

Fluoride distribution in the environment along the gradient of a phosphate-fertilizer production emission (southern Brazil)

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Abstract Airborne fluoride was determined in the rainwater, surface soil and groundwater along a gradient of emission of a phosphate fertilizer factory in Rio Grande, southern Brazil. Concentrations of fluoride in rainwater and groundwater achieved 3 mg l^{-1} and 5 mg l^{-1} , respectively, and were dependent on pH. The fluoride deposited from emissions accumulated in a superficial horizon of soil in quantities comparable to those in the manufactured end-products—up to $23,000 \text{ mg kg}^{-1}$. Fluoride distribution in the environment is controlled by physical–chemical parameters of emission, rain intensity and soil properties. The highest fluoride concentrations were registered at a close distance of up to 2 km from the factory. The distribution of fluoride in groundwater resembled the same distribution in rainwater due to the high permeability of the local soils. Fluoride penetration to the groundwater also depended on the type of vegetation

cover. The groundwater in woodland areas was less affected by contamination of fluoride than in the grassland areas, most probably because of the influence of eucalyptus throughfall, which increases the pH of wet precipitates.

Keywords Airborne fluoride · Groundwater · Phosphate fertilizer · Rainwater · Soil · Vegetation cover

Introduction

The impact of high concentrations of fluoride in the environment is well-known and constantly draws attention (Arnesen, Abrahamsen, Sandvik, & Krogstad, 1995; Ashley & Burley, 1995; Camargo 2003; Fornasiero, 2001; Klumpp, Domingos, & Klumpp, 1996, 1998; Miller, 1997; World Health Organization, 2002). Nevertheless, very few studies are devoted to the dispersion of fluoride in the air from fertilizer production emissions, its deposition on the land surface, accumulation in soil and penetration into the groundwater (Kauranen, 1978; Thompson, Sidhu, & Roberts, 1979). Practically nothing is known about the influence of the vegetation cover on the mobility in soils of fluoride precipitated from air emissions.

The current research aimed to study the dispersion in atmospheric deposits, soil and

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groundwater of airborne fluoride from the emissions of a factory and also the role of the vegetation cover to mobility of fluoride in soils.

The phosphate fertilizer plant in Rio Grande (southern Brazil) has been in operation for more than 40 years. The area surrounding the factory shows visual signs of the impact of the emissions on the environment as thick smoke blanketing the atmosphere, grass withering, tree defoliation, etc. During the existence of the factory the local population has used groundwater for drinking. Cattle and human fluorosis, as well as corrosion of glass and ceramic isolators of electric lines, are known to occur in this area (Brigoni, 1981; Patra, Dwievedi, Bhardwaj, & Swarup, 2000). The area studied represented a favorable case for investigation of the direct contribution of airborne fluoride to environmental pollution for several reasons: (1) the territory had no phospho-gypsum warehousing that could obscure the effects of airborne contamination of soil and groundwater; (2) raw material was unloaded directly from ships and final product was loaded directly on to ships, and the soil surface in the region was free from pollution caused by dispersion of fertilizer and raw material during their transportation; (3) the area was characterized by steady directions of seasonal winds, which would allow us to assess the distribution of emissions; (4) fertilizer application to the soil for agricultural activities did not occur in the area; (5) the vegetation cover in the study area consisted of sharply contrasted vegetation; grassland and woodland of eucalyptus bosks would create the opportunity for us to research the influence of the various vegetation cover on fluoride mobility in the soil.

Materials and methods

Study area

The fertilizer plant of Rio Grande is located on a peninsula in the estuary of the Patos Lagoon (Fig. 1). The area is characterized by a subtropical climate, with seasonal wind directions from the north–northeast in the summer (southern hemisphere) and south–southwest in the winter.

The average precipitation is about 1,300 mm year⁻¹. The relief is plane, with elevations above sea level of no more than 4 m on a ridge of low dunes along the ocean coast. The soils of the peninsula are composed of fine-grained sand with low humus content and are characterized by free water percolation. Groundwater occurs at small depths of up to 2 m and is discharged directly into the estuary or ocean. The vegetation cover is of two types: grassland and stands of planted eucalyptus bosks (woodland). The coastal part of the peninsula is occupied by port constructions; there are two settlements on the peninsula.

Sampling

Samples of raw material (apatite) and fertilizer products (superphosphate, triple superphosphate and NPK complex fertilizer) were obtained directly from the factory. Soil, groundwater and rainwater were sampled at 19 points in open grasslands along the axis of the peninsula from its northern end, at the Rio Grande city, up to the coast, during the period of October 2003–March 2004. The line of sampling was chosen because it passed by the central highest part of the peninsula and did not cross marshes, which were closer to the coastal parts of the estuary of the lagoon (Fig. 1).

Five additional points were sampled in the eucalyptus woodlands along the sampling line (Fig. 1). These points were selected in such a manner as to be closest to the reference sampling points in the grasslands (100–200 m), so that each pair of points was at approximately the same distance from the chimney. At each point manual auger drilling was carried out down to the level of the groundwater. After the level of water in the drill had stabilized (15–20 min) a sample of groundwater was pumped into a 1 l glass bottle with the help of a manual vacuum pump, tube and a siphon.

Samples of surface soil (0–10 cm) were collected with a plastic shovel and placed into polyethylene packages. Rainwater sampling was performed with the help of a simple bulk collector—a bottle coupled to a funnel with a diameter of 12 cm (both of polypropylene) fixed on a

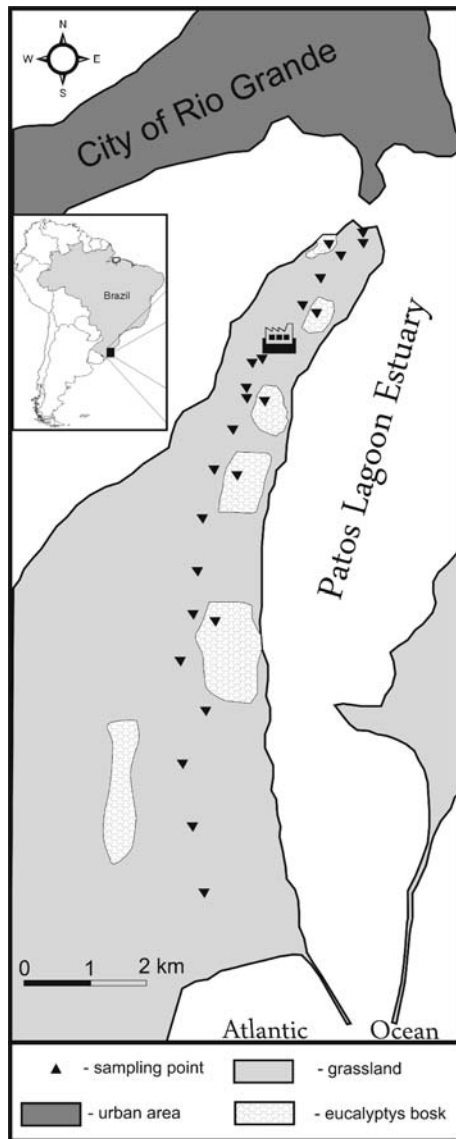


Fig. 1 Sampling location map

wooden pole at a height of 2 m above the soil surface.

All rainwater samples were collected during the rain from the 8th to 9th March 2004. The period and the date of rainwater sampling had been chosen on the basis of local climatic conditions and the short-term meteorological forecast. Two factors determined the sampling of contaminated rainwater: (1) The north–northeasterly wind direction very close to the chosen sampling line; (2) round-the-clock full capacity operation of the factory during the rain.

Collectors had been placed some hours before the rain had begun and were removed immediately after the rain had stopped so that the rainwater samples were not contaminated by dry deposits. At the sampling points inside the woodlands, rainwater (throughfall) sampling was not performed because of the high contamination by leaves and other pieces of vegetation. The direction of the wind during the rain was close to that of the line of collectors (NNE–SSW).

Trace-metal cleaning procedures as detailed in Mart (1982) were employed to minimize the risk of contamination. All sampling containers and fittings were acid-washed in 5% HNO₃, rinsed several times in Milli-Q water, dried, and stored in closed plastic bags for later sampling. Multiple sample blanks consisting of Milli-Q water in sampling bottles were prepared by the procedures described below for rainwater and groundwater sampling.

Sample treatment

Samples of raw material and products were pulverized in an agate mortar. Soil samples in the laboratory were dried at room temperature, sifted through a sieve of 63 μm and then pulverized in an agate mortar.

In this study fluoride determination in soil and fertilizer was performed according to Al-Othman and Sweileh (2000) and Mirlean et al. (2003). About 0.1 g of the sample (soil, raw material, fertilizer) was transferred to a 50 ml disposable plastic tube and followed by the addition of 10 ml of 0.5 mol l⁻¹ of a citric acid solution. The solution was shaken for 45 min at 22±0.5°C, filtered and washed with Milli-Q water. The filtrate was collected in a Nalgene volumetric flask, diluted to 50 ml with Milli-Q water and shaken thoroughly. Of the above solution, 10 ml was transferred to a 50 ml Nalgene beaker; 10 ml of sodium citrate buffer solution 1 M was added to the solution and, after homogenization, the stabilized potential was read.

In the case of water extraction solutions, about 4 g of each soil sample was transferred to a 100 ml disposable plastic tube, and then 40 ml of Milli-Q water was added. The mixture was shaken for 2 h and filtered. Groundwater and rainwater

samples were filtered through a 0.45 μm membrane in the laboratory.

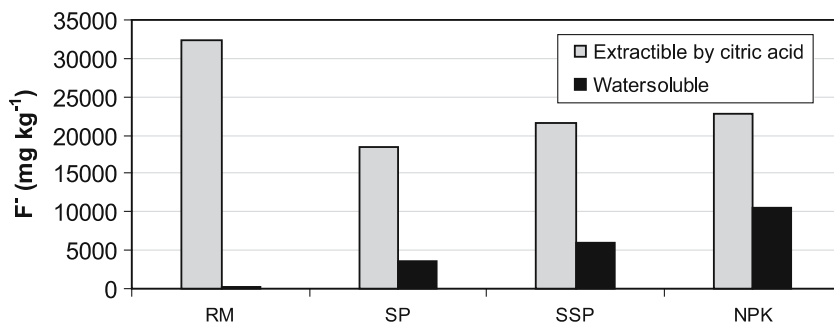
Analytical procedures

Conductivity and pH measurements in water were performed in the laboratory using an Oakton, model WD-35607-10 and Accumet, model no. 15, respectively.

For fluoride analysis in water samples, ion chromatography (Metrohm) was employed, with chemical suppression in a simple column (Metrosep A Supp5-100) and a $\text{NaHCO}_3\text{--Na}_2\text{CO}_3$ solution as eluent. Standard solutions of IsoSol were used for the calibration curve. All water samples were analyzed in triplicate. The coefficients of variation for all triplicates were $<3\%$.

The fluoride measurement in soil and fertilizer extracts was obtained with an Accumet model no. 15 pH/ISE meter equipped with a fluoride ion selective electrode Orion model no. 9609BN, which does not require a separate reference electrode. For instrument calibration [$0.1\text{--}100\text{ mg l}^{-1}$ fluoride (F)], the appropriate volume of fluoride stock solution was transferred to a 25-ml Nalgene flask to which 12.5 ml citrate buffer 1 M (pH 6) had been added and diluted to the mark with deionized water. Next, the solution was transferred into a Nalgene beaker, and the potential was read until a stable value was obtained. The sample solution (10 ml) was transferred to a 50 ml Nalgene beaker, and 10 ml of sodium citrate buffer solution 1 M was added. After homogenization the stabilized potential was read. Extracts were analyzed, with three replicates having a relative standard deviation below 5%.

Fig. 2 Concentration of citric acid extractable and water-soluble fluoride in raw material (RM), superphosphate (SP), triple-superphosphate (SSP) and complex fertilizers (NPK)



Results

Fluoride in raw material and products

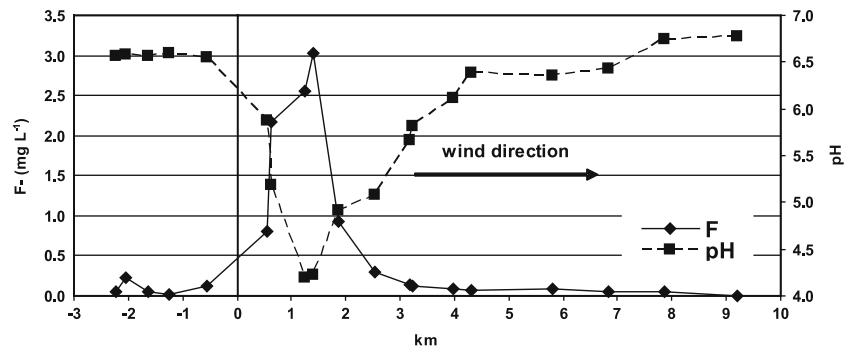
The concentration of fluoride in phosphoric ore (apatite) and in the products of factory varied widely (Fig. 2). In ore [raw material (RM)] the concentration of fluoride extracted by citric acid was $32,270\text{ mg kg}^{-1}$. In the manufactured phosphoric fertilizers the content of fluoride extracted by citric acid was about $20,000\text{ mg kg}^{-1}$, depending on the product type. Water-soluble fluoride was 254 mg kg^{-1} in raw material. Its content in the end-product was tens of times higher, and, in complex fertilizers, it reached $10,000\text{ mg kg}^{-1}$.

Fluoride distribution in rainwater

By the end of precipitation, 31–44 mm of rainwater (average 34 mm, $n = 19$) had been deposited at the sampling points. Distribution of precipitation along the sampling line showed no definite pattern and was obviously influenced by turbulence and impulses of the wind during the rain.

Electrical conductivity of sampled rainwater varied from $31\ \mu\text{S cm}^{-1}$ to $200\ \mu\text{S cm}^{-1}$ (average $82\ \mu\text{S cm}^{-1}$, $n = 19$). A relationship between the electrical conductivity of the rainwater and the distance of the sampling point from the chimney was evident. On the windward side of the chimney the rainwater electrical conductivity did not exceed $40\ \mu\text{S cm}^{-1}$, whereas on the leeward side it was much higher, and, at a distance of 3 km from the chimney, it exceeded $100\ \mu\text{S cm}^{-1}$, gradually reducing to about $50\ \mu\text{S cm}^{-1}$ at a distance of 10 km from the chimney.

Fig. 3 Fluoride and pH in rainwater along the sampling line; 0 km corresponds to the position of the factory



The pH of the rainwater varied strongly, between 4.1 and 6.8, along the sampling line. On the windward side the pH was about 6.5, and right after the chimney it had decreased to 4.1; it was neutral only at a distance of 8–9 km from the chimney (Fig. 3).

The concentration of fluoride in the rainwater varied between 0.01 mg l⁻¹ and 3.04 mg l⁻¹, and the highest concentrations (more than 1.0 mg l⁻¹) were observed at a 2 km distance along the sampling line on the leeward side. These values exceed about ten times the previous reported values for fertilizer factories (Sidhu, 1982). At a greater distance from the chimney the concentration of fluoride in the rainwater decreased sharply and, at a distance of 9 km, was similar to that of the local background (0.01 mg l⁻¹). The fluoride in rainwater showed a negative correlation with pH ($R = -0.85$, $P < 0.05$) and a positive correlation with electrical conductivity ($R = 0.75$, $P < 0.05$).

Fluoride distribution in soil

The concentration of F in the fine fraction (less than 63 μm) of the soil extractable by citric acid

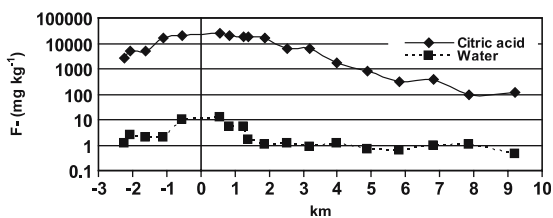


Fig. 4 Distribution of fluoride in surface soil along the sampling line (citric acid and water extracts); 0 km corresponds to the position of the factory

varied from 90 mg kg⁻¹ to 23,700 mg kg⁻¹ (average 8,940 mg kg⁻¹). The highest values of F were found close to the factory. Further from the factory, the concentration of F gradually decreased (Fig. 4). The distribution of water-soluble fluoride in soil followed that of fluoride extractable by citric acid.

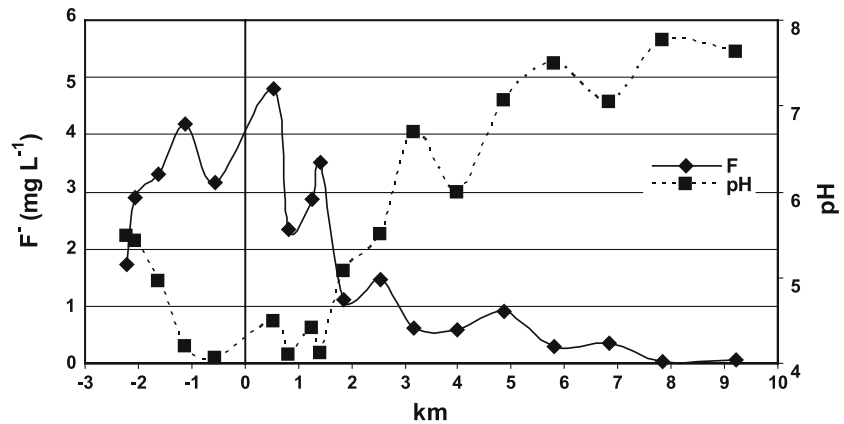
Near the factory the quantity of water-soluble F exceeded 10 mg kg⁻¹, decreasing to 0.43 mg kg⁻¹ at 9 km distance from the factory. Despite a considerable decrease of fluoride concentration with distance from the factory, these concentrations remained ten-times and 30-times higher, respectively, than local background values for extractable and water-soluble fluoride in soil.

When the grassland and woodlands were compared, the concentration of fluoride extracted from the soil by citric acid differed by no more than 5% at the same site, showing that there was no dependence of the F concentration extractable by citric acid on the vegetation cover. At the same time, the quantity of water-soluble F at these point pairs varied from 1% at the point furthest from the factory to more than 20% closest to the factory. The concentration of water-soluble fluoride was higher in the grassland than in the woodland.

Fluoride distribution in groundwater

The pH of the groundwater varied from 4.1 to 7.8. As in the case of rainwater, there was a clear geographical tendency for the pH to increase with distance from the factory (Fig. 5). Concentrations of fluoride in the groundwater varied from 4.79 mg l⁻¹ to 0.1 mg l⁻¹, close to the local background value. Fluoride in groundwater strongly

Fig. 5 Groundwater pH and fluoride concentration along the sampling line; 0 km corresponds to the position of the factory

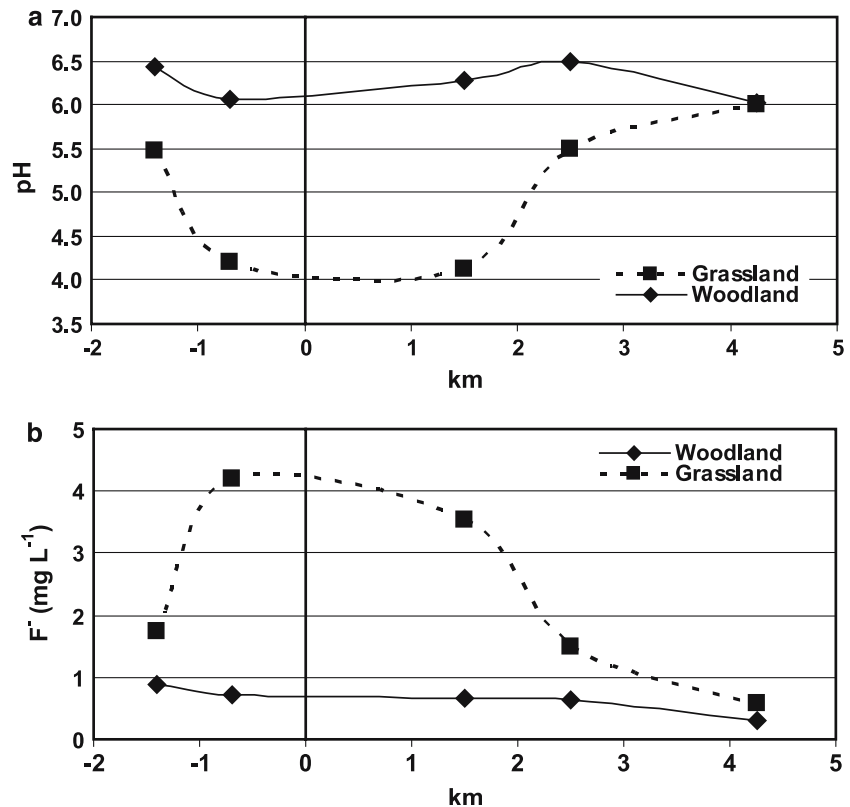


and negatively correlated with pH ($R = -0.86$, $P < 0.05$). As a whole, the leeward distribution of pH and fluoride in groundwater is similar to their distribution in rainwater.

In grassland the pH of the groundwater varied considerably, from 4 to 6, depending on the distance from the chimney, while, in eucalyptus bosk woodlands the pH of the groundwater

showed smaller fluctuations (Fig. 6a). The concentrations of fluoride in groundwater in woodlands at all points along the sampling line were less variable and lower than 1 mg l^{-1} , whereas, in the comparable grasslands, the concentration of fluoride in groundwater was much higher and varied with distance from the chimney (Fig. 6b)

Fig. 6 Influence of vegetation type on groundwater composition: **a** pH, **b** F⁻; 0 km corresponds to the position of the factory



Discussion

The analysis of fluoride in raw material and fertilizers demonstrates that, during ore processing, there are losses of fluoride, i.e. during the industrial processing about 30% of fluoride from apatite is lost to the residual waste. Because in the technological process the volumes of liquid and solid waste products are relatively small, we assume that losses of fluoride occurred mainly as emissions. The processing of raw material transforms the fluoride remaining in the end-product into a water-soluble form (Fig. 2). It is possible that during the manufacture of superphosphates the acid treatment releases fluoride, which reacts with calcium, and, as a result, fluorite is formed, which has much higher solubility than apatite or phosphorite. During manufacture of the fertilizers the addition of potassium chloride and ammonium compounds may have led to the formation of fluorides which have higher solubility. Thus, emissions from the factory of both gas and dust promote the liberation of fluoride into the environment in more mobile forms than in the raw material.

Emissions containing fluoride precipitate to the ground surface, as indicated by its distribution in rainwater (Fig. 4). The high correlation of fluoride with rainwater and pH is most likely due to specific forms of fluoride. It is known that fluoride in fertilizer factory emissions is present mainly in the form of HF and fluorosilicic acid (H_2SiF_6), the product of hydrolysis of SiF_4 (Freedman, 1995). In addition to both of these forms of fluoride, which reduce the pH of rainwater, there are also emissions of sulphuric and phosphoric acids. A low pH of rainwater enhances the leaching of fluoride from dust particles, increasing its concentration in wet precipitations.

The distribution of fluoride extractable by citric acid in the soil surface represents the effect of fluoride deposition in the particulate form. Concentration of fluoride extracted by citric acid from the fine fraction ($<63 \mu\text{m}$) of the soil surface near the factory is almost 500-times higher than that of the local background and is similar to fluoride concentrations in the end-products. It is likely that the fine soil fraction in polluted areas consists, in part, of the dust produced during fertilizer processing.

It is obvious that water does not represent a good agent for the total extraction of fluoride, but it is appropriate to show that the concentrations of current water-soluble fluoride salts recently deposited on the soil surface, have not yet been leached by rainwater or converted to water-insoluble forms. The faster precipitation of emission drops is shown by a drastic reduction in water-soluble fluoride in soil (up to ten times) at a distance of up to 2 km from the chimney. Lighter dust particles are carried away further by the winds, considerably contaminating large areas with less-soluble fluoride. Probably because of this, the tenfold decrease in fluoride extracted by citric acid in the soil surface was observed only at a distance of 5 km from the chimney (Fig. 4). Furthermore, the fluoride extractable by citric acid represents the total long-term effect of the emissions. This explains the smooth decrease in the concentration of water-insoluble F in soil along the sampling line.

The high concentration of fluoride in groundwater at the zone of influence of emissions is not surprising. However, if one takes into account the very high concentration of fluoride in soil and rainwater, high concentrations in groundwater would be expected. The maximum value of fluoride in groundwater only just surpasses that of rainwater. Despite high permeability, the soil retains fluoride, protecting groundwater from excessive enrichment. This is shown by the significant negative correlation between concentration of fluoride in the groundwater and the depth of the phreatic level ($R = -0.68$, $P < 0.05$). Another important factor governing fluoride concentrations in groundwater is the pH. Concentrations of fluoride above 1 mg l^{-1} were found in wells where the water pH was below 5.5.

The vegetation cover had a very strong influence on the fluoride concentration in groundwater. The concentration of fluoride in groundwater did not exceed 1 mg l^{-1} in the woodlands, even in the zone of highest impact. The ability of some types of plants to accumulate fluoride is well known (Fornasiero, 2001). However, uptake by plants does not explain the low mobility of fluoride in the soil of the eucalyptus woodlands, because, after leaf litter has decomposed, most of the fluoride would be realized again. This should

result in high concentrations of fluoride in groundwater, but this did not occur.

The probable limiting factor that controls the lower mobility of fluoride in the eucalyptus woodlands is the higher pH. In all sampling sites under eucalyptus trees, even alongside the factory, the pH of the groundwater was higher than 6.0. In a previous study we showed that throughfall in eucalyptus woodlands always has a neutral character—a pH of about 7.0 (Casartelli, Mirlean, & Peralba, 2004). It has also been shown that eucalyptus foliage is able to neutralize quite acid deposits with a pH below 4.0 and that there are elevated concentrations of calcium and magnesium in the throughfall of eucalyptus. If one takes this information into account, it is possible that the acid deposits from the factory emissions are neutralized by foliage in the eucalyptus woodlands. It is also probable that fluoride in a free ionic form in rainwater transforms to less mobile forms, such as fluoride of calcium or magnesium, and, as a result, the groundwater in the woodlands is less contaminated by fluoride.

Conclusions

The results show, essentially, environmental contamination by fluoride from fertilizer factory emissions. In the zone affected by the emissions, fluoride content in the atmospheric precipitation reached values of several milligrams per liter, and concentration in rainwater was controlled by the pH. The fluoride deposited from emissions accumulated in a superficial soil horizon in quantities comparable to those in the manufactured end-products. The spatial distribution of water-soluble fluoride in the superficial soil horizon was more variable than that of fluoride extractable by citric acid. Fluoride concentrations in groundwater correlated with those in rainwater. The concentration of fluoride in groundwater under grassland was affected by the depth of groundwater and its pH, i.e. the greatest quantities of fluoride were present in shallower and more acid groundwater. Eucalyptus neutralizes acid deposits, and, as a

consequence, the fluoride migrates down to groundwater less intensively than in grassland.

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