Spatiotemporal Evolution of Soil pH and Zinc after the Aznalcóllar Mine Spill

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ABSTRACT

The residual pollution after the Aznalcóllar (southwestern Spain) pyrite mine spill is still a threat due to the continuing oxidation of sulfuric minerals. The objective of this paper was to analyze the combined effect of pyrite oxidation, sugar beet foam applications, and meteorological conditions on the spatiotemporal evolution of the pH and EDTA-extractable Zn concentration, using non co-located data from 11 sampling dates between June 1999 and March 2002. Median pH values ranged from 4.4 at the beginning of the monitoring period to 7.6 at the end, although values near 2.5 were observed throughout the entire period, despite of two sugar beet foam (SBF) applications. Zinc distributions were positively skewed and median concentrations ranged from 17 to 94 mg kg^{-1}. The inverse relationship between pH and Zn became weaker toward the end of the monitoring period as a consequence of the precipitation and posterior dissolution of newly formed minerals from the reaction products of the pyrite oxidation. Normal score maps showed that after the SBF applications only 0.5% of the monitored area was below the pH = 4 threshold, while on other dates up to one-third of the area remained below this value. The better performance of the second SBF application could be explained in terms of pyrite oxidation pathways and environmental conditions. From this analysis, with data obtained under uncontrolled field conditions, it is concluded that SBF should be applied before or during the wet and cold season to alleviate acidification, caused by the oxidation of pyrite or other sulfuric minerals.

The collapse of a wall of the tailings reservoir at the Aznalcóllar pyrite mine (southwestern Spain) on 28 Apr. 1998 released approximately 6 Mm^3 of acid water and sludge into the Agrio and Guadiamar River basins. As a consequence, approximately 2 Mm^3 of pyritic sludge was deposited on the river bed and banks, along a 64-km-long fringe with a mean width of 600 to 700 m, covering approximately 4634 ha of agricultural land. A cleanup program was set up shortly after the spillage and a total volume of 7 Mm^3 of sludge and contaminated soil was removed between May and December 1998. In addition, nearly 1 Mm^3 of contaminated material was removed during 1999 in an effort to further reduce the residual contamination. Finally limestone was applied and mixed with the topsoil layer and the remaining sludge.

The tailings had a particle diameter below 100 μm, and contained between 680 and 780 g kg^{-1} of pyrite (Cabrera et al., 1999; Simón et al., 1999; Vidal et al., 1999). Also, other sulfuric minerals were present, yielding metal concentrations that ranged from 8 g kg^{-1} (Zn) to 0.01 g kg^{-1} (Se) for a broad spectrum of metals such as Zn, Fe, As, Cu, Sb, Co, Tl, Bi, Cd, Ag, Hg, and Se (listed in order of their importance).

Heavy metal dynamics in soils are complex and influenced by numerous factors such as the pH, soil organic matter, soil texture, redox potential, and temperature (Alloway, 1990). Generally, heavy metals become increasingly mobile and available as the pH decreases (Tyler and Olsson, 2001). On exposure to both air and water, pyrite or other sulfuric minerals oxidize and produce sulfuric acid according to a well-known process (Stumm and Morgan, 1981; Xu et al., 2000; Simón et al., 2002):

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad [1]$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad [2]$$

Ferric hydroxide is precipitated and more hydrogen ions are released by the hydrolysis of Fe^{3+} that was formed by the oxidation of Fe^{3+} in Reaction [2]:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad [3]$$

The reaction of pyrite with oxygen is slow (Dent, 1992), but there is another oxidation reaction with Fe^{3+} ions under acid conditions:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad [4]$$

Because of the formation of sulfuric acid in Reactions [1] and [4], the pH of the residual tailings on the land may fall below 3, resulting in an increased mobility and availability of the present metals. Reaction [4] is known to be much faster than Reaction [1]. Xu et al. (2000) reported rate constants of pyrite oxidation by oxygen (Reaction [1]) ranging from 1.1×10^{-10} to 5.3×10^{-10} mol m^{-2} s^{-1}. Those for pyrite oxidation by Fe^{3+} (Reaction [4]) ranged from 9.6×10^{-9} to 1.9×10^{-8} mol m^{-2} s^{-1}. Since the oxidation by Fe^{3+} is faster than by oxygen it is important to know the oxidation rate of Fe^{2+} to Fe^{3+} (Reaction [2]), which becomes, at pH < 4, as slow as 1.53×10^{-10} mol m^{-2} s^{-1}. Nevertheless, under these acid conditions and in presence of dissolved oxygen, *Thiobacillus ferrooxidans* catalyzes Reaction [2] and may increase the oxidation rate by a factor of 10^5. When the pyrite particles are mixed with a porous medium, the above mentioned reactions will be affected by the medium's transport capacity for the re actants to move toward the mineral surface and for the removal of reaction products from it (Doménech et al., 2002). Under the Guadiamar basin field conditions the residual sludge was not mixed homogeneously with the soil, but mainly concentrated within small patches, where Reactions [1–4] could occur.

Common minerals that result from pyrite weathering are iron oxides (e.g., goethite and ferrihydrite), iron

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Abbreviations: MAE, mean absolute error; ME, mean error; ns, normal score; SBF, sugar beet foam.

sulfates (e.g., jarosite), and, under semiarid or arid conditions, sulfate salts (e.g., gypsum and sodium sulfate). This process has mainly been studied in acid sulfate soils (Strawn et al., 2002), in abandoned opencast mining areas (Meyer et al., 1999), in mine spoil piles (Backes et al., 1993), and in dredged materials (Förstner and Calmano, 1998), both under laboratory and field conditions. These studies usually aim at the determination of pyrite oxidation and weathering rates under varying environmental conditions and at understanding the chemical reactions involved to prevent the leaching of the acid soil solution. This concern also led to important efforts in the mathematical modeling of pyrite oxidation and associated reactive transport in saturated and unsaturated porous media (Wunderly et al., 1996; Xu et al., 2000).

Ayora et al. (2001) gave a complete list of the minerals, especially sulfates and hydroxides, that are formed from the ions released during the pyrite oxidation process and that precipitate at the soil surface during periods of intense evaporation. When rainfall starts after a dry period, these minerals are dissolved and form highly acid solutions, which can contribute to pH oscillations that are not directly related with the pyrite oxidation.

During their column and box percolation experiments Ayora et al. (2001) observed a different behavior for the sludge–sand and sludge–clay mixtures. In the latter case, the pH remained constant at 7.5 due to calcite dissolution and due to low pyrite oxidation rates, which were caused by oxygen limited conditions. For the sludge–sand mixture, the pH fell below 2 and the metals present were leached. At pH > 4, Fe and Al hydroxides precipitated and were dissolved when the pH decreased. From these results it can be presumed that, under field conditions, pyrite oxidation and the related precipitation of sulfates and hydroxides would preferably occur during the dry season, when the soil matrix contains more air than water. On the other hand, during the wet season, the lack of oxygen would inhibit pyrite oxidation, but the rainwater would dissolve the previously precipitated minerals and transport the metal containing acid solution toward deeper soil layers.

Simón et al. (2002) analyzed the soil properties and the concentrations of macro and trace elements in a carbonate soil, covered by a 3-cm-thick sludge layer, 15 mo after the spillage and found that only the top 1.2 cm of the soil were affected by the contaminant-holding acidic solution, produced by the oxidation of the tailings. This soil layer was totally decalcified with a pH that in the underlying soil fell from 8 to 3.2. The acidification led to the hydrolysis of the finest soil particles, reducing the fractions of clay, silt, and coarse silt by 65, 60, and 30%, respectively. No hypothesis was made about what would have occurred if the sludge layer had been mixed with the upper soil horizon.

Doménech et al. (2002) analyzed the leachates obtained from a column that contained a mixture of sludge and sandy soil in a 1:9 proportion. After 260 d, the pH of the leachate dropped to 2 and from thereon remained constant. The concentrations of Zn, Co, and Cd in the leachates matched the expected values from flow-through experiments at atmospheric oxygen pressure, which indicated that oxygen diffusion in the gas phase was maximum. Moreover, Zn, Co, and Cd were not retained in the soil by any secondary process (sorption or precipitation of new phases). However, it is not clear how these results can be related to the field conditions in the Guadiamar River basin, where the soil was subjected to intermittent infiltration and exfiltration processes and tilled several times after the cleanup actions.

The Mediterranean climate of the region induces a seasonal variation of the pyrite oxidation rate. Backes et al. (1993) measured pyrite oxidation rates in a mine spoil under both field (lysimeter experiment) and laboratory (pot experiment) conditions over a 53-wk period. They found that the oxidation rates varied primarily with temperature. No influence of the moisture content could be detected in the pot experiments that were maintained close to field capacity and no rainfall or soil moisture data were given for the lysimeter experiment. At the location of the field experiment (Scotland), dry soil conditions occasionally occurred in the summer months. During the summer the oxidation rates were about five to ten times higher than during winter, which was attributed by the authors to the inactivity of *Thiobacillus ferrooxidans* due to the low temperatures of the winter months. The very dry summer conditions for the Guadiamar valley soils, especially near the surface where the major part of the residual pyrite sludge remained, might reduce the pyrite oxidation rates.

According to Backes et al. (1993), liming is one of the most common treatments to neutralize the released acidity and maintain pH above 4 so that there is a fast Reaction [2]. However, microorganisms like *Thiobacillus ferrooxidans* become inactive, and Fe^{3+}, which oxidizes pyrite according to Reaction [4], is removed through the precipitation of $Fe(OH)_3$, which may form a coating on the surface of the pyrite particles. Garrido et al. (2003) evaluated the chemical and mineralogical implications of using industrial by-products as soil acidity amendments under laboratory conditions and found that these are valuable alternatives to mined gypsum and lime for alleviating acidity. In the Aznalcóllar mine spill affected area, sugar beet foam (SBF) was preferred to $CaCO_3$ application because: (i) it is easier to apply on the land; (ii) its reaction with the soil is slower than that of the lime, which prevents the occurrence of extreme alkaline conditions in the case of an overdose; and (iii) its organic matter content is higher than that of lime, which stimulates microbial activity (Antón-Pacheco et al., 2001).

After the remediation actions, the reclaimed land remained locally polluted by a small quantity of pyritic sludge (Antón-Pacheco et al., 2001), which was mixed with the topsoil layer. Depending on the highly variable soil characteristics in the area, the soil surface conditions, and the erratic rainfall occurrence, this mixture still represented a potential risk of contamination. A project was set up to monitor the soil chemical properties at an intensively sampled site, situated downstream from the tailings reservoir, where periodically non co-located soil samples were taken and analyzed. The first six sampling dates of this data set, between June 1999 and September 2000, were used by Vanderlinden et al. (2006) to map the residual pollution at the site by the geostatistical spatial interpolation of the merged normal score–transformed data on pH, Fe, and Zn from different sampling dates, based on the realistic assumption that the spatial pattern of the residual pyrite sludge did not change in time. The non co-located nature of the data prevented them from using traditional multivariate spatiotemporal techniques. Here we build further on the results of this study, using the normal score maps of pH and Zn for the spatiotemporal analysis of the data. Zinc was preferred to Fe since it behaves similarly to this metal and because natural soils usually contain a smaller amount of Zn so that the polluting effect of the mine spoil becomes more evident with respect to Zn.

The aims of this paper are to (i) assess the spatiotemporal evolution of the pH and EDTA-extractable Zn concentrations at the reclaimed site from non co-located observations, (ii) analyze the combined effect of pyrite oxidation and meteorological conditions on the pH and Zn dynamics, and (iii) evaluate the efficiency of the SBF applications to alleviate acidity. These issues are usually studied under laboratory or controlled field conditions. The Aznalcóllar mine spill offers a unique opportunity to evaluate pyrite weathering and related processes, and the alleviation of its consequences under uncontrolled field conditions. Lessons learned from the Aznalcóllar mine spill should be useful for the remediation of the consequences of similar spills elsewhere.

MATERIALS AND METHODS

Site Description and Sampling Scheme

The monitoring site (37°26′ N, 6°13′ W) was situated at a meander in the Guadiamar River, left bank, about 8 km downstream from the tailings reservoir. Figure 1 shows the rainfall record since the spillage at the nearby conventional weather station of Pilas (37°18′ N, 6°18′ W). The hydrologic year 1998–1999 was the driest on record. The study site was cleaned during the summer of 1998. The terrain is rather flat (see Fig. 2) and was flooded by the sludge from north to south. During February and November 2000 SBF was applied and worked into the topsoil layer. The prevailing soil texture at the site is loam to sandy loam, although coarser materials such as gravel and sand may occasionally occur, which reflects the alluvial character of the site. The main soil of the area is a Typic Xerofluvent. These coarse-textured spots form a fast gateway to the underlying aquifer for heavy metals. The very fine granulometry of the pyritic material reduced drastically the in- and exfiltration capacity. The soil–sludge mixture at these spots was observed to form a resistant substrate where tillage and SBF application was only superficial. During the wet season (e.g., December 1999) these spots became marshy, and during the dry season only the surface layer dried while the underlying material remained moist for a longer period.

Periodical sampling took place on 11 different dates between June 1999 and March 2002 (June, September, and December of 1999; March, May, September, and December of 2000; February, March, and May of 2001, and March of 2002). The locations of the 916 sample points, covering an area of approximately 9 ha, are shown in Fig. 2. The samples from June 1999 were intended as a reconnaissance survey and cover only a small section of the study area. Only the May 2000, March 2001, and March 2002 surveys covered almost the entire area, while the others covered adjacent or partly overlapping areas. All soil samples were taken from the 0- to 15-cm horizon using a 7-cm-diameter auger and were transported in marked plastic bags to the laboratory. On each date the positions of the samples were measured with a Topcon (Livermore, CA) topographic total station and represented in a coordinate system with the *x* axis parallel to the direction of the remaining sludge bands (see Vanderlinden et al., 2006).

Analytical Methods

The soil samples were air-dried and subsequently sieved (< 2 mm). Both water and $CaCl_2$ solutions were used for pH measurement (Lab pH-meter Basic 20; Crison SA, Alella, Barcelona, Spain). The EDTA-extractable Zn concentrations,

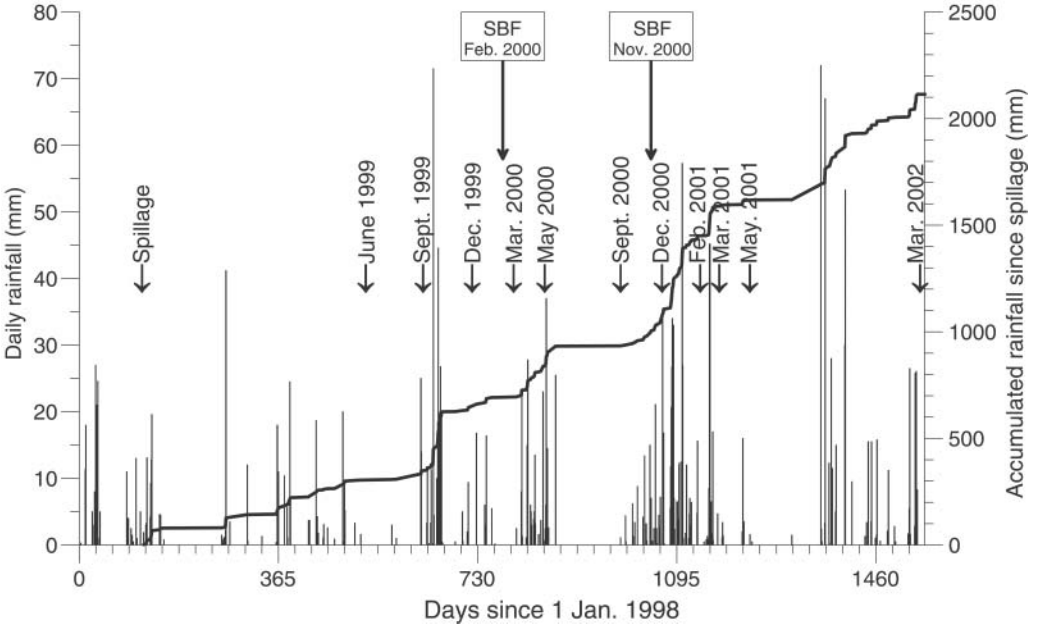

Fig. 1. Rainfall at the nearby weather station of Pilas from 1 Jan. 1998 to 31 Mar. 2002. Also the sampling dates and the dates of two sugar beet foam (SBF) applications are shown.

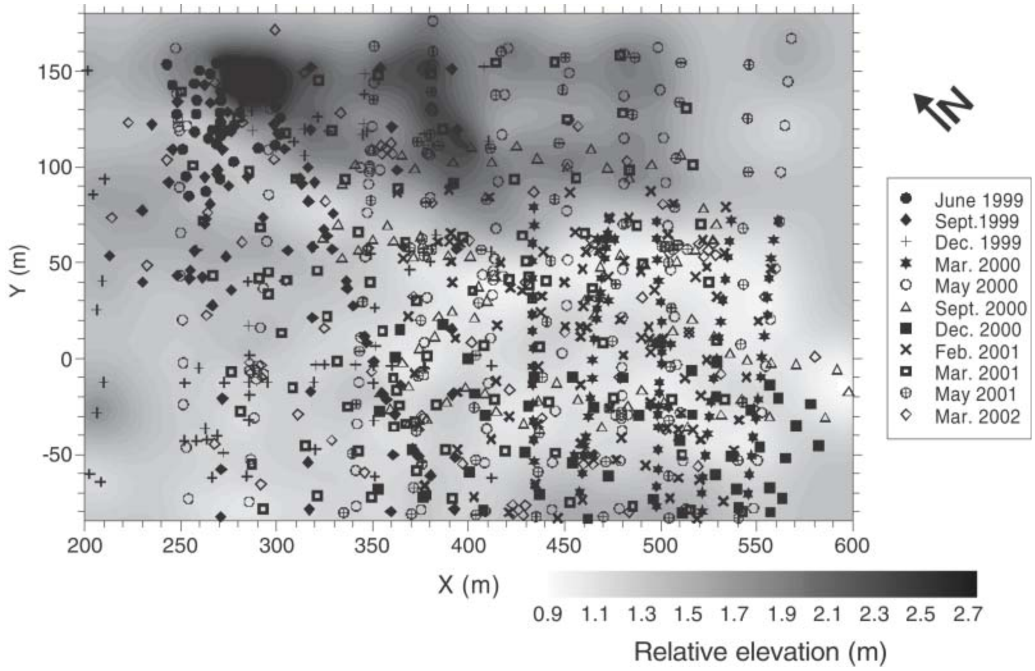

Fig. 2. Location of the 916 sampling points within the study area, according to the 11 sampling dates. The background gray-scale map represents local relative topography.

hereafter denoted by Zn, were extracted with a solution of CH_3COONH_4 0.5 M + CH_3COOH 0.5 M + $EDTANa_2$ 0.02 M and their concentrations were subsequently measured by atomic absorption spectrophotometry (Atomic Absorption Spectrometer 3110; PerkinElmer, Wellesley, MA).

Statistical Analysis and Mapping of pH and EDTA-Extractable Zinc

The temporal evolution of both soil chemical properties is represented by means of box-and-whisker plots. The caps at the end of each box indicate the extreme values (minimum and maximum), the box is defined by the lower and upper quartiles (LQ, UQ, respectively), and the line in the center of the box is the median. The length of the box is the interquartile range (IQR). Outliers (circles) are points that fall below LQ − 1.5IQR or above UQ + 1.5IQR.

The spatial distribution of the residual pyrite sludge did not change in time, but those of the soil chemical properties that reflect this pollution did, as a consequence of reactions like pyrite oxidation or of the application of SBF. Taking this into account, Vanderlinden et al. (2006) merged the data from the different sampling dates together after a normal score transformation, ns, $y(x) = \Phi[z(x)]$, with $z(x)$ the original data, $\Phi(\cdot)$ the transformation function, and $y(x)$ the transformed data, or normal scores (ns), with a standard normal histogram (Goovaerts, 1997; Deutsch and Journel, 1998). They compared several geostatistical interpolation methods and found that ordinary kriging with anisotropic variogram models (Goovaerts, 1997) produced the most representative ns maps for the pH and Zn concentrations. Applying the corresponding back-transformation, it is possible to obtain maps of the entire area for each sampling date. However, this back-transformation is not straightforward since the optimal character of the kriging estimates is lost and unbiasedness is no longer guaranteed. The back-transformation, $\Phi^{-1}(\cdot)$, magnifies the interpolation errors of the ns estimates in a nonlinear way, yielding biased back-transformed estimates although the ns estimates are unbiased. In this particular case, any underestimation (negative bias) of the highest metal concentrations and, although less serious, overestimation (positive bias) of the lowest pH values were important.

To avoid the loss of unbiasedness during the back-transforms, each ns map can be classified according to an ns threshold value that corresponds to a certain value of the soil chemical property on a certain sampling date. These indicator maps can then be overlaid or added up to detect the areas where the threshold value is most often exceeded.

Cross-validation (Goovaerts, 1997) was used here to evaluate the quality of the back-transformed maps and to assess the bias introduced. This was done by back-transforming the ns cross-validation estimates and comparing them with the observed values using different statistical parameters. Here we used the mean error (ME), which quantifies the average bias of the estimator and is a measure of the accuracy of the estimates:

$$\mathrm{ME} = \frac{1}{n}\sum_{i=1}^{n}[z^*(x_i) - z(x_i)] \qquad [5]$$

and the mean absolute error (MAE):

$$\mathrm{MAE} = \frac{1}{n}\sum_{i=1}^{n}|z^*(x_i) - z(x_i)| \qquad [6]$$

which gives the precision of the back-transformed estimates, $z^*(x_i)$, compared to the observations, $z(x_i)$, at locations x_i.

Since we were interested in the spatiotemporal evolution of the chemical properties it was sufficient to calculate difference maps of the back-transformed estimates for each successive pair of sampling dates. In this way, the effect of the bias introduced was filtered out because the bias was similar for all sampling dates. Probability plots of the observations and the grid estimates illustrate this, and are used with the difference maps to assess the two applications of SBF and their effect on the soil chemical properties. The overall evolution of the spatial pattern of the soil chemical properties during the entire monitoring period of 33 mo is also represented in this way.

RESULTS AND DISCUSSION

Exploratory Temporal Data Analysis

The pH distributions (Fig. 3) were slightly skewed toward the lowest values, especially for the last five sampling dates. The median pH values ranged from 4.4 in June and September 1999 to 7.6 in March 2002. Significant increases in the pH were observed after the application of SBF, combined with tillage, during February and November 2000. Zinc concentrations showed positively skewed distributions toward the largest data values (see Fig. 3). Median concentrations ranged from 17 (December 1999) to 94 mg kg^{-1} (September 1999).

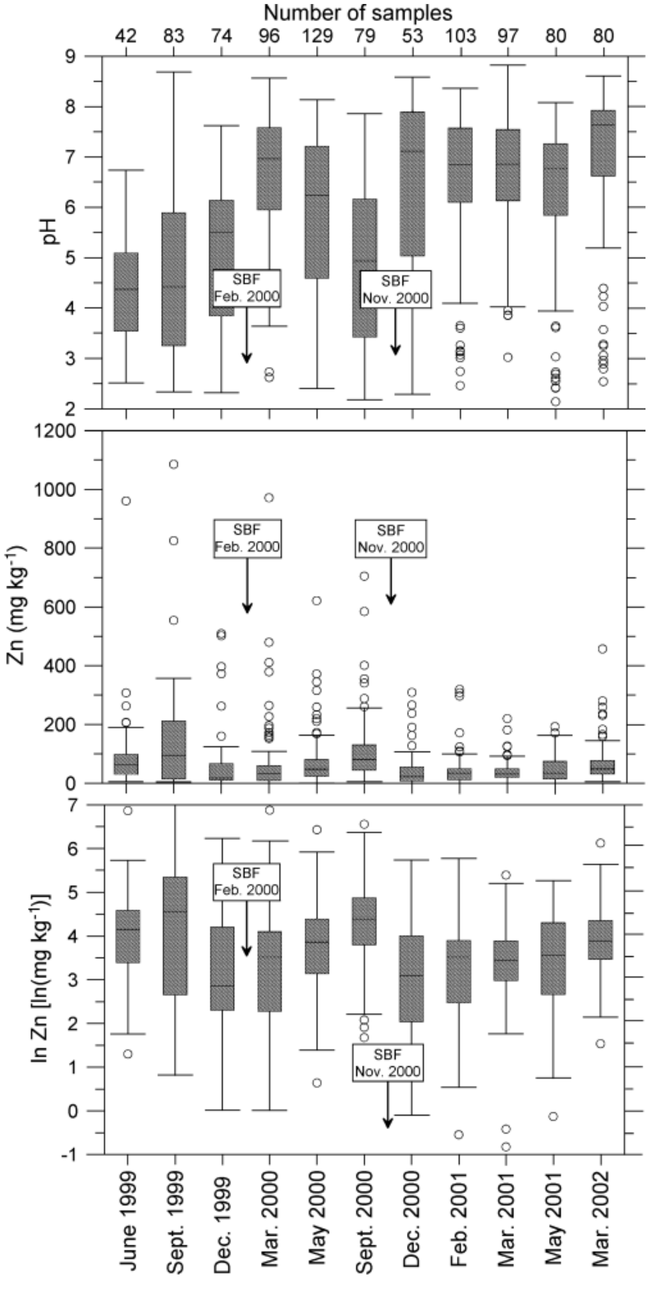

Fig. 3. Box-and-whisker plots for pH, EDTA-extractable Zn concentration (Zn), and ln-transformed EDTA-extractable Zn (ln Zn) concentration, on the 11 sampling dates. Also, the moment of both sugar beet foam (SBF) applications is indicated.

To improve the interpretation of these graphs and to facilitate their subsequent analysis, the data were ln-transformed. Box-and-whisker plots of the transformed data are also shown in Fig. 3. It can be clearly observed, especially for the ln-transformed data, that Zn became increasingly available as the pH decreased. Three periods, separated by the dates of the SBF applications, could be distinguished. During the period from June 1999 until December 1999 the increasing pH corresponded to a decrease in the Zn concentrations, especially on the last date. After the SBF application of February 2000, from March 2000 until September 2000 the pH decreased steadily, while the Zn concentrations increased. Due to the second application of SBF in November 2000, the pH and Zn, observed in December 2000, increased and decreased, respectively. After this date, the pH and Zn values, respectively, dropped and increased only slightly.

The total rainfall between December 2000 and March 2001 (rainy season) was 540 mm. After December 2000, especially the LQ of the pH distributions increased (see Fig. 3), indicating a substantial improvement in the situation, although still very low values were observed. Median Zn concentrations were lower than for previous sampling dates, but were higher than expected according to the high pH measured. These results indicate that the relationship between the pH and Zn changed during this last period, probably due to the precipitation and dissolution of newly formed minerals from the reaction products of the pyrite oxidation.

Changing Relations between the Chemical Properties

As suggested in the previous section, the relationship between the analyzed soil chemical properties changed during the monitoring period. In Fig. 4, scatter plots and regression lines for the December 1999 and March 2001 data are compared. For the first data set, a moderate linear relationship between pH and ln Zn was found, explaining 42% of the variance. The March 2001 data did not fit the linear relationship well, explaining only 14% of the variance. From December 1999 to March 2001, after two applications of SBF, the Zn availability increased consistently at higher pH values, while its concentration at the lowest pH values remained similar. This suggests the difficulty in correcting the metal concentrations caused by the increased acidity with pH-increasing amendments like SBF.

The correlation coefficient between the pH and ln Zn is also represented in Fig. 4 to evaluate the quality of the assumed linear relationships. All correlation coefficients, except for May 2001, were significant at the $\alpha = 0.01$ level. Similar correlation coefficients of about -0.70 were obtained from June 1999 until December 1999. After the SBF application of February 2000, in March 2000 higher Zn concentrations were observed at the highest pH values and the correlation coefficient dropped to -0.50. Due to the SBF application, the

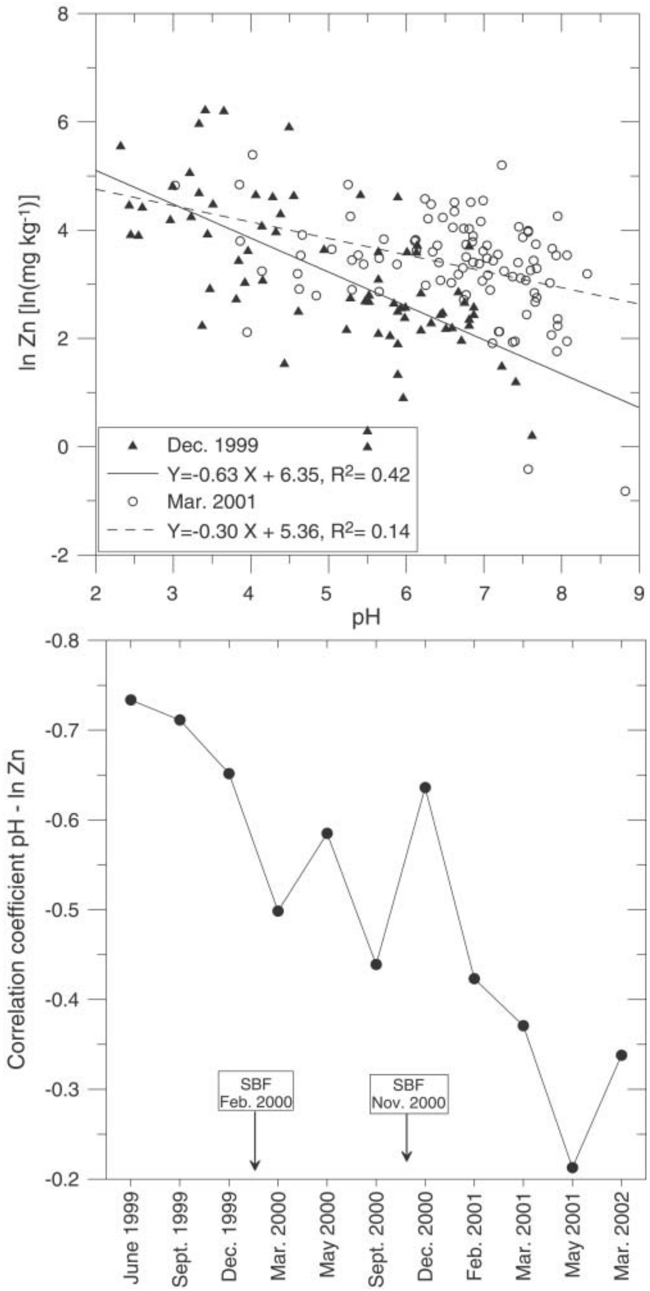

Fig. 4. Changing relationship between pH and ln-transformed EDTA-extractable Zn (ln Zn) concentrations during the monitoring period. All correlation coefficients, except for May 2001, were significant at the $\alpha = 0.01$ level.

measured pH increased, but the Zn concentration remained similar. From May 2000 until December 2000 FeS_2 oxidation might have increased the acidity and the Zn concentration. The correlation coefficient increased in May 2000 to –0.58, but decreased again to –0.44 in September 2000. The effect of the second SBF application was not apparent until February 2001, when higher Zn concentrations were observed at the highest pH values (similar to what occurred in March 2000). For February, March, and May 2001 the correlation coefficients dropped to below –0.40. These results suggested a different behavior of the most polluted samples as a consequence of the precipitation and dissolution of newly formed minerals.

Effect of Environmental Conditions and Sugar Beet Foam on pH and Zinc Evolution

The large pH values observed after the application of SBF during February and November 2000 might have catalyzed the oxidation of Fe^{2+} to Fe^{3+} in Reaction [2]. After the first application, the pH decreased from March 2000 until September 2000, probably because the oxidation of the FeS_2 particles was resumed due to (i) the increased availability of oxygen in the soil matrix after tillage, (ii) the high temperatures that are usual during this period of the year, and (iii) the increased availability of Fe^{3+}.

The relatively small amount of rainfall during this period (242 mm, see Fig. 1) in combination with high evapotranspiration rates probably did not saturate the soil matrix, but may have dissolved the newly formed minerals at the beginning of the period, contributing in this way to the increasing acidification. The probable lack of soil moisture during this period might also have inhibited the reaction of the SBF constituents and the buffering of the potential increase in acidity. After the second SBF application, from December 2000 until May 2001 no significant decrease in the pH was observed. Probably the large amount of rainfall (400 mm) between December 2000 and February 2001 saturated the soil matrix and inhibited the FeS_2 oxidation. During this period the SBF applied reacted with the soil solution reducing its acidity. Anyway, pH values of about 2.5 were recorded on all sampling dates, indicating that the pH remained very low in some profiles of the most polluted zones, during the entire monitoring period.

Spatiotemporal Evolution of the Residual Pollution

Classified ns pH Maps

Vanderlinden et al. (2006) found that pH was a good indicator of the residual pollution. Showing an almost normal distribution, the pH was less affected by the bias of the ns back-transformation. We used it here, considering a threshold value of pH = 4 since at lower pH values the oxidation rate of Fe^{2+} to Fe^{3+} becomes very slow, constituting a pyrite oxidation rate-limiting step, while at higher pH values *Thiobacillus ferrooxidans* becomes inactive and Fe-holding minerals precipitate (e.g., Jaynes et al., 1984). Also, plant and tree growth is limited at $pH < 4$ due to phytotoxic metal concentrations and macronutrient deficiencies (Kramer et al., 2000).

For each sampling date, the ns map was classified according to the corresponding ns threshold values for pH = 4. Figure 5 shows the classified pH maps for each sampling date. The last map at the lower right-hand corner shows the number of sampling dates on which the pH was below 4 and indicates that low pH values persisted mostly in the central parts of the polluted areas. In March 2000 and 2001 only 0.5% of the area showed pH values of below 4, while in September 1999

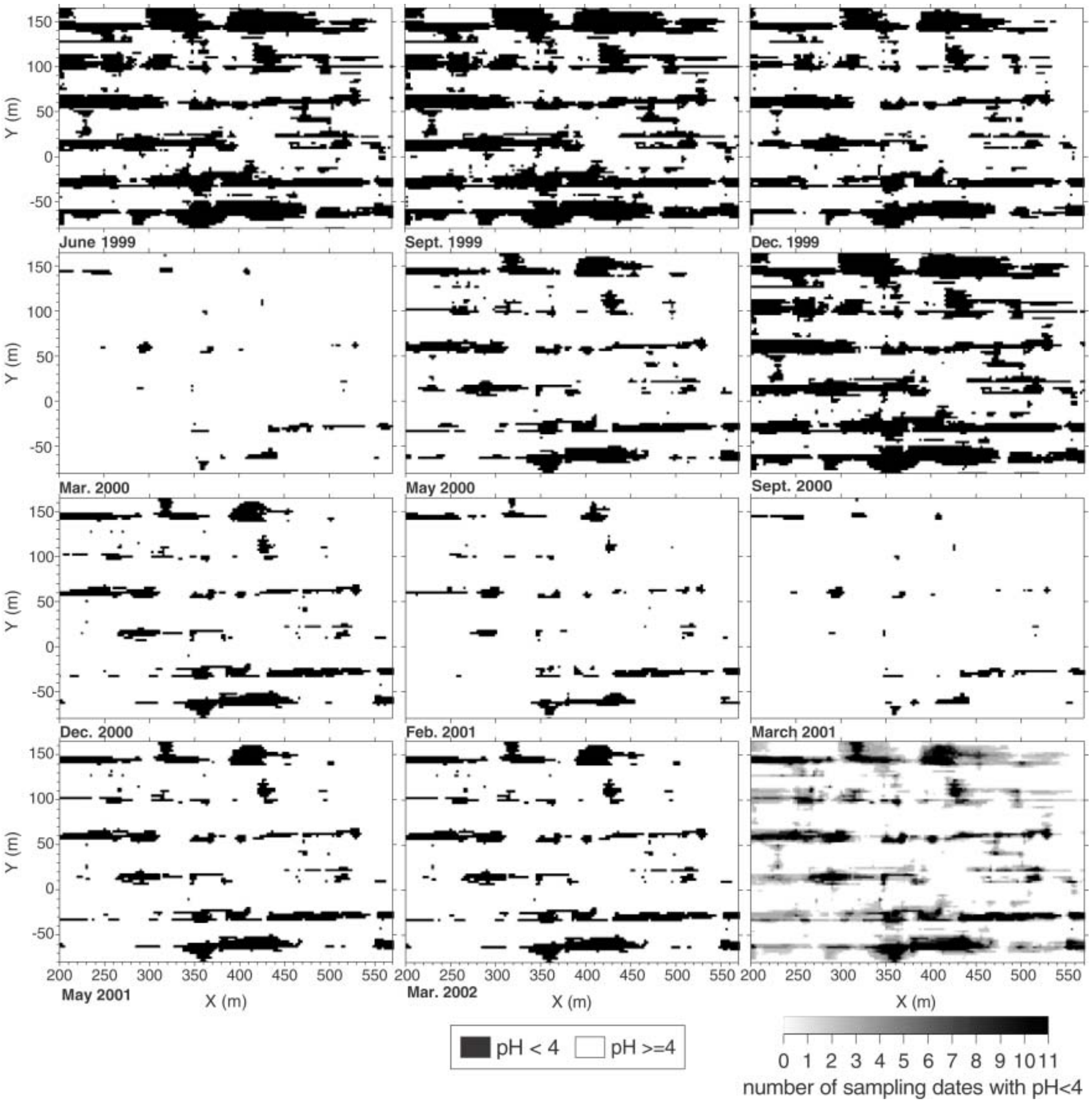

Fig. 5. Classified normal score pH maps for the 11 sampling dates, according to a threshold value of pH = 4. The map at the lower right-hand corner shows the number of sampling dates on which pH < 4.

and 2000 the area was approximately one-third. Less than 10% of the area was below the threshold value on the last sampling date. The classified ns maps in Fig. 5 only required back-transformation of one data value of the distribution. Therefore, these maps were not affected by the bias that is usually incorporated when the entire distribution is back-transformed. In the next section the back-transformed estimates of the pH and Zn are evaluated and an alternative mapping approach is used to minimize the effects of the back-transform.

Cross-Validation of the Back-Transformed Estimates

Figure 6 shows the cross-validation results for pH and Zn. The ME for the pH ranges from –0.36 in September 2000 to 0.27 in December 1999. Except for September 1999 and 2000, a small positive error was observed due to the overestimation of the smallest pH values. Box-and-whisker plots of the errors (Fig. 7) indicated near normal error distributions and showed that the underestimation in September 1999 and 2000 was caused by some large negative errors. The MAE ranges from 1.35 in September 2000 to 0.53 in June 1999 and was on average near 0.90.

For Zn the ME ranged from –46 in June 1999 to –5 mg kg^{-1} in September 2000, due to an important underestimation of the highest data values. This fact can be clearly observed in Fig. 7, showing how the amount of large negative errors decreased in time. The MAE ranged from 97 in September 1999 to 20 mg kg^{-1} in March 2001, with, in general, a decrease in time and an average value of 47 mg kg^{-1}.

For the pH, the skew was negligible, but for Zn, the bias observed, which originated from the underestimation of some high data values, became important for some sampling dates. This can be observed in Fig. 7, where the medians of the error distributions were all

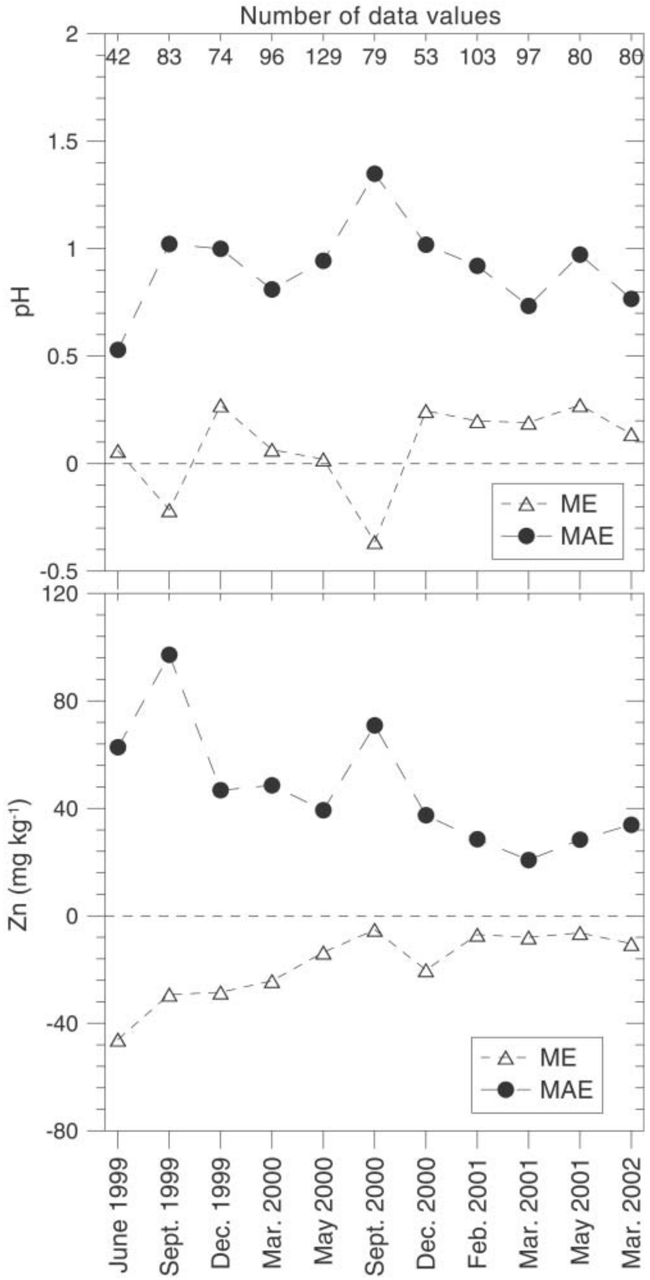

Fig. 6. Cross-validation mean error (ME) and mean absolute error (MAE) for pH and EDTA-extractable Zn concentration (Zn) on the 11 sampling dates.

very close to zero. Therefore, no global additive or multiplicative correction could be applied without increasing the MAE. In the next section, the bias is circumvented by using difference maps to assess the spatiotemporal evolution of the chemical properties.

Assessing the Efficiency of Sugar Beet Foam Applications with Difference Maps and Cumulative Frequency Distributions

Difference maps and cumulative frequency distributions were used to analyze the effect of the SBF applications in February and November 2000. Figure 8 shows the probability plots of the observed pH and Zn concentrations and grid-estimates on one date before the applications and two dates after. The differences between the probability plots of the observations and the grid estimates were similar on successive sampling dates for both the pH and Zn, indicating that the over- and underestimations were filtered out of the difference maps in Fig. 9.

For the first SBF application, between December 1999 and March 2000, an overall increase in the pH was detected, especially in the outer parts of the areas that contained residual sludge. In the inner parts of these spots, where the lowest pH values were found, the increase was smaller. No clear response of this decrease in acidity could be found in the Zn. In the zones with values of between 10 and 40 mg kg^{-1} the Zn concentration increased, while small fluctuations were noted in the tails of the distributions. The SBF application was not very effective, because on the next sampling date, May 2000, an overall increase in the acidity was observed, especially in the outer part of the polluted zones. The pH of the most polluted points (pH < 3) remained almost unchanged. As a consequence, the number of Zn concentrations below 100 mg kg^{-1} increased, while the highest values remained approximately constant since they were located at the most acid spots. This general increase in the acidity and the Zn concentration 3 mo after the application demonstrated

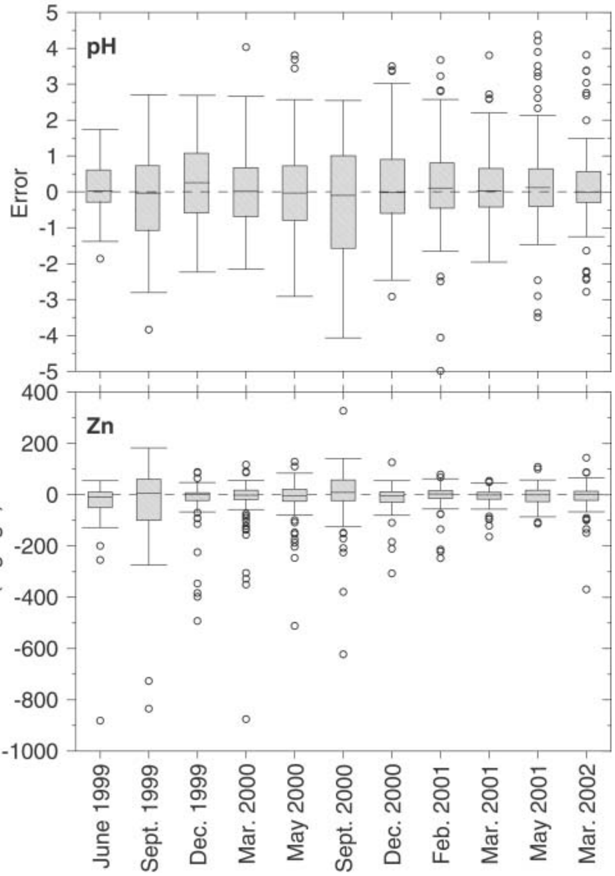

Fig. 7. Box-and-whisker plots of the cross-validation errors for pH and EDTA-extractable Zn concentration (Zn), on the 11 sampling dates.

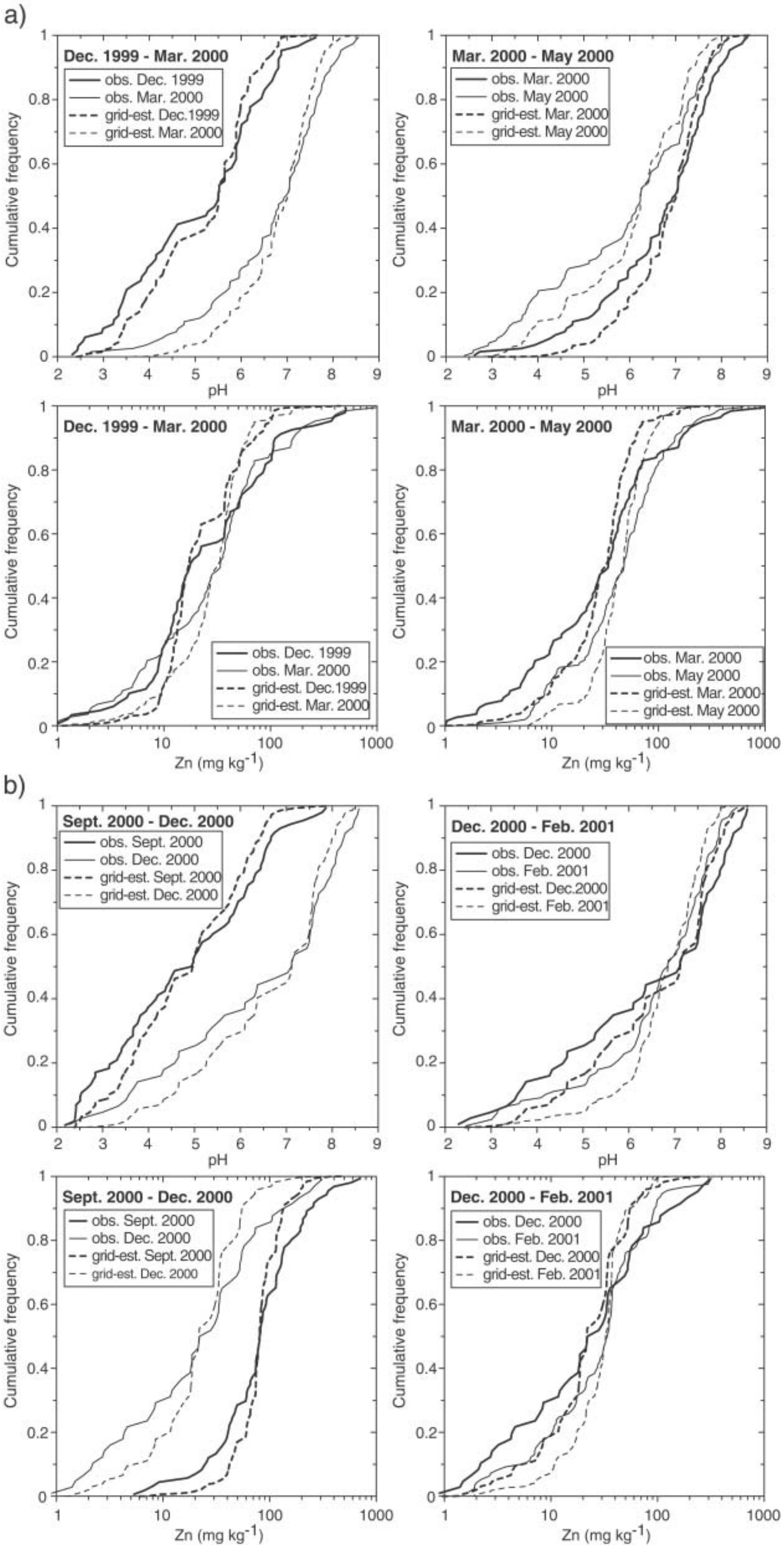

Fig. 8. Cumulative frequency distributions of pH and EDTA-extractable Zn concentration on consecutive sampling dates before and after the sugar beet foam (SBF) applications of (a) February 2000 and (b) November 2000.

the continuing oxidation of pyrite, due to the higher temperatures and to the availability of oxygen in the unsaturated soil matrix.

On the next sampling date at the end of the dry and hot season, in September 2000, even more acid conditions and higher Zn concentrations were observed.

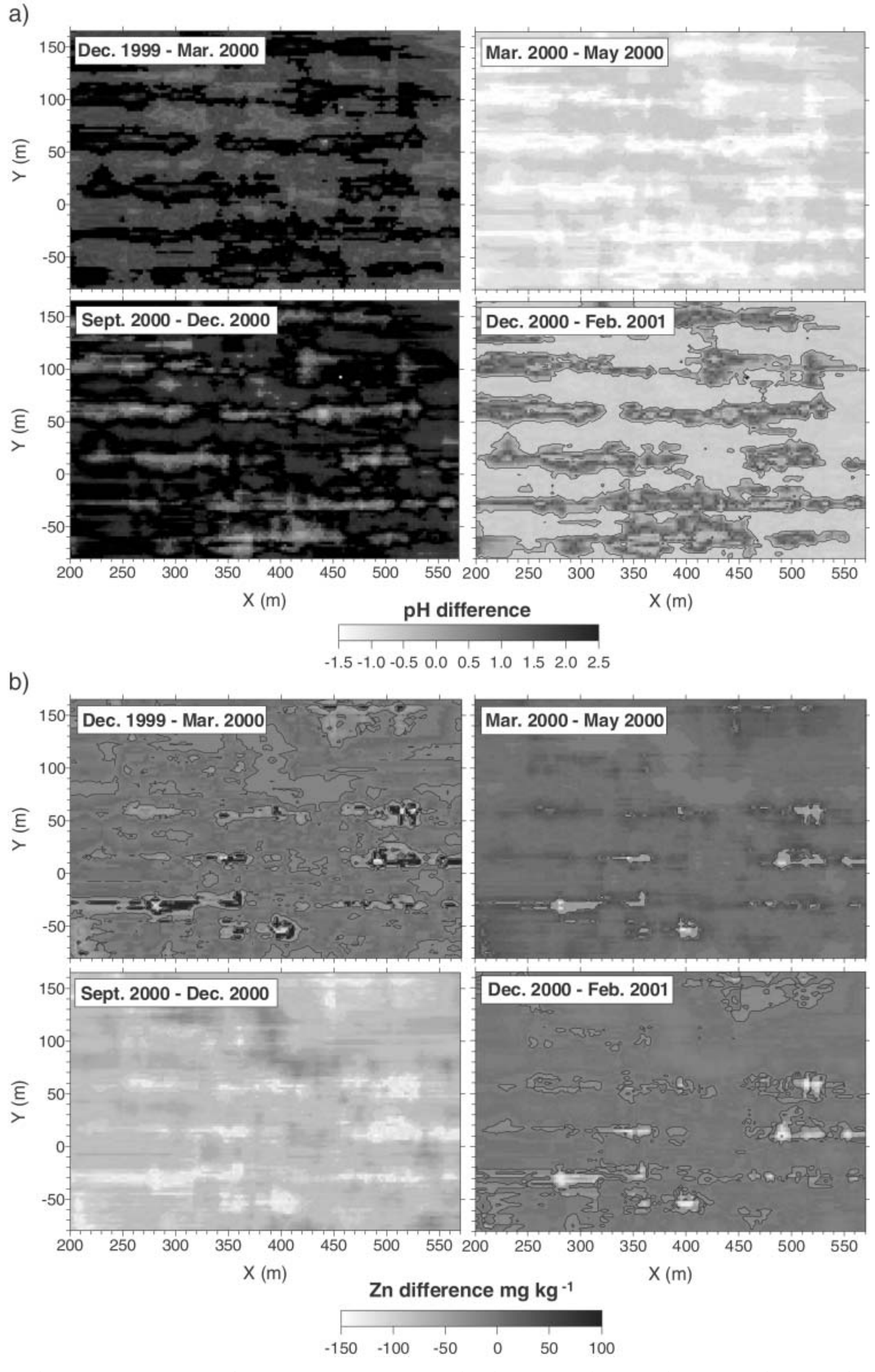

Fig. 9. Difference maps for (a) pH and (b) EDTA-extractable Zn concentration for consecutive sampling dates before and after the sugar beet foam (SBF) applications of February 2000 and November 2000. The zero difference contour is also represented.

After the SBF application of November 2000, the pH increases noticeably except in the polluted areas, where it remained almost constant. This decrease in acidity led to a noticeable decrease in the Zn in December 2000, especially in the polluted zones. Due to the moist soil conditions the SBF constituents might have been able to react with the soil solution, while the FeS_2 oxidation seemed to be inhibited due to the lower temperatures and the lack of oxygen in the moist soil matrix.

On the next sampling date, in February 2001, pH values below 6.5 were further increased, while the highest pH values decreased. The Zn concentration in

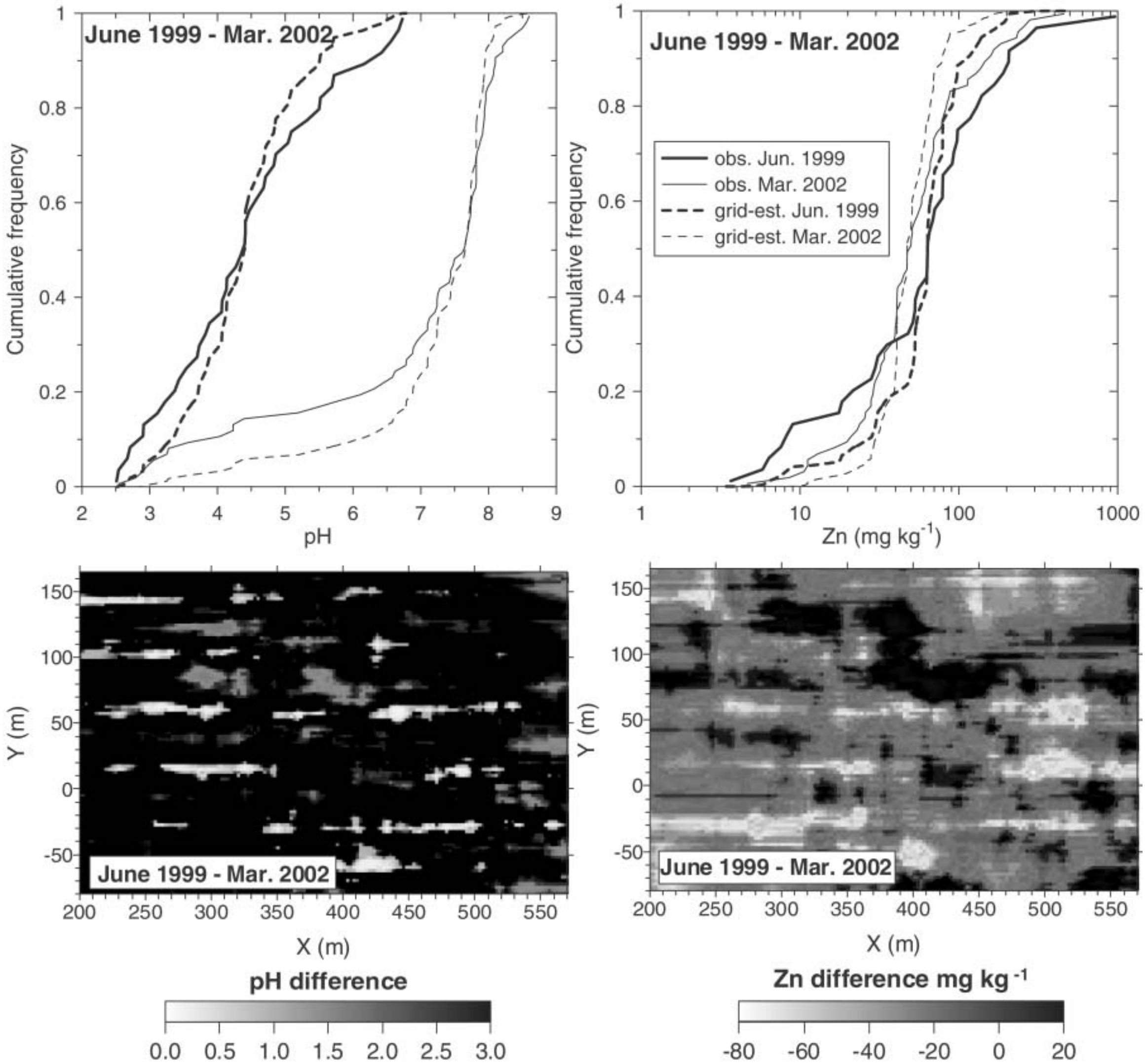

Fig. 10. Cumulative frequency distributions and difference maps for pH and EDTA-extractable Zn concentration on the first and last sampling date of the monitoring period. The zero difference contour is also represented.

the polluted places, with values of above 100 mg kg^{-1}, decreased, while the lowest values increased, in accordance with the evolution of the pH.

The analysis of both situations indicated that SBF should be applied before the rainy and cold season. The pyrite oxidation rate can be minimized only under these conditions, and the SBF constituents are able to react with the soil solution to buffer the produced acidity. Once the acidity was neutralized, newly formed metal-holding minerals precipitated on the pyrite particle surface and inhibited further reactions with oxygen or Fe^{3+}.

To evaluate the effect of the SBF applications and the overall spatiotemporal evolution of the residual pollution, the pH and the Zn concentrations on the last sampling date (March 2002) were compared with those observed in June 1999, in Fig. 10. The probability plots show a significant increase in the pH during the monitoring period of almost 3 yr, raising the median values from 4.4 to 7.6. The lowest values, however, had only slightly increased, indicating that the acid production due to the oxidation of the tailings was still continuing. The median Zn concentration had decreased from 64 to 49 mg kg^{-1}, although higher and lower values were observed on intermediate dates. Especially, the highest values had been reduced. The difference maps in Fig. 10 confirm this trend. A general increase in the pH was observed, except for the central parts of the residual sludge locations where the pH remained almost constant. The Zn concentration only increased in the nonpolluted zones and decreased markedly in the polluted areas.

CONCLUSIONS

The data from the 11 sampling dates showed a general increase of pH and decrease of Zn at the monitoring site between June 1999, shortly after the cleanup actions, and March 2002, almost 4 yr after the spillage, although pH values near 2.5 and Zn concentrations of more than 200 mg kg^{-1} were observed throughout the entire period, despite the SBF applications in February and November 2000.

The spatiotemporal methodology applied, which consisted of the geostatistical spatial interpolation of the merged normal score–transformed data from different sampling dates, followed by a back-transformation for each sampling date of the previously obtained normal score maps, produced suitable maps of pH and Zn for the entire monitoring site on each sampling date. Data set deficiencies such as a small number of data points and non-overlapping sampling areas on successive sampling dates, and the skewed Zn distributions, prevented independent spatial analysis on each sampling date, but were overcome by this methodology. Although the cross-validation results indicated that, especially for Zn, unbiasedness could no longer be guaranteed after back-transformation, no global additive or multiplicative correction could be applied without loss of precision. Classified normal score maps were found to be a valuable alternative for mapping the temporal evolution of pH and indicated that during the monitoring period the area with pH values of below 4 ranged from 0.5 to 33%, and was approximately 10% in March 2002, almost 4 yr after the spillage. The use of difference maps, calculated for consecutive sampling dates, constituted a second alternative to circumvent the problems related with the back-transformation. Since the back-transformed distributions for the different sampling dates were affected in a similar way by the bias, it was filtered out by subtracting back-transformed maps. This enabled the identification of the areas with the largest changes and major chemical activity.

The box-and-whisker plots and the difference maps elucidated the different performance of the two SBF applications. The first application increased the pH significantly, but 6 mo later, in September 2000 (after the summer), the pH had decreased again to values similar to those observed before the application, while the Zn concentrations became even larger. The observed inefficiency of this SBF application can be explained by the resumed oxidation of the pyrite particles due to: (i) SBF induced increments of the pH that might have catalyzed the oxidation of Fe^{2+} to Fe^{3+}, (ii) the tillage after the application and the dry soil conditions during this period that enhanced oxygen availability in the soil matrix and prohibited the SBF to react with the soil solution, and (iii) the usual high temperatures during this period of the year. Also, the dissolution of the newly formed minerals by the small amount of rainfall at the beginning of this period may have contributed to the increasing acidification. The second SBF application increased pH again and decreased Zn, but afterward no significant changes could be observed. In this case the large amount of rainfall shortly after the application, in combination with the low evaporation rates that characterized the winter period, probably moistened the soil matrix enough to inhibit pyrite oxidation and to let the SBF react with the soil solution, reducing its acidity. Finally, newly formed metal-holding minerals could precipitate on the pyrite particle surface and inhibited further reactions with oxygen or Fe^{3+}. The analysis of both situations gave evidence of the importance of applying SBF before the rainy and cold season.

Our experience with the data from the Guadiamar River basin in southwestern Spain, after the Aznalcóllar mine spill, should be useful for resolving similar problems in other studies related with the alleviation of acidity or the remediation of other adverse consequences of similar spills elsewhere.

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