et al., 2006). On the other hand, the annual precipitation was 616-494 mm between 2000 and 2002 and 716-793 mm from 2003-2006 (except for 2004 (322mm), which was a very dry year), and rainfall could dissolve sulfate minerals formed during the previous dry season. The significant decrease in EC over time (Fig. 1b) could be due to leaching of salts by the frequent rainfall occurring in the years 2003-2006, though sorption phenomena may also have contributed (see below). Rainfall also enhances wild plant or weed growth (shoot biomass production has been estimated at 150g FW per m<sup>2</sup> with a third more for root biomass; unpublished results), which could explain the slight increase in OM content toward the end of the monitoring period, especially in 2005 (Fig. 1c). In any case, the existing OM-rich topsoil layers were mechanically removed together with the sludge during remediation efforts in 1998, and the remaining top soil containing normal levels of OM (2%) is very shallow. The lower soil horizons display a sharp decrease in OM content (Álvarez-Ayuso et al., 2008). For this reason, no correlations with OM were observed (Table 1).

The increase in Fe oxides over time (Fig. 1d) indicates a continuous release of Fe from pyrite after oxidation and subsequent precipitation. Effects such as natural sludge weathering that promote continuous oxidation of pyritic minerals and the subsequent penetration of the oxidized products into the topsoil have been widely

described (Clemente et al., 2006; Aguilar et al., 2007; Álvarez-Ayuso et al., 2008). Iron oxides including goethite and ferrihydrite are important in influencing the mobility of As in soils. Studies using soil and pure Fe hydroxides have demonstrated that As solubility increases with pH within the range commonly measured in soil (pH 3-8) (Fitz and Wenzel, 2002). At low pH, the solubility of As decreases due to surface charges on the Fe oxides. However, the availability of As in soils can increase under acidic conditions (mainly below 5) as the increased solubility of the Fe oxides releases more immobilized As (Alloway, 1995). Due to these soil processes affecting the availability of As, moderate correlations between Fe oxide content and As were observed (Table 1).

Both the strong negative correlation of pH and the strong positive correlation of EC with the elemental composition of the soil (table 1) indicate that the general decrease metal concentration with time (except for Cd and Al, (Fig. 3)) could be due to continuous leaching of elements from the most available fractions in the soil, and that the available concentration increases at lower pH. This behavior is clearer for the total levels than for the available and soluble fractions because the elements in these fractions are continuously replaced from non-available residual fractions as soon as the element is leached (Alloway, 1995). Aluminum is not present in the pyritic sludge but rather is an acidity-induced pollutant. As the pH decreases large amounts of Al are released to the soil through dissolution of Al oxides (Alloway, 1995). This trait of Al could be a reason for the unclear pattern of concentration with time (Figs. 3m-o). The increase in total soil Cd concentration in later years (Fig. 3p) could be a consequence of increasing soil acidity. This would be in agreement with Álvarez-Ayuso et al., (2008) who reported a vertical distribution of elements across the soil profile, with the greatest levels of Cd and Zn occurring in deeper soil layers (50-60cm) but higher leachable Cd and Zn levels in the upper layers (10-20cm and 20-30cm). Therefore, environmental monitoring of adjacent areas and groundwater is still strongly recommended.

In 2000 all trace elements except As were below maximum permissible levels. The general trend of decreasing levels of metals except for Cd and Al over time seems to indicate a natural ability to attenuate metals in these soils. In the last year, the total concentration of As was decreased 47% with respect to 2000 level, reaching a median value of 99.8 mg Kg<sup>-1</sup>, that is just under the maximum permissible level (Table 2).

In addition to the total concentration, the availability of a given element is essential to assessing the potential risk. In this study, leaching processes are important for Mn, Cu, Zn, and Cd (high availability elements) as the amount capable of being mobilized is greater than for low availability elements (Fe, Al, As). This behavior has been widely reported (Kraus and Wiegand, 2006; Vanderlinden et al., 2006; Aguilar et al., 2007). There were also significant reductions in the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable percentages of Mn, Cu, Zn, and Cd during later years (Figs. 4b, c, d and f), indicating that the natural attenuation effect not only acts on the total concentration but also on the element availability. Similar decreases in availability were observed by Clemente et al. (2006), though the total concentration of As was not reduced during their experiments.

The spatial distributions may be organized into two groups, *pH-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable Zn* and *(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable fractions of Fe-Al-As* (Fig.5). The variables comprising these groups were also those displaying higher Pearson coefficients (Table 1). Therefore, the spatial distribution was closely related to the correlation analysis. The results pertaining to the *pH-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable Zn* group were in accordance with Vanderlinden et al. (2006), who described an inverse relationship between pH and Zn due to precipitation and further dissolution of minerals formed from the products of pyrite oxidation. The high correlation and similar spatial distribution observed for Fe, Al, and As (Table 1; Fig. 5) are due to the close relationship of these elements and the soil chemistry, particularly under acidic conditions (Clemente et al., 2006; Aguilar et al., 2007; Álvarez-Ayuso et al., 2008). Evolution of the spatial distribution with time indicated a progressive and continuous soil acidification, together with a significant dispersion of available elements similar to that described for Zn. In contrast, the evolution of the dispersion of non-available elements such as Fe, Al, and As was not as clear (Fig.5). This would suggest that elemental availability is the main factor controlling mobility in soils, and highly available elements are the most sensitive to dispersion-driving forces (acidification and leaching) in sludge-contaminated soil. Therefore, correlation and spatial distribution analysis are complementary studies allowing us to establish relationships between variables (soil properties and elements) and assess the evolution of these variables with time. This in turn enables us to study the dispersion of contamination in a given area.

## Conclusions

A capacity for natural attenuation was identified in the pyritic sludge-contaminated soils of the Vicario area (Guadamar banks), responsible for reductions in both total element concentration (particularly As) below maximum permissible levels, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable percentages of Mn, Cu, Zn, and Cd. Soil acidification by pyrite oxidation and leaching by rainfall were the main factors contributing to temporal and spatial evolution of the highly available elements Mn, Cu, Zn and Cd, and of the low availability elements Fe, Al, and As to a lesser extent. Periodic use of correlation and spatial distribution analysis proved to be useful tools in studying the dispersion of elements/contaminants in pyritic-contaminated areas.

## Acknowledgements

Financial support from the Spanish MICINN (CTM 2007-66401-CO2-02/TECNO; CTM 2004-06715-CO2-01), and from Comunidad de Madrid (EIADES S2009/AMB-1478) is acknowledged. Authors are grateful for the experimental plot cession in “El Vicario” by “Consejería de Medio Ambiente, Junta de Andalucía.”

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263



264 **Table 1.** Correlation matrix (Pearson coefficient) for soil properties and element concentrations in  
265 soil samples

266 **Table 2.** Maximum permissible levels of trace elements ( $\text{mg Kg}^{-1}$ ) established by the Spanish  
267 Ministry of Environment and the ‘Junta de Andalucía’ compared to maximum statutory limits  
268 established in other countries (Bernal et al., 2007).

269

## 270 **Figure captions**

271 **Fig. 1.** Soil temporal variation of pH (a), CE (b), OM (c) and iron oxides (d). Diagrams depict the  
272 median (line), percentiles (boxes and bars), and outliers (circles). Significant differences among  
273 years are indicated by different characters ( $P < 0.05$ ;  $n = 32$ ).

274 **Fig. 2.** Soil temporal variation of total, EDTA-extractable and  $(\text{NH}_4)_2\text{SO}_4$ -extractable Fe (a-c), Mn  
275 (d-f), Cu (g-i), and Zn (j-l) concentrations. Diagrams depict the median (line), percentiles (boxes  
276 and bars), and outliers (circles). Significant differences among years are indicated by different  
277 characters ( $P < 0.05$ ;  $n = 32$ ).

278 **Fig. 3.** Soil temporal variation of total, EDTA-extractable and  $(\text{NH}_4)_2\text{SO}_4$ -extractable Al (m-o), Cd  
279 (p-r) and As (s-u) concentrations. Diagrams show the median (line), percentiles (boxes and bars)  
280 and outliers (circles). Significant differences among years are indicated by different characters ( $P <$   
281  $0.05$ ;  $n = 32$ ).

282 **Fig. 4.** Percentage of  $(\text{NH}_4)_2\text{SO}_4$ -extractable and EDTA-extractable element concentrations with  
283 respect to total concentrations.

284 **Fig. 5.** Spatial distribution of the best-correlated variables (pH and  $(\text{NH}_4)_2\text{SO}_4$ -extractable fractions  
285 of Zn, Fe, Al and As). Relative values are plotted in a thermographic scale with hot colors (red)  
286 indicating low pH and high element levels, and cold colors (blue) indicating the opposite.

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288

289 **Table 1.** Correlation matrix (Pearson coefficient) of the soil properties and the element  
290 concentrations determined in the soil  
291

	pH	CE	OM	Fe oxides	(NH4)SO4- Fe	EDTA Fe	Total Fe	(NH4)SO4- Mn	EDTA Mn	Total Mn	(NH4)SO4- Cu	EDTA Cu	Total Cu
pH	1	-.372**	.174*	-.649**	-.484**	-.515**	-.540**	-.519**	.127	.540**	-.660**	.044	-.205**
CE	-.372**	1	-.129	.250*	.538**	.558**	.564**	.585**	.287**	.050	.599**	.112	.320**
OM	.174*	-.129	1	.147*	-.057	-.153*	.024	-.165*	-.166*	-.114	-.119	.330**	.347**
Fe oxides	-.649**	.250**	.147*	1	.372**	.421**	.552**	.177*	-.273**	-.586**	.458**	.142*	.286**
(NH4)SO4- Fe	-.484**	.538**	-.057	.372**	1	.707**	.583**	.423**	-.005	.199**	.842**	.022	.404**
EDTA Fe	-.515**	.558**	-.153*	.421**	.707**	1	.542**	.435**	.320**	.192**	.635**	.286**	.202**
Total Fe	-.540**	.564**	.024	.552**	.583**	.542**	1	.453**	-.011	-.179*	.671**	.168*	.516**
(NH4)SO4- Mn	-.519**	.585**	-.165*	.177*	.423**	.435**	.453**	1	.374**	.036	.649**	.075	.415**
EDTA Mn	.127	.287**	-.166*	-.273**	-.005	.320**	-.011	.374**	1	.383**	.018	.408**	.000
Total Mn	.540**	.050	-.114	-.586**	-.199**	-.192**	-.179*	.036	.383**	1	-.206**	.002	-.053
(NH4)SO4- Cu	-.660**	.599**	-.119	.458**	.842**	.635**	.671**	.649**	.018	-.206**	1	.035	.518**
EDTA Cu	.044	.112	.330**	.142*	.022	.286**	.168*	.075	.408**	.002	.035	1	.512**
Total Cu	-.205**	.320**	.347**	.286*	.404**	.202**	.516**	.415**	.000	-.053	.518**	.512**	1
(NH4)SO4- Zn	-.668**	.647**	-.129	.336**	.623**	.587**	.566**	.895**	.238**	-.104	.822**	.022	.413**
EDTA Zn	-.117	.476**	-.079	.024	.233**	.587**	.251**	.489**	.856**	.128	.264**	.494**	.163*
Total Zn	.117	.388**	.090	-.203**	.252**	.104	.255**	.561**	.444**	.497**	.324**	.027	.404**
(NH4)SO4- Al	-.474**	.402**	-.266**	.411**	.493**	.412**	.432**	.500**	.116	-.230**	.603**	.011	.305**
EDTA Al	-.614**	.570**	-.167*	.531**	.677**	.888**	.553**	.493**	.298**	-.308**	.717**	.268**	.250**
Total Al	-.060	-.014	.111	.070	-.014	.008	.368**	-.174*	-.222**	.138*	-.014	.059	-.061
(NH4)SO4- Cd	-.550**	.418**	.063	.361**	.507**	.355**	.331**	.699**	.124	-.230**	.655**	-.075	.392**
EDTA Cd	.150*	.333**	-.186**	-.160*	.094	.423**	.162*	.192**	.704**	.318**	.052	.454**	.031
Total Cd	-.038	-.191**	.048	.046	-.118	-.109	-.127	-.181*	-.069	.002	-.144*	.002	-.097
(NH4)SO4- As	-.289**	.396**	-.056	.238**	.646**	.417**	.414**	.350**	.030	-.053	.612**	.007	.351**
EDTA As	-.384**	.579**	-.151*	.301**	.619**	.909**	.536**	.442**	.453**	-.057	.551**	.291**	.187**
Total As	-.506**	.694**	-.071	.437**	.758**	.667**	.794**	.660**	.200**	-.119	.821**	.085	.546**

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297

	(NH4)SO4- Zn	EDTA Zn	Total Zn	(NH4)SO4- Al	EDTA Al	Total Al	(NH4)SO4- Cd	EDTA Cd	Total Cd	(NH4)SO4- As	EDTA As	Total As
pH	-0.668**	-.117	.117	-.474**	-. .614**	-.060	-.550**	.150*	-.038	-.289**	-. .384**	-. .506**
CE	.647**	.476**	.388**	.402**	.570**	-.014	.418**	.333**	-. 0.191**	.396**	.579**	.694**
OM	-.129	-.079	.090	-.266**	-.167*	.111	.063	-.186**	.048	-.056	-.151*	-.071
Fe oxides	.336**	.024	-. .203**	.411**	.531**	.070	.361**	-.160*	.046	.238**	.301**	.437**
(NH4)SO4- Fe	.623**	.233**	.252**	.493**	.677**	-.014	.507**	.094	-.118	.646**	.619**	.758**
EDTA Fe	.587**	.587**	.104	.412**	.888**	.008	.355**	.423**	-.109	.417**	.909**	.667**
Total Fe	.566**	.251**	.255**	.432**	.553**	.368**	.331**	.162*	-.127	.414**	.536**	.794**
(NH4)SO4- Mn	.895**	.489**	.561**	.500**	.493**	-.174*	.699**	.192**	-.181*	.350**	.442**	.660**
EDTA Mn	.238**	.856**	.444**	.116	.298**	-. .222**	.124	.704**	-.069	.030	.453**	.200**
Total Mn	-.104	.128	.497**	-.230**	-. .308**	.138*	-.230**	.318**	.002	-.053	-.057	-.119
(NH4)SO4- Cu	.822**	.264**	.324**	.603**	.717**	-.014	.655**	.052	-.144*	.612**	.551**	.821**
EDTA Cu	.022	.494**	.027	.011	.268**	.059	-.075	.454**	.002	.007	.291**	.085
Total Cu	.413**	.163*	.404**	.305**	.250**	-.061	.392**	.031	-.097	.351**	.187**	.546**
(NH4)SO4- Zn	1	.454**	.505**	.526**	.649**	-.123	.808**	.137*	-.117	.444**	.569**	.774**
EDTA Zn	.454**	1	.470**	.275**	.573**	-. .241**	.321**	.728**	-.090	.175*	.693**	.461**
Total Zn	.505**	.470**	1	.210**	.108	-. .226**	.494**	.312**	-.090	.312**	.260**	.523**
(NH4)SO4- Al	.526**	.275**	.210**	1	.558**	-. .199**	.479**	.163*	-.069	.469**	.385**	.553**
EDTA Al	.649**	.573**	.108	.558**	1	-.055	.504**	0.311**	-.069	.476**	.765**	.689**
Total Al	-.123	-. .241**	-. .226**	-.199**	-.055	1	-.350**	-.003	.034	-.020	-.027	-.101
(NH4)SO4- Cd	.808**	.321**	.494**	.479**	.504**	-. .350**	1	-.088	.084	.387**	.312**	.614**
EDTA Cd	.137*	.728**	.312**	.163*	.311**	-.003	-.088	1	-.103	.088	.553**	.252**
Total Cd	-.117	-.090	-.090	-.069	-.069	.034	.084	-.103	1	-.193**	-.150*	-. .204**
(NH4)SO4- As	.444**	.175*	.312**	.469**	.476**	-.020	.387**	.088	-.193**	1	.345**	.583**
EDTA As	.569**	.693**	.260**	.385**	.765**	-.027	.312**	.553**	-.150*	.345**	1	.703**
Total As	.774**	.461**	.523**	.553**	.689**	-.101	.614**	.252**	-.204**	.583**	.703**	1

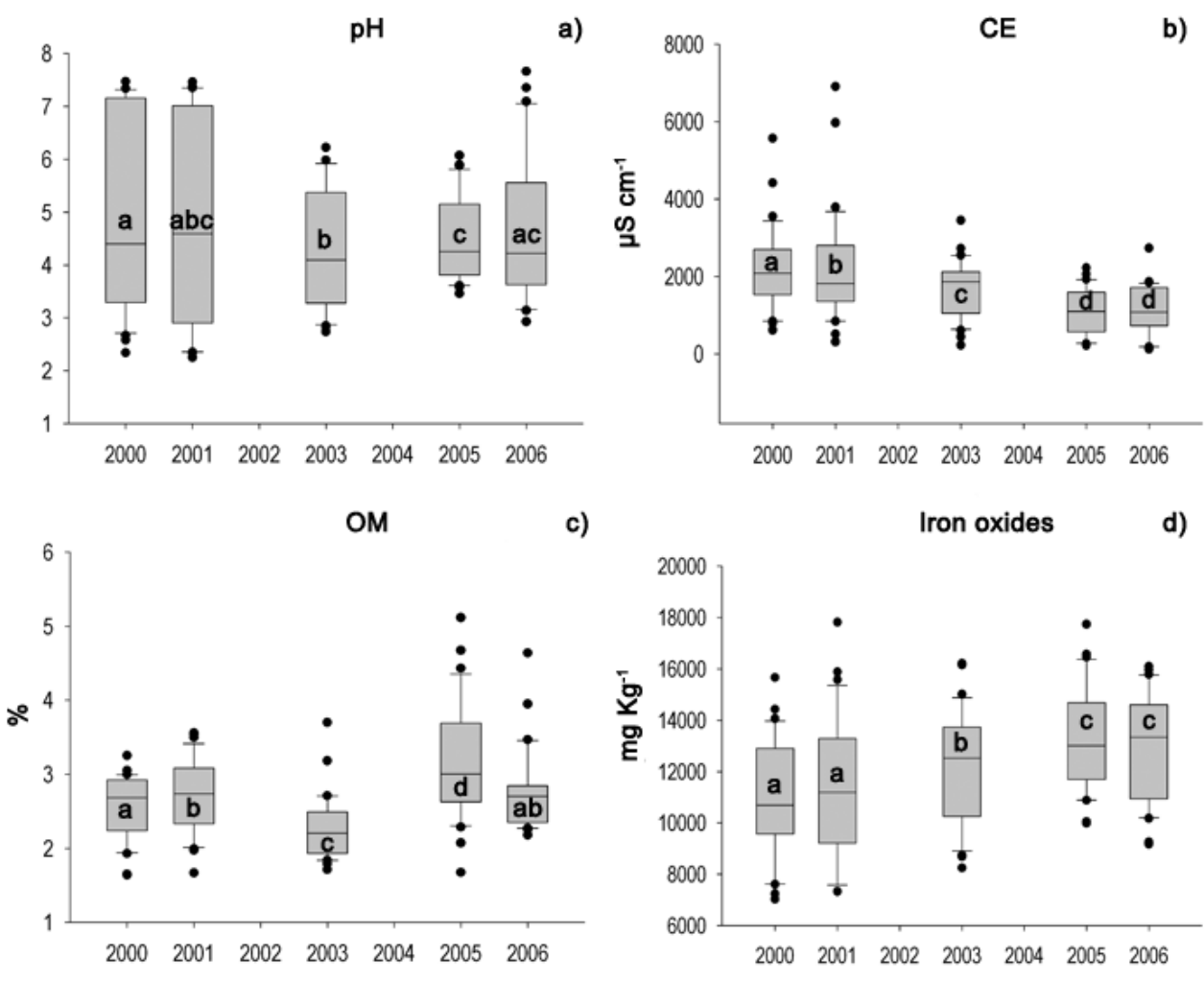
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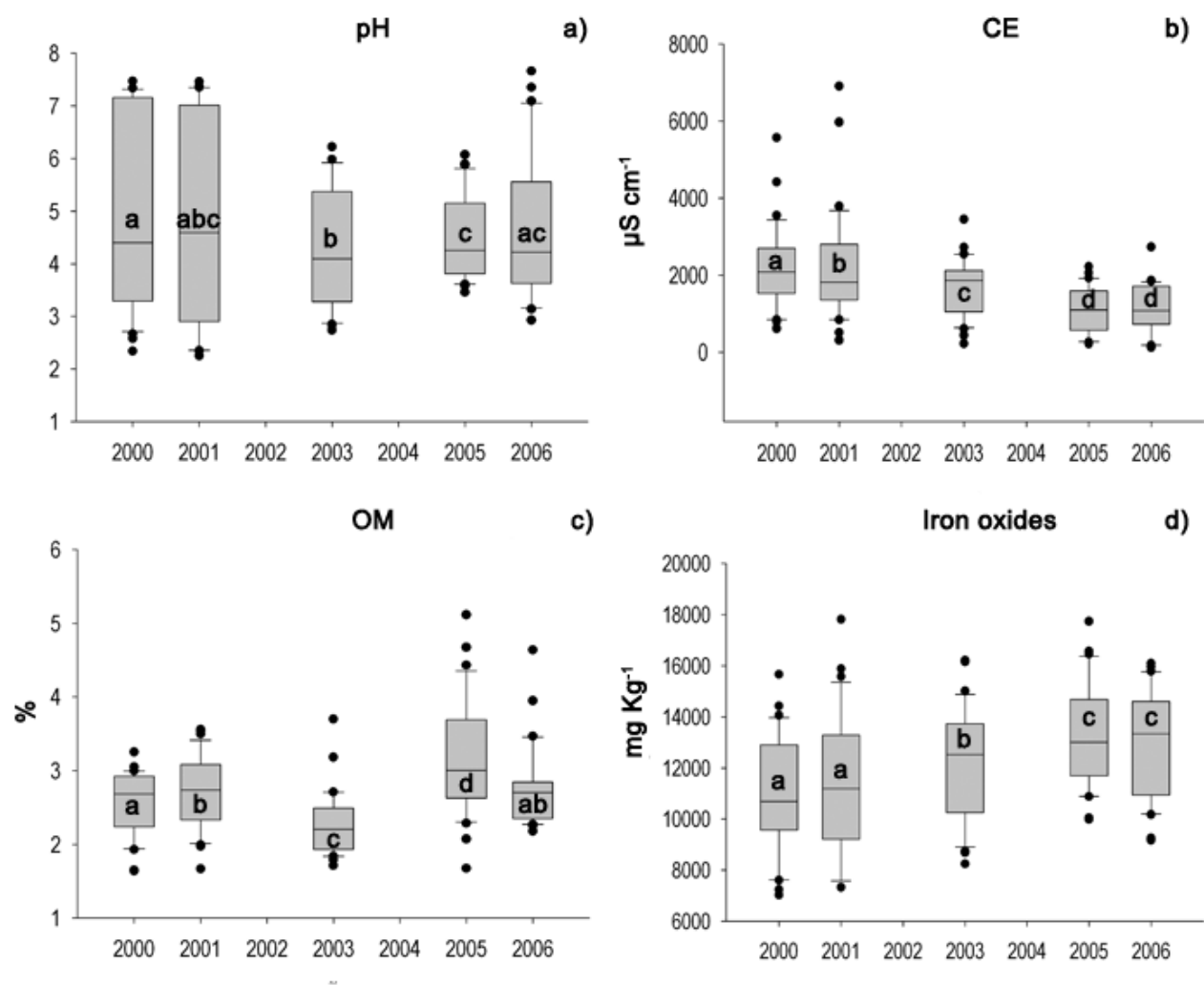
Correlation is significant at the \* $P < 0.05$  level, \*\* $P < 0.01$  level.

305 **Fig.1.** Temporal variation of pH (a), CE (b), OM (c) and iron oxides (d) in the soil. Diagrams  
306 represent the median (line), percentiles (boxes and bars) and outliers (circles). Significant  
307 differences among years are indicated by different characters ( $P < 0.05$ ;  $n = 32$ ).  
308



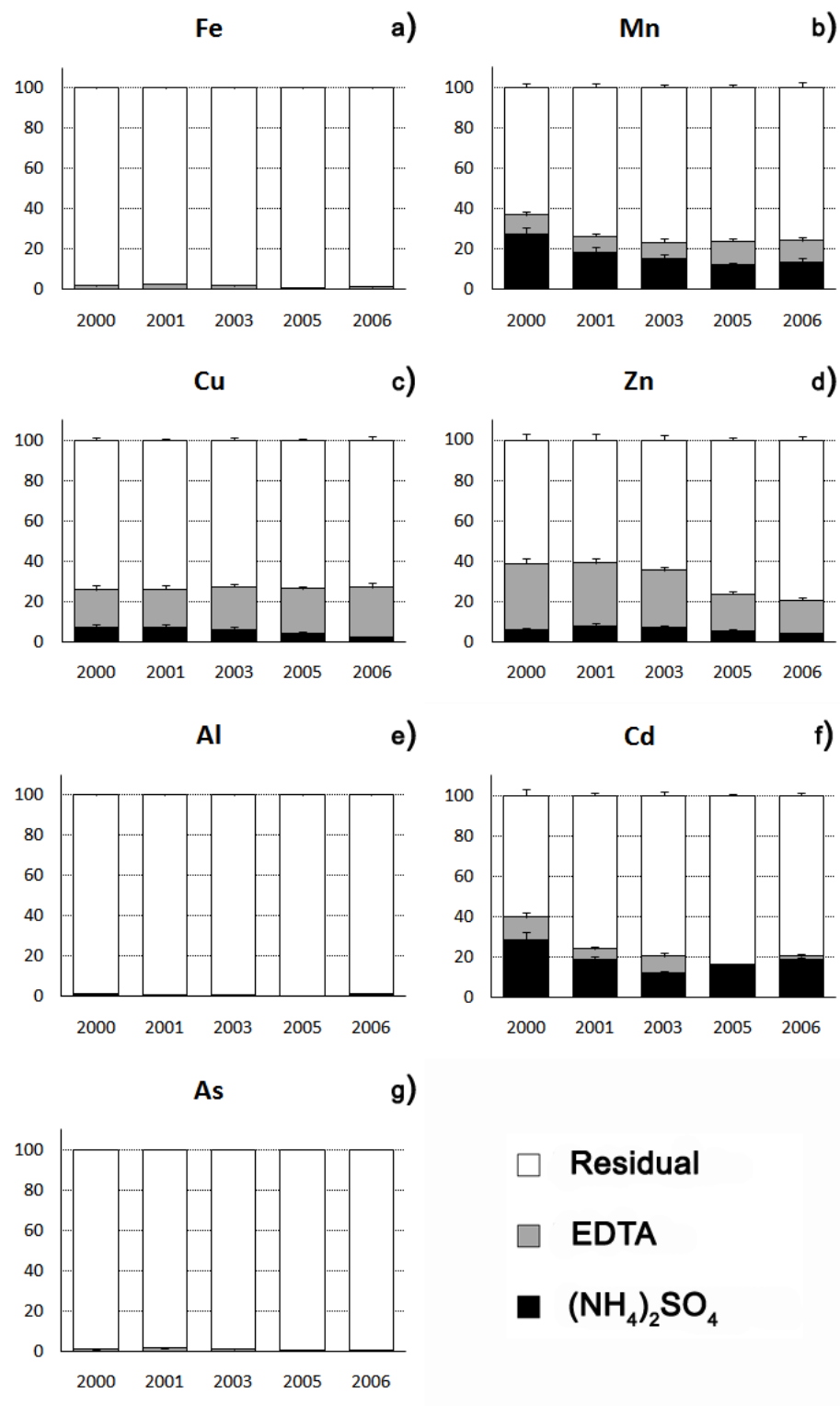
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314 **Fig.2.**  
 315



316 **Fig. 2.** Soil temporal variation of total, EDTA-extractable and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable Fe (a-c), Mn  
 317 (d-f), Cu (g-i), and Zn (j-l) concentrations. Diagrams depict the median (line), percentiles (boxes  
 318 and bars), and outliers (circles). Significant differences among years are indicated by different  
 319 characters ( $P < 0.05$ ;  $n = 32$ ).  
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 321

322  
323 Fig 3.  
324



325 Fig 4.  
326

