

Pollution of carbonate soils in a Mediterranean climate due to a tailings spill

M. SIMÓN, C. DORRONSORO, I. ORTIZ, F. MARTÍN & J. AGUILAR

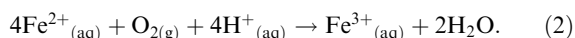
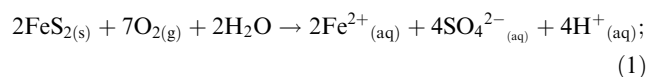
Departamento de Edafología y Química Agrícola, Facultad de Ciencias, Universidad de Granada, 18002 Granada, Spain

Summary

The retention walls in a pond containing the residues from the pyrite mine of Aznalcóllar (southern Spain) broke open on 25 April 1998, spilling approximately $6 \times 10^6 \text{ m}^3$ of polluted water and toxic tailings, which affected some 55 km^2 . Drying and aeration of the tailings resulted in oxidation, forming an acidic solution with high pollutant contents, the effects of which were studied in a calcareous soil. The infiltration of this solution markedly affected only the first 12 mm of the soil, where strong acidification caused the weathering of the carbonates, and where the fine mineral particles were hydrolysed. The SO_4^{2-} ions in the acidic solution precipitated almost entirely at this depth, forming gypsum, hydroxysulphates and complex sulphates. The Fe^{3+} ions also precipitated there, mainly in amorphous or poorly crystallized forms, adsorbing to As, Sb, Tl and Pb dissolved in the acidic solution. The Al^{3+} ions, though partly precipitating in the acidic layer, accumulated mostly where the soil pH exceeded 5.5 (12–14 mm in depth). They did so primarily as amorphous or poorly crystallized forms, adsorbing to Cu dissolved in the acidic solution. The Zn^{2+} and Cd^{2+} ions accumulated mainly at $\text{pH} > 7.0$ (19–21 mm in depth), being adsorbed chiefly by clay mineral. After 15 months, only the first 20 mm of the soil were acidified by the oxidation of the tailings and most of the pollutants did not penetrate deeper than 100 mm. Consequently, the speed of the cleanup of the toxic spill is not as important as a thorough removal of tailings together with the upper 10 cm of the soil.

Introduction

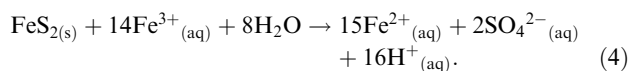
When the tailings from a pyrite mine are exposed to oxygen and water, sulphides oxidize to sulphates, the pH falls markedly as a result of the formation of sulphuric acid, and the pollutants solubilize (Förstner & Wittmann, 1983). In the case of pyrite, the most abundant sulphide in these tailings, the oxidation can be represented by the following reactions:



The Fe^{3+} released in reaction (2) may hydrolyse to form ferric hydroxide:

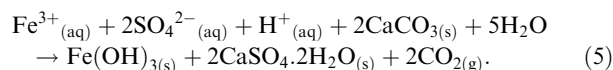


or it may oxidize additional pyrite by the reaction



Reaction (2) is very slow at $\text{pH} < 4.0$ and has been described as the rate-determining step in pyrite oxidation; nevertheless, Fe-oxidizing bacteria (e.g. *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*) increased the oxidation rate of Fe^{2+} by 10^5 (Singer & Stumm, 1970), and thus oxidation rates for pyrite are 10- to 20-fold larger than those resulting from purely chemical oxidation (Battaglia *et al.*, 1998; Boon & Heijnen, 1998).

When CaCO_3 is present in the soils the acidity is neutralized, the oxidation of Fe^{2+} to Fe^{3+} proceeds rapidly (Singer & Stumm, 1968), iron precipitates and the calcium and sulphate ions form gypsum (Ritsema & Groenenberg, 1993; Kashir & Yanful, 2000):



On 25 April 1998 the retention walls in a pond containing the residues from the pyrite mine of Aznalcóllar (southern Spain) broke open, and approximately $4 \times 10^6 \text{ m}^3$ of polluted water (solution phase) and $2 \times 10^6 \text{ m}^3$ of toxic tailings (solid phase) were spilled into the Agrío and Guadiamar River Basin, affecting some 55 km^2 (Grimalt *et al.*, 1999). The solid phase consisted of several sulphides such as pyrite (75–80%), sphalerite and galene (5%), chalcopyrite (1.5%) and arsenopyrite (1%), as well as minor amounts of bournonite, boulangerite, nuffieldite,

Correspondence: M. Simón. E-mail: msimon@goliat.ugr.es
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jaskolkiite and numerous trace metals (Almodóvar *et al.*, 1998; López-Pamo *et al.*, 1999). The principal pollutants were Zn, Pb, Cu, As, Sb, Bi, Cd and Tl (Cabrera *et al.*, 1999; Simón *et al.*, 1999; Vidal *et al.*, 1999).

After the spill, the soils of the basin were covered by a layer of tailings some 7 cm thick on average (López-Pamo *et al.*, 1999). At the time of the deposition the tailings were saturated with water, and afterwards began to dry progressively. As the tailings dried and aerated, sulphides oxidized to sulphates, the pH fell, and the pollutants solubilized (Alastuey *et al.*, 1999). The concentration of water-soluble SO_4^{2-} , Cd^{2+} and Pb^{2+} in the tailings increased logarithmically with declining moisture (Simón *et al.*, 1999). These solubilized elements, with evaporation, rose by capillary action to the surface, forming a white salty crust composed of $\text{Fe}^{(II)}$ -, Zn- and Mg-hydrated sulphates and large contents of Cu, As, Cd and Sb (López-Pamo *et al.*, 1999). Subsequent rains would dissolve these soluble salts, forming an acidic solution, which would then infiltrate the soil, raising the pollution level.

In the present work our aim is to determine the impact that the acidic solution from the oxidation of the tailings exerted on the different soil properties, estimating both the concentration reached by the pollutants in the soils as well as their penetration in depth.

Materials and methods

On 4 May 1998 (9 days after the toxic spill), in a project aimed at studying the pollution of the soils affected by the spill, we sampled the soils in various sectors throughout the basin, analysing the concentration of trace elements in the soils (0–10 cm in depth). In one of these sectors, 18 km from the origin of the spill, the colour of the soil was uniformly pale brown (10YR 6/3). Nevertheless, by 25 July 1999 (15 months after the spill), the first 12 mm of the soil of this sector had changed to reddish-yellow (7.5YR 6/8), presumably because of infiltration into the soil of the strongly acidic solution from the oxidation of the tailings, in which the various elements were dissolved. On this date, we sampled four locations in this sector which were still covered by a layer of tailings some 3 cm thick. At each location we made a detailed study of the soil properties and their pollutant concentrations, sampling the reddish-yellow band every 2 mm (0–2, 2–4, 4–6, 6–8, 8–10, 10–12 mm in depth) and sampling the underlying soil at different depths to 101 mm (12–14, 19–21, 29–31, 39–41, 59–61 and 99–101 mm).

In each sample, the particle-size distribution was determined by the pipette method after removal of organic matter with H_2O_2 and dispersion with sodium hexametaphosphate (Loveland & Whalley, 1991). The pH was measured potentiometrically in a 1:2.5 soil-water suspension. The CaCO_3 equivalent was determined by a manometric method (Williams, 1948). Total carbon was analysed by dry combustion with a LECO instrument, and the organic carbon was determined by the difference between total carbon and inorganic carbon from

CaCO_3 . Extracts of tailings:water and soil:water (1:10) were prepared, and the sulphates were precipitated as BaSO_4 (US Salinity Laboratory Staff, 1954). Total iron (Fe_d) and aluminium (Al_d) oxides of the soil samples were extracted with citrate–dithionite (Holmgren, 1967) and the amorphous or poorly crystallized oxides (Fe_o and Al_o) with ammonium oxalate (Schwertmann & Taylor, 1977). Iron and aluminium in the extracts were measured by atomic absorption spectroscopy. Pills of soil and lithium tetraborate (0.6:5.5) were prepared, and the total content of silica (SiO_2), iron (Fe_t) and aluminium (Al_t) was measured by X-ray fluorescence in a Philips PW-1404 instrument. Iron and aluminium within the structure of silicates were estimated by the differences $\text{Fe}_t - \text{Fe}_d$ and $\text{Al}_t - \text{Al}_d$, respectively, while well-crystallized oxides were estimated by the differences $\text{Fe}_d - \text{Fe}_o$ and $\text{Al}_d - \text{Al}_o$, respectively (Arduino *et al.*, 1984). X-ray diffraction patterns of powdered soil samples were made with a Philips PW-1700 instrument, using $\text{CuK}\alpha$ radiation. Samples of the soils, very finely ground (<0.05 mm), were digested in strong acids ($\text{HNO}_3 + \text{HF} + \text{HCl}$). In each digested sample and in each extract of tailings:water, the Cu, Zn, Cd, As, Pb, Sb, Bi and Tl contents were measured by ICP-MS with a PE SCIEX ELAN-5000 A spectrometer. The accuracy of the method was corroborated by analyses (six replicates) of Standard Reference Material: SRM 2711 (soil with moderately large trace-element concentrations; Gills & Kane, 1993) (Table 1). A Zeiss-950 scanning electron microscope with a Tracor Northern 523 X-ray energy-scattering microanalyser (SEM-EDS) was used to examine the morphology and analyse the composition of certain minerals present in the first 12 mm of the soil.

The climate of this area is typically Mediterranean (hot dry summers, cold wet winters, temperate autumns, and springs with variable rainfall). The rainfall from 4 May 1998 to 25 July 1999 was 695 mm, the average temperature 17.9°C, and the

Table 1 Analysis of Standard Reference Material 2711 (Gills & Kane, 1993)

Element	SRM 2711			
	Certified		Experimental	
	Mean	SD	Mean	SD
As	105.0	8.0	102.4	1.1
Cd	41.7	0.25	40.8	0.27
Cu	114.0	2.0	115.0	1.6
Pb	1162.0	31.0	1138.1	11.0
Tl	2.47	0.15	2.57	0.08
Zn	350.4	4.8	350.3	3.4
Bi	ND	–	2.66	0.17
Sb	ND	–	21.0	0.18

ND, not determined; SD, standard deviation.

potential evapotranspiration 975 mm (taken from the Aznalcázar weather station, at 21 km from the spill).

Results and discussion

Soil properties and macroelements

The chemical characteristics of the acidic solution from the oxidation of the tailings, although these must have changed over time, can be estimated from extracts of tailings:water on 25 July 1999 (Table 2). The infiltration of this solution into the soil resulted in the total decalcification and strong acidification of the reddish-yellow band (Table 3). The mean pH for the four locations analysed fell to a minimum of 3.2 compared with a maximum of 8.1 in the underlying calcareous soil. This strong acidification led to the hydrolysis of the finest mineral particles, reducing the mean clay content by roughly 65%, fine silt by 60% and coarse silt by 30%, with respect to the

Table 2 Mean, maximum and minimum values of pH and soluble-pollutant concentrations on 25 July 1999 in the extracts of tailings: water (1:10), in mg l^{-1}

	Mean	Maximum	Minimum
pH	2.51	2.62	2.43
SO_4^{2-}	2305.9	2419.6	2086.7
Fe	312.6	342.2	279.2
Al	0.96	1.27	0.80
Cu	58.6	66.2	53.3
Zn	332.1	385.9	304.2
Cd	1.03	1.21	0.87
As	28.6	31.7	26.1
Sb	0.60	0.71	0.48
Bi	0.82	0.93	0.68
Tl	0.001	0.001	0.001
Pb	3.81	3.96	3.70

Table 3 Mean, maximum and minimum values of the particle size, pH, CaCO_3 , and organic carbon content at different depths of the soils sampled on 25 July 1999 (data from the reddish-yellow band in *italic*)

Depth /mm	Clay /%			Fine silt /%			Coarse silt /%		
	Mean	Maximum	Minimum	Mean	Maximum	Minimum	Mean	Maximum	Minimum
0–2	<i>3.7</i>	<i>4.3</i>	<i>3.4</i>	<i>4.6</i>	<i>5.0</i>	<i>4.1</i>	<i>7.1</i>	<i>7.7</i>	<i>5.7</i>
2–4	<i>3.8</i>	<i>4.1</i>	<i>3.5</i>	<i>4.7</i>	<i>5.3</i>	<i>4.4</i>	<i>9.1</i>	<i>9.4</i>	<i>8.6</i>
4–6	<i>3.6</i>	<i>3.9</i>	<i>3.2</i>	<i>4.4</i>	<i>4.9</i>	<i>3.9</i>	<i>9.3</i>	<i>9.6</i>	<i>8.8</i>
6–8	<i>3.9</i>	<i>4.2</i>	<i>3.6</i>	<i>5.6</i>	<i>6.1</i>	<i>4.7</i>	<i>8.5</i>	<i>8.9</i>	<i>7.9</i>
8–10	<i>4.1</i>	<i>4.3</i>	<i>3.9</i>	<i>4.5</i>	<i>5.5</i>	<i>3.7</i>	<i>8.9</i>	<i>9.5</i>	<i>8.1</i>
10–12	<i>4.1</i>	<i>4.4</i>	<i>3.7</i>	<i>4.4</i>	<i>4.9</i>	<i>3.9</i>	<i>9.7</i>	<i>10.2</i>	<i>9.4</i>
12–14	8.7	9.8	7.4	9.6	10.8	8.2	11.6	12.7	10.8
19–21	11.8	12.2	11.2	11.3	13.3	9.6	10.8	11.4	10.1
29–31	11.6	12.0	11.1	12.6	14.2	9.7	11.4	13.1	10.8
39–41	11.9	12.7	10.5	12.1	13.9	9.1	11.3	12.8	10.3
59–61	11.7	12.4	11.5	13.2	15.1	9.9	12.0	12.4	11.6
99–101	12.2	13.1	10.6	12.8	14.5	10.3	12.1	13.2	11.1

Depth /mm	pH			CaCO_3 /%			Organic C /%		
	Mean	Maximum	Minimum	Mean	Maximum	Minimum	Mean	Maximum	Minimum
0–2	<i>3.2</i>	<i>3.5</i>	<i>3.1</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.61</i>	<i>0.68</i>	<i>0.57</i>
2–4	<i>3.3</i>	<i>3.5</i>	<i>3.1</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.58</i>	<i>0.61</i>	<i>0.55</i>
4–6	<i>3.4</i>	<i>3.6</i>	<i>3.3</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.64</i>	<i>0.70</i>	<i>0.59</i>
6–8	<i>3.4</i>	<i>3.7</i>	<i>3.1</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.64</i>	<i>0.69</i>	<i>0.61</i>
8–10	<i>3.7</i>	<i>4.1</i>	<i>3.5</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.61</i>	<i>0.66</i>	<i>0.54</i>
10–12	<i>4.1</i>	<i>4.4</i>	<i>3.9</i>	<i>0.2</i>	<i>0.3</i>	<i>0.1</i>	<i>0.69</i>	<i>0.73</i>	<i>0.62</i>
12–14	6.0	6.1	5.9	1.1	1.4	0.8	0.72	0.78	0.65
19–21	7.4	7.8	7.1	5.8	6.6	5.4	0.77	0.82	0.73
29–31	7.8	8.0	7.7	6.4	6.9	6.1	0.73	0.77	0.70
39–41	8.0	8.1	7.9	6.8	7.2	6.5	0.71	0.74	0.69
59–61	8.1	8.2	8.0	6.7	7.0	6.5	0.66	0.68	0.65
99–101	8.1	8.2	8.0	6.8	7.4	6.6	0.53	0.55	0.51

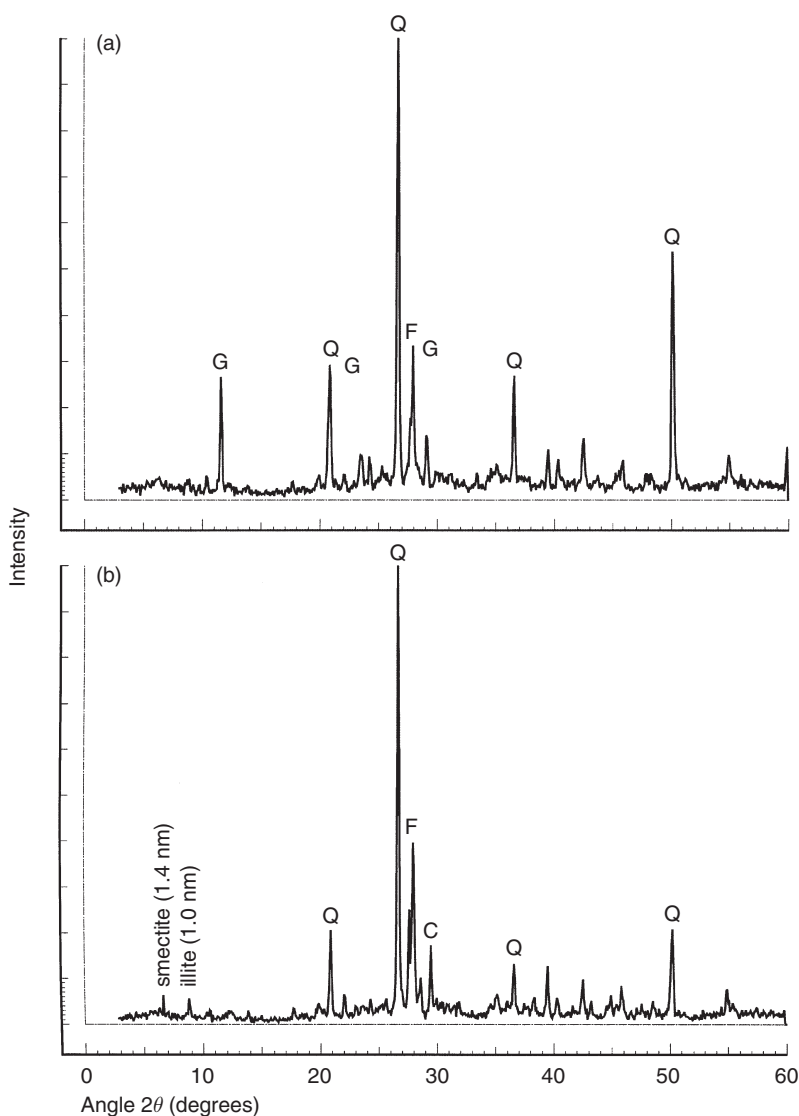


Figure 1 X-ray diffraction diagrams, obtained at the same instrument setting, of the soil-powder samples within (a) and beneath (b) the first 12 mm in the profile: G, gypsum; F, feldspars; C, calcite; Q, quartz.

underlying soil. The X-ray of the soil-powder samples (Figure 1) revealed that, within the first 12 mm, the reflections of the calcite disappeared, the relative intensities of feldspars diminished, and the intensity and sharpness of the basal reflections at 1.0 (illite) and 1.4 nm (smectite) of the clay minerals also decreased; by contrast, the reflections of the minerals resistant to hydrolysis, such as quartz, increased in relative intensity. The content in organic carbon was hardly affected by the acid solution, the values remaining nearly constant in the first 100 mm of the soil.

The SO_4^{2-} ions in the acid solution precipitated upon making contact with the soil, accumulating in the reddish-yellow band (Figure 2a), where their mean concentration increased by approximately 30 g kg^{-1} with respect to the underlying soil at 100 mm in depth. This precipitation occurred primarily in the form of gypsum (Miedema *et al.*, 1974; Ritsema & Groenenberg, 1993; Kashir & Yanful, 2000), as reflected by the X-ray

diffraction diagram showing the peaks for gypsum (Figure 1a). The SEM-EDS analysis, in addition to identifying crystals composed of S and Ca and a tabular habit (Figures 3a,b) typical of gypsum (Eswaran & Shoba, 1983), also shows needle-like crystals composed of S and Fe projecting from a mass made up of S, Zn, Fe, Mn and Al (Figure 3c), as well as raised scaly crystals composed of S and Al (Figure 3b) and aggregate microcrystals with pseudo-cubic morphology and composed of S, Fe and K (Figure 3d), presumably jarosite (Wagner *et al.*, 1982; Eswaran & Shoba, 1983). These results indicate that, in addition to the precipitation as gypsum, sulphate may also be adsorbed by various Fe and Al oxides and hydrous oxides, this being assumed to be the primary mechanism for SO_4^{2-} retention in a variety of soils (Parfitt & Smart, 1978; Johnson & Todd, 1983; Singh, 1984).

The iron in the acid solution also precipitated in this band (Figures 2c,d), increasing the concentration of Fe_t by

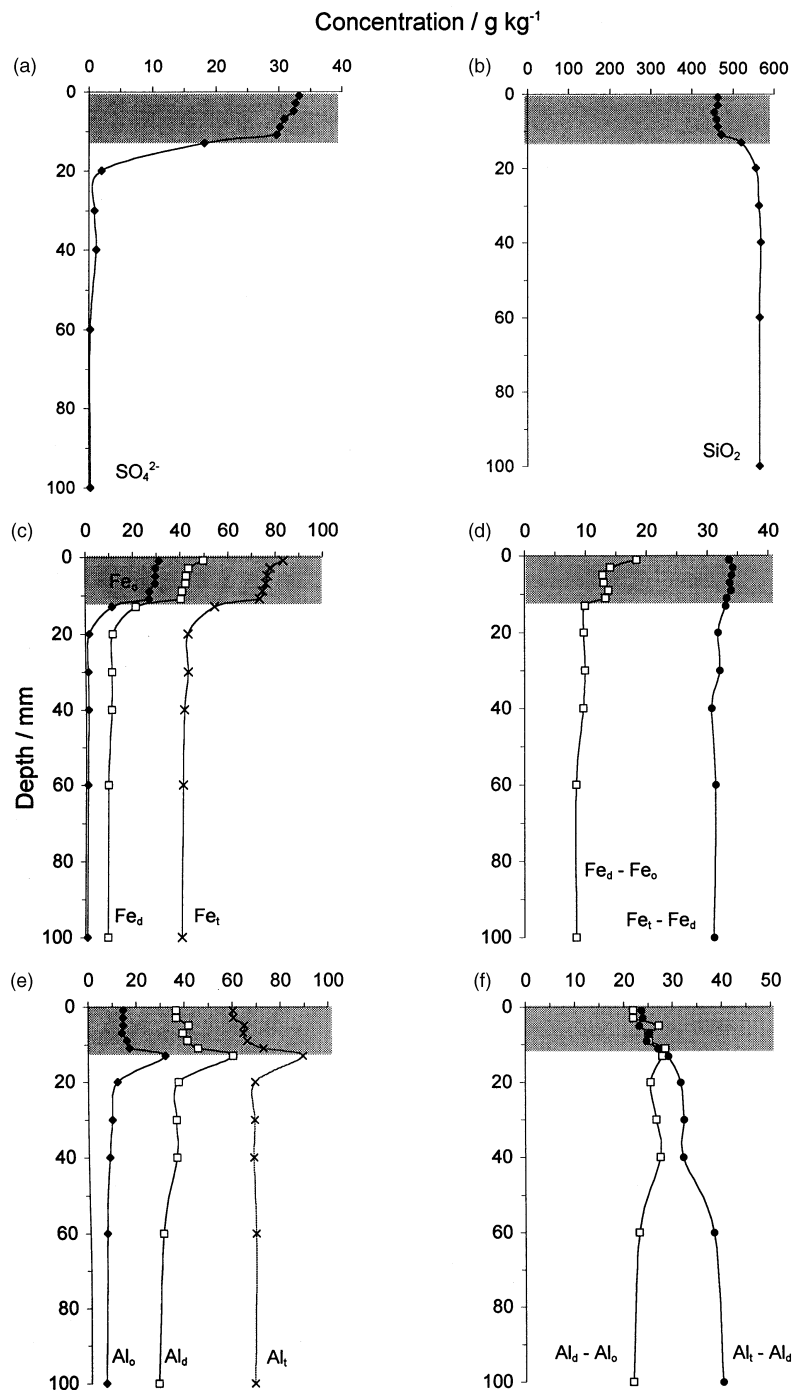


Figure 2 Mean concentrations of sulphates (a), silica (b) and iron (c,d) and aluminium (e,f) forms with depth of the soils sampled on 25 July 1999 (reddish-yellow band shaded).

approximately 36 g kg^{-1} with respect to the soil at 100 mm in depth. This precipitation must have resulted from the neutralization of the acidic solution on contact with the calcareous soil, accelerating the oxidation of Fe^{2+} to Fe^{3+} (Singer & Stumm, 1968). The Fe oxidized eventually reached saturation with respect to a variety of less soluble oxyhydroxides and hydroxy-sulphate minerals, forming ochreous precipitates (Bigham & Nordstrom, 2000) responsible for the reddish-yellow colour of

the uppermost soil layer. From the 36 g kg^{-1} of the Fe_t accumulated in the first 12 mm, almost all (33 g kg^{-1}) was extracted with citrate-dithionite (Fe_d), and $\text{Fe}_t - \text{Fe}_d$ remained practically constant with depth. The iron extracted with ammonium oxalate (Fe_o) was approximately 28 g kg^{-1} , indicating that the iron precipitated basically in the amorphous or poorly crystallized form (85%) and only a small portion (15%) in a well-crystallized form ($\text{Fe}_d - \text{Fe}_o$).

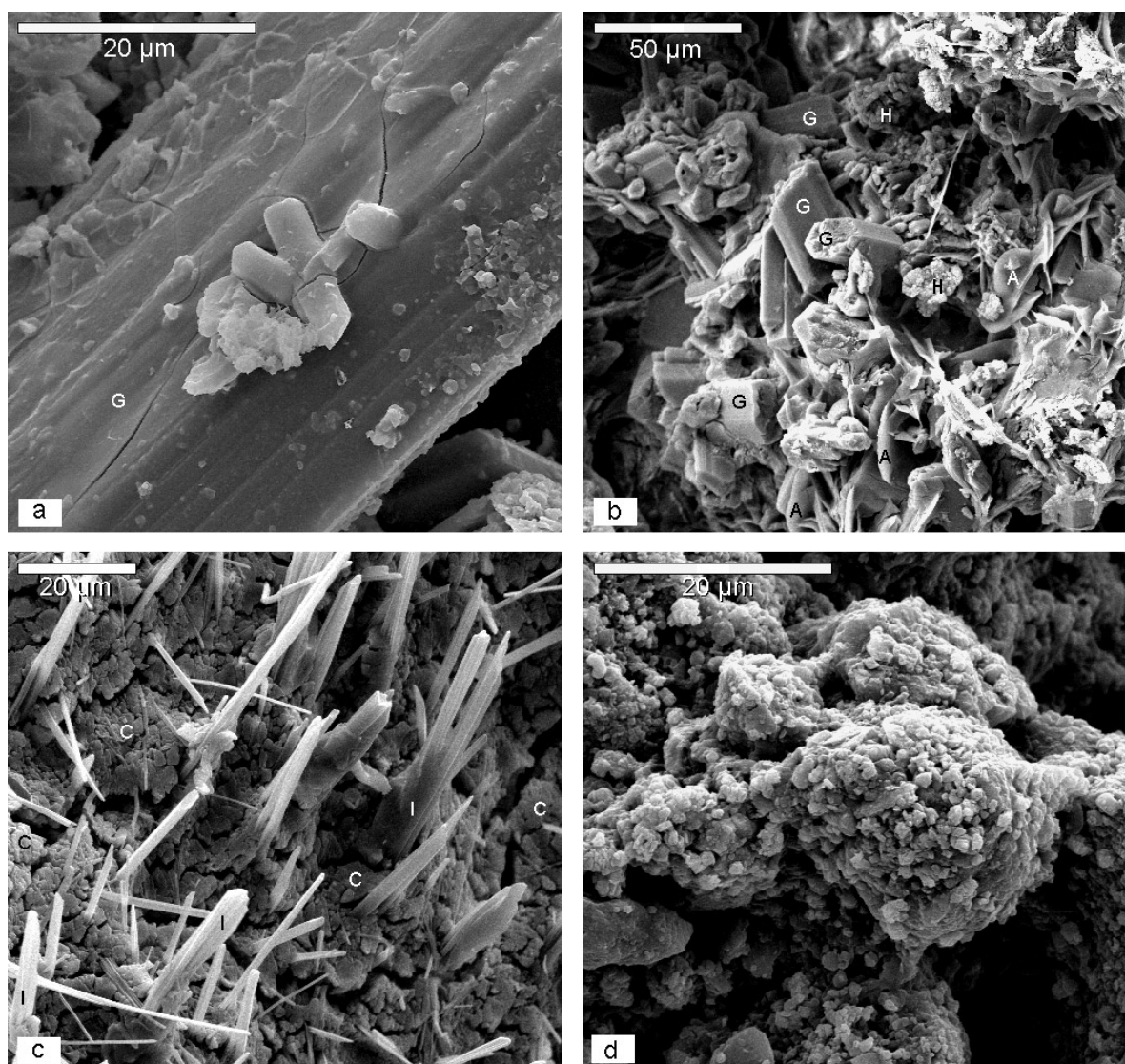


Figure 3 SEM-EDS analysis of certain minerals present in the first 12 mm of the soil: (a) crystal with tabular habit and composed of S and Ca (gypsum); (b) gypsum (G), raised scaly mineral composed of S and Al (A), aggregate microcrystals made up of Fe only (H); (c) needle-like minerals composed of S and Fe (I) projecting from a mass composed of S, Zn, Fe, Mn and Al (C); (d) aggregate microcrystals with pseudo-cubic morphology and made up of S, Fe and K (presumably jarosite).

The Fe_d content proved to be closely related to the sulphate content, both in $g\ kg^{-1}$, by the linear regression

$$Fe_d = 8.925 + 1.071SO_4^{2-}; r^2 = 0.973, p < 0.0001,$$

supporting the idea that iron and sulphate precipitate together (this also being reflected in the SEM-EDS analysis). The poorly crystallized iron hydroxysulphate formed appeared to be schwertmannite (Nordstrom, 1982; Bigham *et al.*, 1996; Bigham & Nordstrom, 2000); also, a minor fraction of the iron precipitated as aggregate microcrystals composed exclusively of iron (Figure 3b). In addition, the colour 7.5YR 6/8 of the uppermost 12 mm coincides with that characteristic of

schwertmannite (Scheinost & Schwertmann, 1999). The well-crystallized form could be jarosite, also visible in the SEM-EDS analysis.

The aluminium incorporated in silicates such as feldspars, illite and smectite, which can be estimated by the difference between the total aluminium and the total aluminium oxides ($Al_t - Al_d$), diminished substantially from $40\ g\ kg^{-1}$ at 100 mm depth to $24\ g\ kg^{-1}$ in the first 12 mm of the soil (approximately 40%), reflecting the intense hydrolysis process that affected this sector (Figure 2f). The Al that was dissolved in the acidic solution, although a minor part accumulated in the first 12 mm (Figure 3b), was more mobile than iron, a large portion being leached from the very acidic layer and accumulating in the

layer between 12 and 14 mm in depth with pH = 6.0 (Figure 2e). From the total hydrous Al oxides accumulated (Al_d), roughly 80% precipitated in the amorphous or poorly crystallized form (Al_o) and only 20% in a well-crystallized form ($Al_d - Al_o$). The relatively large sulphate content in this layer (18.3 g kg^{-1}), the pH > 5.0 and the predominance of the poorly crystallized form appear to indicate that this precipitation could have occurred fundamentally as basic aluminium sulphate (Van Breemen, 1973), presumably basaluminite (Nordstrom & May, 1996). The well-crystallized form could be jurbanite (Bigam & Nordstrom, 2000). The Al_d content was not related to sulphate content because the majority of the SO_4^{2-} precipitated in the first 12 mm as gypsum and iron hydroxysulphate.

The hydrolysis of the aluminium silicates also caused the partial solubilization and leaching of the silica (SiO_2) in the first 12 mm of the soil, where its concentration diminished by some 100 g kg^{-1} in relation to 100 mm in depth (Figure 2b). However, in contrast to the Al, silica showed no clear accumulation within the first 100 mm depth, and thus the accumulation may have occurred at a greater depth.

Trace elements

On 4 May 1998 the oxidation rate of the tailings and the concentration of water-soluble pollutants were found to be negligible (Simón *et al.*, 1999), and no rain fell between 25 April 1998 (spill) and 4 May 1998 (first sampling). Consequently, the concentration of the various pollutants in the soils sampled on 4 May 1998 would be attributable only to the soil concentrations prior to the spill (background) and the amount that penetrated the soil from the solution and solid phases of the toxic spill (initial pollution). The increase of pollutants in the soils sampled on 25 July 1999 with respect to those on 4 May 1998 can be ascribed to the oxidation of the tailings (Alastuey *et al.*, 1999), solubilization of the pollutants in the rainwater (Table 2), and infiltration into the soils. This increase will be termed 'oxidative pollution'.

The concentration of the pollutant elements between 0 and 10 cm in depth in the soil sampled on 4 May (this soil concentration will hereafter be termed SC4M) was very similar to mean concentrations between 99 and 101 mm in depth of the soils sampled on 25 July 1999 (Table 4). This indicates that almost all the elements which were dissolved in the acidic solution of the tailings remained in the first 100 mm of the soil. Only Zn and Cd, with average concentrations between 99 and 101 mm in depth clearly greater than SC4M, appear to have penetrated beyond the first 100 mm.

Nevertheless, although all the elements dissolved in the acidic solution tended to accumulate in the first 100 mm of the soil, there were clear differences between them. Thus, the mean concentrations of Zn and Cd in the first 12 mm of the soil were equal to or even less than SC4M, and therefore these elements did not accumulate in this highly acidic layer of soil

(pH < 4.5); it even appears that the acidic solution from the tailings solubilized and leached part of the Zn already present in the soil. The accumulation began in the soil layer with a pH = 6.0 (12–14 mm in depth) and reached its maximum in the soil layer with a pH > 7.0 (19–21 mm in depth). Deeper than 21 mm, concentrations progressively decreased. The difference between the mean concentration at each depth and that of SC4M, defined above as oxidative pollution (P_{OZn} and P_{OCd}), proved to be significantly related to the clay content and pH ($p < 0.05$). This indicates that these elements were adsorbed on to or diffused through the clay structure, this process increasing with the pH (Harter, 1983; Shuman, 1985; Brummer, 1986).

In addition, as with Al_d , some Cu accumulated in the strongly acidic layer (pH < 4.5), where the mean concentration was greater than SC4M, reaching its maximum accumulation at pH = 6.0 (12–14 mm in depth) and accumulating almost totally in the first 40 mm of the soil. The oxidative pollution (P_{OCu}) proved to be significantly related to Al_d ($p < 0.001$), indicating that this element is fundamentally adsorbed by amorphous or poorly crystallized hydrous Al oxides (Baker & Senft, 1995).

Like Fe_d , As tended to accumulate fairly uniformly in the reddish-yellow, strongly acidic band (pH 3.0–4.5). The oxidative pollution (P_{OAs}) was strongly correlated with Fe_d and SO_4^{2-} ($p < 0.001$), indicating that the As, probably as H_2AsO^- (the major species in this pH interval), was highly adsorbed by iron hydroxysulphates (O'Neill, 1995; Waychunas *et al.*, 1995). The Pb accumulated in the first 2 mm of the soil, with values decreasing sharply below this depth. The oxidative pollution (P_{OPb}) proved not to be related to the hydrous oxides (Al_d or Fe_d), despite the amorphous Fe oxides having a strong affinity for Pb (Kinniburgh *et al.*, 1976; McKenzie, 1980). This affinity, and propensity to precipitate as $PbSO_4$ (Brookins, 1988), may have caused the Pb to accumulate in the first 2 mm of the soil, while the Fe_d content was distributed fairly uniformly throughout the first 12 mm, masking any statistical relationship between the two. The other elements (Sb, Tl and Bi) showed a behaviour intermediate between As and Pb, with a maximum accumulation in the first 2 mm of the soil but with a progressive decline in depth. The oxidative pollution of each element (P_{OSb} , P_{OTl} and P_{OBi}) proved to be significantly related to Fe_d ($p < 0.001$) and SO_4^{2-} ($p < 0.01$), revealing that they were adsorbed by iron hydroxysulphates (Edwards *et al.*, 1995). The oxidative pollution of these elements was also significantly related to P_{OPb} ($p < 0.001$), which confirms the adsorption of Pb by Fe_d .

To estimate the mobility of the different pollutants in the soil we calculated a mobility index (M) using the equation

$$M = \sum_{n=1}^{12} (P_{Oin}/TP_{Oi})d_n,$$

where n represents the layers sampled, P_{Oin} is the oxidative pollution of each element i in each layer sampled n , TP_{Oi} is the

Table 4 Mean, maximum and minimum concentrations of the pollutants (in mg kg⁻¹) at different depths of the soils sampled on 25 July 1999 (data from the reddish-yellow band in *italic*), and the concentrations for the soil sampled on 4 May 1998 between 0 and 10 cm depth (SC4M)

Depth /mm	Cu			Zn			As			Cd		
	Mean	Maximum	Minimum	Mean	Maximum	Minimum	Mean	Maximum	Minimum	Mean	Maximum	Minimum
0–2	<i>104.1</i>	<i>123.6</i>	<i>90.5</i>	<i>377.6</i>	<i>485.9</i>	<i>211.9</i>	<i>1128.9</i>	<i>1480.5</i>	<i>925.9</i>	<i>0.7</i>	<i>0.9</i>	<i>0.6</i>
2–4	<i>95.1</i>	<i>119.0</i>	<i>81.1</i>	<i>334.5</i>	<i>431.2</i>	<i>238.8</i>	<i>1012.0</i>	<i>1204.1</i>	<i>893.1</i>	<i>0.8</i>	<i>1.0</i>	<i>0.6</i>
4–6	<i>90.0</i>	<i>111.8</i>	<i>79.2</i>	<i>274.7</i>	<i>368.2</i>	<i>195.0</i>	<i>1014.7</i>	<i>1297.5</i>	<i>796.1</i>	<i>0.6</i>	<i>0.9</i>	<i>0.4</i>
6–8	<i>93.4</i>	<i>113.6</i>	<i>80.9</i>	<i>234.1</i>	<i>267.0</i>	<i>178.8</i>	<i>1034.4</i>	<i>1309.9</i>	<i>856.2</i>	<i>0.8</i>	<i>1.0</i>	<i>0.6</i>
8–10	<i>109.1</i>	<i>126.9</i>	<i>99.2</i>	<i>264.5</i>	<i>327.1</i>	<i>232.9</i>	<i>746.1</i>	<i>918.3</i>	<i>622.6</i>	<i>0.8</i>	<i>1.1</i>	<i>0.7</i>
10–12	<i>210.7</i>	<i>238.6</i>	<i>181.8</i>	<i>214.3</i>	<i>233.2</i>	<i>203.5</i>	<i>514.9</i>	<i>546.6</i>	<i>488.7</i>	<i>0.9</i>	<i>1.1</i>	<i>0.7</i>
12–14	728.2	827.0	686.4	1742.4	2102.9	1535.4	188.9	308.7	135.7	7.5	10.2	6.5
19–21	451.0	593.9	362.5	2857.8	3547.8	2134.5	29.6	33.8	26.6	13.2	16.9	10.6
29–31	87.8	112.0	75.1	1606.7	2036.4	1366.2	23.5	26.3	20.4	7.0	8.7	5.6
39–41	31.2	37.1	27.7	1020.3	1250.6	818.8	20.0	22.4	17.9	4.1	5.7	3.4
59–61	25.5	30.5	21.2	749.5	918.8	622.3	19.5	21.4	16.1	1.9	2.8	1.4
99–101	26.1	30.1	22.8	512.3	653.0	432.9	18.9	22.8	15.1	1.9	2.5	1.4
CS4M	23.5			405.9			18.6			0.8		

Depth /mm	Sb			Bi			Tl			Pb		
	Mean	Maximum	Minimum	Mean	Maximum	Minimum	Mean	Maximum	Minimum	Mean	Maximum	Minimum
0–2	<i>20.0</i>	<i>23.0</i>	<i>18.0</i>	<i>7.7</i>	<i>9.2</i>	<i>6.6</i>	<i>2.8</i>	<i>3.3</i>	<i>2.5</i>	<i>215.9</i>	<i>267.7</i>	<i>173.2</i>
2–4	<i>11.3</i>	<i>12.6</i>	<i>9.7</i>	<i>6.9</i>	<i>8.9</i>	<i>6.1</i>	<i>1.9</i>	<i>2.7</i>	<i>1.5</i>	<i>89.3</i>	<i>102.4</i>	<i>79.6</i>
4–6	<i>9.5</i>	<i>11.2</i>	<i>8.4</i>	<i>5.1</i>	<i>5.4</i>	<i>4.7</i>	<i>1.6</i>	<i>2.2</i>	<i>1.4</i>	<i>81.3</i>	<i>97.1</i>	<i>68.2</i>
6–8	<i>7.6</i>	<i>9.2</i>	<i>6.6</i>	<i>4.4</i>	<i>5.3</i>	<i>3.5</i>	<i>1.2</i>	<i>1.6</i>	<i>0.8</i>	<i>52.4</i>	<i>64.4</i>	<i>42.4</i>
8–10	<i>6.9</i>	<i>8.4</i>	<i>5.4</i>	<i>3.2</i>	<i>4.2</i>	<i>2.3</i>	<i>1.0</i>	<i>1.4</i>	<i>0.7</i>	<i>50.4</i>	<i>62.6</i>	<i>39.3</i>
10–12	<i>6.1</i>	<i>7.6</i>	<i>5.1</i>	<i>2.8</i>	<i>4.0</i>	<i>2.2</i>	<i>0.8</i>	<i>1.1</i>	<i>0.6</i>	<i>46.9</i>	<i>51.9</i>	<i>40.5</i>
12–14	4.6	5.3	4.3	2.6	3.9	2.0	0.8	1.0	0.6	47.4	55.2	32.1
19–21	3.3	3.7	3.0	2.8	3.4	1.9	0.5	0.6	0.4	47.3	51.8	44.4
29–31	3.4	3.7	3.1	2.3	3.2	1.8	0.5	0.6	0.4	45.8	49.7	40.5
39–41	3.1	3.4	2.9	2.5	3.9	1.9	0.4	0.5	0.3	44.9	46.0	43.1
59–61	3.1	3.3	2.8	2.1	2.7	1.7	0.4	0.4	0.3	44.9	46.4	42.4
99–101	2.4	2.5	2.2	1.6	2.0	1.5	0.5	0.7	0.3	43.8	50.0	40.1
CS4M	2.2			1.4			0.5			44.3		

sum of the oxidative pollution of each element i of all layers sampled, and d_n is the depth (mm) of the lower limit of each layer sampled n . The value of this index would range from 2 (if the element accumulated entirely in the first 2 mm) to 101 (if the element accumulated entirely between 99 and 101 mm). The mobility in descending order was (the M values in parentheses)

$$\text{Zn}(29.7) > \text{Cd}(28.1) \gg \text{Bi}(15.6) > \text{Cu}(14.7) \gg \text{Sb}(8.3) \\ > \text{As}(6.6) > \text{Tl}(5.4) > \text{Pb}(4.8).$$

For the same spill, comparable results were reported by Vidal *et al.* (1999) three months after the accident, with the exception of Bi, which these authors include among the elements of low mobility such as Pb. This appears to indicate that Bi can increase in mobility over time.

Conclusions

The infiltration into the soil of the strongly acid solution formed by the oxidation of pyrite tailings gave rise to acidification, weathering of the carbonates, and hydrolysis of the mineral particles (more intense the finer the particle size), but only in the first 12 mm of the soil. The SO_4^{2-} ions present in the acidic solution precipitated almost entirely at this depth, forming gypsum, hydroxysulphates and complex sulphates. The Fe^{3+} ions also precipitated at this depth, mainly in amorphous or poorly crystallized forms (probably schwertmannite), adsorbing to As, Sb, Tl and Pb dissolved in the acidic solution. The Al^{3+} ions, though partly precipitating in the acidic layer, accumulated most when the soil pH exceeded 5.5. Similarly to Fe^{3+} , the Al^{3+} ions precipitated primarily as amorphous

or poorly crystallized forms (probably basaluminite), adsorbing to Cu dissolved in the acidic solution. The Zn^{2+} and Cd^{2+} ions precipitated mainly at $pH > 7.0$, being adsorbed chiefly by the clay mineral. Most of these pollutants did not penetrate beyond 100 mm in depth.

After 15 months, the solution from the oxidation of the tailings acidified only the first 20 mm of the soils, and most of the pollutants did not penetrate deeper than 100 mm and did not contaminate the subsoil or groundwater. This implies that under a Mediterranean climate in calcareous soils, the speed of the cleanup is not as important as a thorough removal of the spill without leaving behind remains of tailings mixed with soils. Also, the upper 10 cm layer of the soils should be removed together with the toxic tailings.

References

- Alastuey, A., García-Sánchez, A., López, F. & Querol, X. 1999. Evolution of pyrite mud weathering and mobility of heavy-metals in the Guadiamar valley after the Aznalcóllar spill, south-west Spain. *Science of the Total Environment*, **242**, 41–55.
- Almodóvar, G.R., Sáez, R., Pons, J.M., Maestre, A., Toscano, M. & Pascual, E. 1998. Geology and genesis of the Aznalcóllar massive sulphide deposits, Iberian Pyrite Belt, Spain. *Mineralium Deposita*, **33**, 111–136.
- Arduino, E., Barberis, E., Carraro, F. & Forno, M.G. 1984. Estimating relative ages from iron-oxide/total-iron ratios of soils in the western Po valley, Italy. *Geoderma*, **33**, 39–52.
- Baker, D.E. & Senft, J.P. 1995. Copper. In: *Heavy Metals in Soils* (ed. B.J. Alloway), pp. 179–205. Blackie Academic and Professional, London.
- Battaglia-Brunet, F., d'Hugues, P., Cabral, T., Cezac, P., García, J.L. & Morin, D. 1998. The mutual effect of mixed *Thiobacilli* and *Leptospirilli* populations on pyrite bioleaching. *Mineral Engineering*, **11**, 195–205.
- Bigham, J.M. & Nordstrom, D.K. 2000. Iron and aluminum hydroxy-sulfates from acid sulfate waters. In: *Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance* (eds C.N. Alpers, J.L. Jambor & D.K. Nordstrom), pp. 351–403. Mineralogical Society of America, Washington, DC.
- Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L. & Wolf, M. 1996. Schwertmannite and the chemical modeling of iron in acid sulfate waters. *Geochimica et Cosmochimica Acta*, **60**, 2111–2121.
- Boon, M. & Heijnen, J.J. 1998. Chemical oxidation kinetics of pyrite in bioleaching processes. *Hydrometallurgy*, **48**, 27–41.
- Brookins, D.G. 1988. *Eh-pH Diagrams for Geochemistry*. Springer-Verlag, Berlin.
- Brummer, G.W. 1986. Heavy metal species, mobility and availability in soils. In: *The Importance of Chemical Speciation in Environmental Processes* (eds M. Bernhard, F.E. Brinckman & P.J. Sadler), pp. 169–192. Springer-Verlag, Berlin.
- Cabrera, F., Clemente, L., Díaz Barrientos, E., López, R. & Mutillo, J.M. 1999. Heavy metal pollution of soil affected by the Guadiamar toxic flood. *Science of the Total Environment*, **242**, 117–129.
- Edwards, R., Lepp, N.W. & Jones, K.C. 1995. Other less abundant elements of potential environmental significance. In: *Heavy Metals in Soils* (ed. B.J. Alloway), pp. 306–352. Blackie Academic and Professional, London.
- Eswaran, H. & Shoba, S.A. 1983. Scanning electron microscopy in soil research. In: *Soil Micromorphology: Volume 1, Techniques and Applications* (eds P. Bullock & C.P. Murphy), pp. 19–51. A B Academic Publishers, Berkhamsted.
- Förstner, U. & Wittmann, G.T.W. 1983. *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin.
- Gills, T.E. & Kane, J.S. 1993. *Certificate of Analysis, Standard Reference Material 2711*. National Institute of Standards and Technology, Gaithersburg, MD.
- Grimalt, J.O., Ferrer, M. & Macpherson, E. 1999. The mine tailing accident in Aznalcóllar. *Science of the Total Environment*, **242**, 3–11.
- Harter, R.D. 1983. Effect of soil pH on adsorption of lead, copper, zinc and nickel. *Soil Science Society of America Journal*, **47**, 47–51.
- Holmgren, G.G.S. 1967. A rapid citrate-dithionite extractable iron procedure. *Soil Science Society of America Proceedings*, **31**, 210–211.
- Johnson, D.W. & Todd, D.E. 1983. Relationships among iron, aluminum, carbon, and sulfate in a variety of forest soils. *Soil Science Society of America Journal*, **50**, 776–783.
- Kashir, M. & Yanful, E.K. 2000. Compatibility of slurry wall backfill soils with acid mine drainage. *Advances in Environmental Research*, **4**, 252–268.
- Kinniburgh, D.G., Jackson, M.L. & Syers, J.K. 1976. Adsorption of alkaline earth, transition, and heavy metal cations by hydrous oxide gels of iron and aluminum. *Soil Science Society of America Journal*, **40**, 796–799.
- López-Pamo, E., Baretino, D., Antón-Pacheco, C., Ortiz, G., Arránz, J.C., Gumiel, J.C. *et al.* 1999. The extent of the Aznalcóllar pyritic sludge spill and its effects on soils. *Science of the Total Environment*, **242**, 57–88.
- Loveland, P.J. & Whalley, W.R. 1991. Particle size analysis. In: *Soil Analysis: Physical Methods* (eds K.A. Smith & C.E. Mullis), pp. 271–328. Marcel Dekker, New York.
- McKenzie, R.M. 1980. The adsorption of lead and other heavy metals on oxides of manganese and iron. *Australian Journal of Soil Research*, **18**, 61–73.
- Miedema, R., Jongmans, A.G. & Slager, S. 1974. Micromorphological observations on pyrite and its oxidation products in four Holocene alluvial soils in the Netherlands. In: *Soil Microscopy* (ed. G.K. Rutherford), pp. 772–794. Limestone Press, Kingston.
- Nordstrom, D.K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In: *Acid Sulfate Weathering* (eds J.A. Kittrick, D.S. Fanning & L.R. Hossner), pp. 37–56. Soil Science Society of America, Madison, WI.
- Nordstrom, D.K. & May, H.M. 1996. Aqueous equilibrium data for mononuclear aluminum species. In: *The Environmental Chemistry of Aluminum* (ed. G. Sposito), pp. 39–80. CRC Press/Lewis Publishers, Boca Raton, FL.
- O'Neill, P. 1995. Arsenic. In: *Heavy Metals in Soils* (ed. B.J. Alloway), pp. 105–121. Blackie Academic and Professional, London.
- Parfitt, R.L. & Smart, R.St.C. 1978. The mechanism of sulphate adsorption on iron oxides. *Soil Science Society of America Journal*, **42**, 48–50.
- Ritsema, C.J. & Groenenberg, J.E. 1993. Pyrite oxidation, carbonate weathering, and gypsum formation in a drained potential acid sulfate soil. *Soil Science Society of America Journal*, **57**, 968–976.
- Scheinost, A.C. & Schwertmann, U. 1999. Color identification of iron oxides and hydroxysulfates: use and limitations. *Soil Science Society of America Journal*, **63**, 1463–1471.

- Schwertmann, U. & Taylor, R.M. 1977. Iron oxides. In: *Minerals in Soil Environments* (eds J.B. Dixon & S.B. Webb), pp. 148–180. Soil Science Society of America, Madison, WI.
- Shuman, L.M. 1985. Zinc, manganese and copper in soil fractions. *Soil Science*, **140**, 11–22.
- Simón, M., Ortiz, I., García, I., Fernández, E., Fernández, J., Dorronsoro, C. & Aguilar, J. 1999. Pollution of soils by the toxic spill of a pyrite mine (Aznalcóllar, Spain). *Science of the Total Environment*, **242**, 105–115.
- Singer, P.C. & Stumm, W. 1968. Kinetics of the oxidation of ferrous iron. In: *Second Symposium on Coal Mine Research*, pp. 12–34. Mellon Institute, Pittsburgh, PA.
- Singer, P.C. & Stumm, W. 1970. Acidic mine drainage: the rate-determining step. *Science*, **167**, 1121–1123.
- Singh, B.R. 1984. Sulfate sorption by acid forest soils: 2. Sulfate adsorption isotherms with and without organic matter and oxides of aluminum and iron. *Soil Science*, **138**, 294–297.
- US Salinity Laboratory Staff 1954. *Diagnosis and Improvement of Saline and Alkaline Soils*. Handbook 60, US Department of Agriculture, Washington, DC.
- Van Breemen, N. 1973. Dissolved aluminum in acid sulfate soils and in acid mine waters. *Soil Science Society of America Proceedings*, **37**, 694–697.
- Vidal, M., López-Sánchez, J.F., Sastre, J., Jiménez, G., Dagnac, T., Rubio, R. & Rauret, G. 1999. Prediction of the impact of the Aznalcóllar toxic spill on the trace element contamination of agricultural soils. *Science of the Total Environment*, **242**, 131–148.
- Wagner, D.P., Fanning, D.S., Foss, J.E., Patterson, M.S. & Snow, P.A. 1982. Morphological and mineralogical features related to sulfide oxidation under natural and disturbed land surfaces in Maryland. In: *Acid Sulfate Weathering* (eds J.A. Kittrick, D.S. Fanning & L.R. Hossner), pp. 109–125. Soil Science Society of America, Madison, WI.
- Waychunas, G.A., Xu, N., Fuller, C.C., Davis, J.A. & Bigham, J.M. 1995. XAS study of arsenate and selenate substituted schwertmannite. *Physica B*, **208**, 481–483.
- Williams, D.E. 1948. A rapid manometric method for the determination of carbonate in soils. *Soil Science Society of America Proceedings*, **13**, 127–129.