



Heavy metal concentrations in soils in the vicinity of a fertilizer factory in Southern Brazil¹⁾

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Abstract

A peninsula in Rio Grande do Sul (Southern Brazil) has been known to be influenced by the immissions of a phosphorus fertilizer factory since four decades. As other industries are assumed to affect the spatial distribution of metals at this site as well, this study was conducted to identify and differentiate between potential contamination sources and their impact on accumulation of environmentally relevant elements in soils and groundwater. The concentrations of major elements (Al, Ca, Fe, K, Mg, Na, and P) and heavy and trace metals (Cu, Co, Ni, Nb, Pb, Sr, Th, U, V, Zn, and rare earth elements including Y (REY)) were determined in top and sub soils and groundwater along a transect. High enrichment factors for all trace metals in the top soil showed a strong contamination at the site of the factory. A petroleum refinery and a wood preservation factory were identified as potential sources for Ni, V, Cu, and As accumulation in soils. Phosphorus fertilizer samples used in Southern Brazil were analyzed to explore coherences with metal emission patterns potentially released by processing of the rock phosphate. High variation coefficients of all metal concentrations in fertilizers indicate different origins and show the potential contamination hazard for soils through agricultural fertilization. The REY patterns of the fertilizers allowed for the identification of the sedimentary or igneous origin of the phosphate rock used for fertilizer production. The REY patterns of top soil in the vicinity of the factory confirm that the fertilizer factory is a major source of contamination in the surrounding environment.

Keywords: Southern Brazil, soil contamination, fertilizer factory, phosphorus fertilizer, heavy metals, rare earth elements, trace elements

Zusammenfassung

Schwermetallgehalte in Böden im Umfeld einer Düngemittelfabrik in Südbrasilien

Eine Halbinsel in Rio Grande do Sul (Südbrasilien) wird seit vier Jahrzehnten durch die Immissionen einer Fabrik zur Herstellung von Phosphordüngemitteln beeinflusst. Diese Studie hatte zum Ziel, diese und andere industrielle Kontaminationsquellen in Ober- und Unterböden und Grundwasser zu identifizieren und ihren Einfluss auf die räumliche Verteilung von Hauptelementen (Al, Ca, Fe, K, Mg, Na und P) und Schwermetallen bzw. Spurenelementen (Cu, Co, Ni, Nb, Pb, Sr, Th, U, V, Zn und Seltene Erd-Elemente inklusive Y (REY)) zu untersuchen. Hohe Anreicherungsfaktoren aller Spurenelemente in der Nähe der Fabrik belegen eine starke Kontamination durch die Düngemittelproduktion. Weiterhin wurden eine Holzimprägnierungsfabrik und eine Erdölraffinerie als mögliche Emissionsquellen von Cu und As bzw. V und Ni identifiziert. Hohe Variationskoeffizienten der Spurenmetall-Konzentrationen in Düngemitteln aus Südbrasilien kennzeichnen deren unterschiedliche Herkunft. Durch Untersuchung der REY-Muster der Düngemittel und Böden konnte die sedimentäre oder magmatische Herkunft identifiziert werden. Die Dünger zeigen Zusammenhänge mit Emissionsmustern der Elemente, die bei der Rohphosphat-Verarbeitung freigesetzt wurden und weisen die Düngemittelfabrik als Hauptverursacher der Kontamination der näheren Umgebung aus. Entsprechend kann auch landwirtschaftliche Düngung zum Eintrag von Schwermetallen in Böden führen.

Schlüsselworte: Südbrasilien, Bodenkontamination, Düngemittelfabrik, Phosphor-Düngemittel, Schwermetalle, Seltene Erden, Spurenelemente

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1 Introduction

Chemical production sites are known as potential emitters of organic and inorganic contaminants, which may pollute the environment. The understanding of the dispersion and spatial distribution of the emitted substances from any kind of factory is important to assess the risk of environmental pollution. Fertilizer production is among these potential sources of environmental pollution, which has to be controlled and regulated by the industry (FAO, 2004). For example, the release of silicon tetrafluoride (SiF_4), hydrogen fluoride (HF), and particulates composed of fluoride and phosphate material has to be minimized in phosphate processing factories (USEPA, 1995). Standard quality of emission for the release of fluorine at the reaction unit of a factory should not be higher than 30 mg m^{-3} (FAO, 2004). Besides fluorine, sulfur dioxide, nitrogen dioxide, and the total particle release from phosphorus (P) fertilizer factories, a regulation of other hazardous trace elements (heavy metals, radionuclides, rare earth elements, and other trace elements) does not exist. The production of P fertilizers requires rock phosphates as raw material, which can be found as a mixture of fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$, hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, chlorapatite $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$, and francolite $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{F,OH})_{2+x}$. The rock phosphate has to be ground and treated with concentrated sulfuric or phosphoric acid for the destruction of the calcium phosphate mineral to extract the final product P fertilizer and the by-product phosphogypsum (PG).

Rock phosphates contain trace elements in a range of 1 to 100 mg kg^{-1} Cd, 70 to 110 mg kg^{-1} Cr, 1 to 1000 mg kg^{-1} Cu, < LLD (lower limit of detection) -117 mg kg^{-1} Ni, < LLD -45 mg kg^{-1} Pb, 4 to 1000 mg kg^{-1} Zn, 710 mg kg^{-1} F, and 8 to 220 mg kg^{-1} U (Malavolta, 1994; Da Conceicao and Bonotto, 2006; Kratz et al., 2008). Depending on the origin of the rock phosphates mineral fertilizers show trace element concentrations in a range of < LLD -58.8 mg kg^{-1} Cd, 10.4 to 72.7 mg kg^{-1} Cr, 1 to 183 mg kg^{-1} Cu, 5 to 26.9 mg kg^{-1} Ni, 0.6 to 30.7 mg kg^{-1} Pb, 8.8 to 181 mg kg^{-1} Zn, and 39.7 to 206 mg kg^{-1} U (Hamamo et al., 1995; Camelo et al., 1997; Abdel-Haleem et al., 2001; McBride and Spiers, 2001, Smidt et al., 2011b).

Phosphogypsum (PG) is usually deposited, but is also used for liming of tropical arable soils in Brazil. PG contains high concentrations of Cd (15 mg kg^{-1}), Cu (32 mg kg^{-1}), Ni (43 mg kg^{-1}), Sr (963 mg kg^{-1}), Zn (263 mg kg^{-1}), U (135 mg kg^{-1}), and of the radionuclides ^{226}Ra , ^{40}K , and U (Perez-Lopez et al., 2007; Abril et al., 2009). Its use for agricultural practices as a soil amendment is banned in the US since 1992 unless the Ra activity is lower than 370 Bq kg^{-1} (USEPA, 1999).

The minimization of the total loads of trace elements by agricultural fertilizer application to arable fields are dis-

cussed worldwide and many countries developed limits for certain heavy metals in fertilizers (USEPA 1999, DÜMV 2008). Phosphorus fertilizer-derived pollutants may reach the food chain by cropping and carry-over into dairy products, or leaching into groundwater resources. The diffuse pollution pathway of trace element co-application by fertilizers is intensively discussed in the scientific community (Rogasik et al., 2008; Kratz et al. 2008; Tunney et al., 2009; Smidt et al., 2011a and 2011b).

The cumulative load of gaseous and particulate pollutants from a P fertilizer factory into the neighboring environment can be considerably high. Elevated concentrations of toxic elements (Hg, F, Cd, and As) were found in soils and waters around a P fertilizer factory on a peninsula close to the city of Rio Grande (Southern Brazil) (Mirlean et al., 2003a; 2003b; 2006, and 2007). This study site has been known to be strongly influenced by the emissions from a P fertilizer factory since 40 years. However, so far nothing is known about the input of other rock phosphate-derived trace elements into the environment at this site. In this study the concentrations of numerous trace elements in soils and groundwater, potentially released from the P fertilizer factory in Rio Grande have been investigated. Additionally a collection of fertilizers traded in southern Brazil was analyzed to identify possible contaminants in the products and to source the sedimentary or igneous origin of the raw material. It was tested if coherences between emission patterns released by the factory through particulate emission enable to identify the origin of the processed phosphate rock type.

2 Materials and methods

2.1 Study area

The study site is located on a peninsula "Superporto" in the Patos Lagoon estuary in the vicinity of the city of Rio Grande in the federal state of Rio Grande do Sul (RS) – Brazil (Figure 1). This peninsula is part of a Holocene barrier-lagoon system having very fine-grained quartzose beach sands, derived probably from the inner continental shelf. The overall geological setting of the study area consists of Paleozoic and Mesozoic sedimentary and volcanic rocks of the Paraná Basin in the northern part of RS and the igneous and metamorphic rocks of the Precambrian shield in the southern part of RS (Tomazelli et al., 2000). The subtropical oceanic climate with an average annual precipitation of 1300 mm and prevailing wind directions from north-northeast in summer and south-southwest in winter formed a dune sand vegetation with different grass species in the north of the peninsula. Only small areas are used as pasture for cattle grazing and eucalyptus plantations can be found randomly. The southern end of the peninsula is directly influenced by the oceanic sea spray and brackish

groundwater, which is shown by the halophyte plant community at this site (Mirlean and Roisenberg, 2006).

The soil is a sandy soil with low organic carbon content, which is influenced by the groundwater level at 1 to 2 m depth forming anoxic gleyic soil conditions, identified through the typical Fe(III)-rich oxidized horizon (Go) and the anoxic reduced horizon (Gr). At the southern part of the peninsula the groundwater is influenced by diurnal tidal changes, resulting in temporal water logged conditions. A container freight terminal, a shipyard, a wood factory and a rural settlement are located at the southern part and one rural settlement at the northern part of the 11.5 km long peninsula.

2.2 Sampling

In 2008 soil samples (N = 21) were taken at seven sites along a transect from north to south across the production site from different depths (0 to 10, 10 to 40, and 40 to 100 cm; Figure 1). Corresponding to the location of the P fertilizer factory (km 0) one soil sampling point is located in northern direction (km -1.1) of and five soil samples were taken southwards (km 1, km 1.9, km 5.1, km 6.3, km 9.3). The north-south transect across the fertilizer factory was chosen to determine the distribution of pollutants potentially released by the factory effected by seasonal changes in the prevailing wind direction. The spatial distribution of the sampling sites follows the transect studied by Mirlean and Roisenberg (2006 and 2007). In this study the selection of the seven sampling sites was based on the results of the named authors, who showed increased Cd and As concentration in top soils (N = 19) at the factory site with decreasing concentrations towards km 5.1 and increasing concentration of As at the southern end of the peninsula. In our study the soil horizons were opened with a shovel to a sampling depth of 100 cm to study the vertical distribution of trace elements in soils. The time consuming sampling procedure did not allow opening more than seven horizons at one day. Samples were taken with a stainless steel knife out of the different horizons and stored in polyethylene (PE) bags. The groundwater level depths varied along the transect and samples could only be collected at the sampling points km -1.1, km 0.9, km 6.1, and km 9.3. After the opening of the soil horizon the pit was cleaned and the groundwater was sampled with PE bottles after sedimentation of dispersed soil particles.

Phosphorus fertilizer samples (N = 39) traded in Southern Brazil in 2007 and 2008 were collected to determine typical trace element concentrations of local products. Out of the 39 samples 29 are multi component fertilizers (13 NPK, 11 NP, and 5 PK) and 10 straight P fertilizers (4 single superphosphate and 6 triple superphosphate). Phosphorus contents vary between 14 to 52 %.

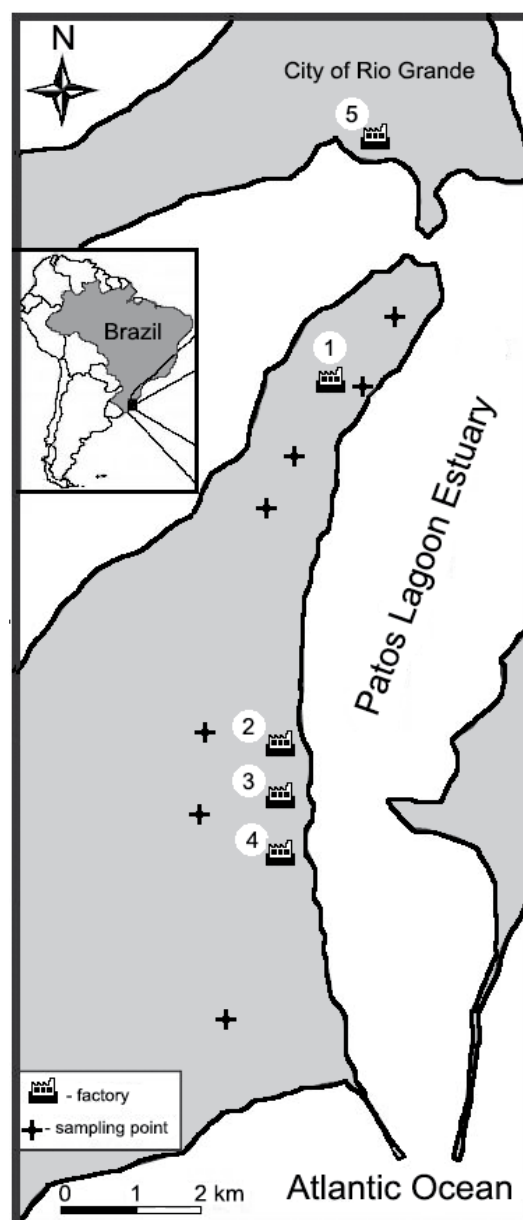


Figure 1:

Sampling site on the peninsula south of Rio Grande (Southern Brazil) showing the spatial distribution of seven sampling points and the location of a P fertilizer factory (1), a wood factory (2), a container freight terminal (3), a ship yard (4), and a petroleum refinery (5) (map modified after Mirlean and Roisenberg, 2006).

2.3 Sample preparation and chemical analysis

The collected soil samples were air-dried and stored in plastic bags. The samples were sieved (2 mm) and ground in an agate ball mill to a particle size of < 20 µm and dried overnight at 105 °C before further chemical treatment. For the determination of the total elemental content the procedure for trace element analyses described by Dulski (1994 and 2001) and Alexander (2008) was used. 100 mg of each sample was digested with 3 ml of HCl, 1 ml HNO₃

and 1 ml HF (all acids used are concentrated and supra-pure grade) for 16 hours at > 180 °C in a closed acid pressure digestion system (Picotrace). Prior to the analyses the acids were evaporated in the open teflon vessel at a temperature of 120 °C. The evaporation step was repeated two times with 5 ml HCl for the complete evaporation of fluoride complexes, which affect the rare earth element analysis. The final sample solution was taken up in 50 ml of 0.5M HCl. The groundwater samples were filtered with 0.2 µm cellulose acetate filters immediately after the sampling. The groundwater samples were acidified with concentrated suprapure HNO₃ to pH 2.

The fertilizer samples (N = 39) were hand-ground with a mortar and pestle and together with two certified P rock standard reference material (NIST 120b and NIST 694) dried overnight at 105 °C, and then digested by microwave (MLS Start 1500). The samples (0.05 g) were extracted with aqua regia (3.6 ml concentrated HCl and 1.2 ml concentrated HNO₃) at constant temperature of 210 °C for 60 minutes. Filtered samples were diluted to 100 g with de-ionized water.

2.4 Analytical procedures

Trace element concentrations in soil and fertilizer samples were determined in a 0.5M HNO₃ matrix with a Perkin-Elmer/SciexElan Model 5000 inductively coupled plasma mass spectrometer (ICP-MS) following the procedures of Dulski (2001). Beside the trace elements Cd, Co, Ni, Nb, Pb, Sr, Th, U, and Zr, the rare earth elements La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y (REY) were analysed via ICP-MS. The major elements Al, K, Fe, Ca, Na, Mg, and P and the trace elements Zn and V contents were determined using an inductively couple plasma optical emission spectrometer (Spectro Ciros Vision – ICP-OES). The Cu concentrations in the soil samples were determined using cathodic stripping voltammetry (Metrohm 757 VA Computrace). The accuracy of the measurements was tested using certified reference material (BHVO-2, NIST 120b, and NIST 694). The pH value of the soils was measured in 0.01 M CaCl₂ with a 1:5 soil to solution ratio according to ISO 10390. Major and trace element concentrations in groundwater samples were analyzed via ICP-MS and ICP-OES. Additionally the pH was measured and the anion concentrations (F⁻, Cl⁻, NO₃⁻, and SO₄²⁻) were determined using ion chromatography (Metrohm IC 462).

2.5 Statistical analysis and calculation of enrichment factors for trace elements (EF_{TE})

The statistical description of the dataset, including mean, minimum, maximum values, and standard deviation was carried out with SPSS 12.

The evaluation of the enrichment of the investigated trace elements in the top soils along the transect cannot be done with simple calculation of the top soil/sub soil quotients. The different geochemical behavior and the multiple sources of the trace elements require different calculation of the trace element enrichment factors (EF_{TE}). Therefore a modified calculation model based on methods by Zoller et al. (1974) and Reimann and Caritat (2000) was used. The concentration of the trace element at the site X is divided by the concentration of the trace element at the control site (ctrl). In addition, these values are normalized to a "conservative" element (Zr), which is not anthropogenically enriched in top soils along the transect.

$$EF_{TE} = (\text{conc}(TE)_x / \text{conc}(Zr)_x) / (\text{conc}(TE)_{ctrl} / \text{conc}(Zr)_{ctrl})$$

- with EF_{TE} = enrichment factor for a certain trace element
 conc(TE)_x = concentration of trace element in top soil at sampling point x
 conc(TE)_{ctrl} = concentration of trace element in top soil at sampling point km 5.1
 conc(Zr)_x = concentration of zirkonium in top soil at sampling point x
 conc(Zr)_{ctrl} = concentration of zirkonium in top soil at sampling point km 5.1

3 Results and discussion

3.1 Major and trace elements in P fertilizers traded in Brazil

All Brazilian P fertilizers analyzed in this study show typical ranges of major and trace element concentrations. The mean, median, minimum, and maximum concentration of P₂O₅, K₂O, Ca, Fe, Al, Mg, and Na are given in Table 1. High variation coefficients (RSD) between 41 to 210 % indicate the broad concentration range in the studied P fertilizers. The results in Table 1 and 2 are separated into two classes, which represent a sedimentary (s) (N = 34) and igneous (i) (N = 5) origin of the raw phosphate material. The identification of different geological origin of the raw phosphates is based on the different geochemical composition of the rare earth elements in the two sources (see section 3.5).

The mean, median, minimum, and maximum concentrations of trace elements (Sr, Zn, V, Ce, U, La, Ni, Zr, Cd, Pb, Nb, and Th) are listed in Table 2. While high mean concentrations of the potentially environmental harmful heavy metals Zn (306 mg kg⁻¹), U (78 mg kg⁻¹), Ni (33 mg kg⁻¹), Cd (16 mg kg⁻¹), and Pb (6.9 mg kg⁻¹) were found in fertilizers of sedimentary origin, the mean concentrations of these elements are low in fertilizers of igneous origin (12 mg Zn kg⁻¹, 2 mg U kg⁻¹, 7.7 mg Ni kg⁻¹, < LLD mg Cd kg⁻¹, and 2.9 mg Pb kg⁻¹). In contrast other trace ele-

Table 1:

Concentrations of major components (P_2O_5 , K_2O , Ca, Fe, Al, Mg, and Na) in % in fertilizer samples with sedimentary (s) (N = 34) and igneous (i) (N = 5) origin with a P_2O_5 -content of > 5 % traded in southern Brazil in 2007 and 2008

	P_2O_5		K_2O		Ca		Fe		Al		Mg		Na	
	s	i	s	i	s	i	s	i	s	i	s	i	s	i
Mean	29	35	9.9	3.0	8.9	1.0	0.63	0.26	0.56	0.31	0.51	0.06	0.36	0.26
Median	22	34	2.2	0.14	8.9	0.6	0.54	0.33	0.42	0.35	0.28	0.07	0.32	0.21
RSD (%)	48	45	131	210	83	114	79	60	72	41	99	61	55	64
Minimum	14	18	0.05	0.13	0.16	0.17	0.06	0.03	0.13	0.15	0.09	0.03	0.12	0.06
Maximum	53	51	58	14	22	2.9	1.9	0.40	1.6	0.42	2.58	0.12	1.13	0.51

Table 2:

Concentrations of selected trace elements (Sr, Zn, V, Ce, U, La, Ni, Zr, Cd, Pb, Nb, and Th) in $mg\ kg^{-1}$ in fertilizer samples with sedimentary (s) (N = 34) and igneous (i) (N = 5) origin with a P_2O_5 -content of > 5 % traded in southern Brazil in 2007 and 2008

	Sr		Zn		V		Ce		U		La	
	s	i	s	i	s	i	s	i	s	i	s	i
Mean	309	1588	306	12	118	105	35	566	78	2	28	317
Median	237	241	235	12	102	116	15	385	61	2.9	20	165
RSD (%)	93	196	79	34	43	17	119	102	74	64	83	131
Minimum	0.16	72	44	8.0	63	85	0.05	54	0.01	0.25	0.06	24
Maximum	1072	7148	1005	16	229	116	171	1558	200	3.5	93	1048
	Ni		Zr		Cd		Pb		Nb		Th	
	s	i	s	i	s	i	s	i	s	i	s	i
Mean	33	7.7	20	22	16	< LLD	6.9	2.9	1.3	18	5.5	11
Median	25	8.4	18	16	9.7	< LLD	4.0	1.3	0.6	19	3.7	16
RSD (%)	58	24	52	63	98		107	114	119	67	98	76
Minimum	0.35	5.1	0.21	7.7	1.3	< LLD	0.32	0.59	0.01	0.25	0.01	0.13
Maximum	82	9.7	57	44	56	< LLD	31	8.5	6.8	30	20	19

LLD = lower limit of detection

ments were determined in higher mean concentrations in P fertilizers of igneous origin (1588 $mg\ Sr\ kg^{-1}$, 566 $mg\ Ce\ kg^{-1}$, 317 $mg\ La\ kg^{-1}$, and 18 $mg\ Nb\ kg^{-1}$) in comparison to fertilizers of sedimentary origin (309 $mg\ Sr\ kg^{-1}$, 35 $mg\ Ce\ kg^{-1}$, 28 $mg\ La\ kg^{-1}$, and 1.3 $mg\ Nb\ kg^{-1}$). Such variation in trace element contents of fertilizers in relation to the geogenic origin of the material is confirmed by a study from Niedergesäss et al. (1992), who analyzed mineral fertilizers processed from either igneous or sedimentary P rock sources. A comparison of the values of this study with concentrations in P fertilizer products traded in Germany (Smidt et al., 2011b) shows that Brazilian fertilizers contain distinctly higher mean concentrations of P_2O_5 , Cd, and U. The high concentrations of heavy metals (Zn, U, Ni, Cd, and Pb) in the analyzed fertilizers indicate the potential contamination hazard for arable soils which receive regularly applications.

3.2 Major and trace elements in top and sub soils

The mean, minimum, maximum, and variation coefficient (RSD) of major elements in the top soils of the seven sampling sites along the transect are given in Table 3. The broad ranges of all major element concentrations reflect the variation of top soil element contents along the sampled transect. Especially P and Ca, which are the main components of apatite rock phosphates, show extreme maximum concentrations of 5225 and 15035 $mg\ kg^{-1}$ in comparison to the mean concentrations (1095 $mg\ P\ kg^{-1}$ and 4318 $mg\ Ca\ kg^{-1}$). The mean, minimum, maximum, and variation coefficient (RSD) of trace elements (Sr, Zn, V, Ce, U, La, Ni, Zr, Cu, Pb, Nb, Th, and Co) (Table 4) show a high variation in the top soils along the investigated transect, which is especially pronounced for Sr, La, Ce, Zn, Nb, Th, and U.

Table 3:
Concentrations of major components (P, K, Ca, Fe, Al, Mg, and Na) in seven top soils from Southern Brazil (mg kg⁻¹)

	P	K	Ca	Fe	Al	Mg	Na
Mean	1 095	5 498	4 318	4 532	13 097	510	3 199
Median	398	4977	3 180	4 072	15 658	540	2 660
RSD (%)	170	36	112	68	43	72	49
Minimum	80	3 245	1 200	1 726	6 109	113	1 683
Maximum	5 225	8 675	15 035	10 267	19 438	1 121	5 912

Table 4:
Concentrations of selected trace elements (Sr, Zn, V, Ce, U, La, Ni, Zr, Cu, Pb, Nb, Th, and Co) in seven top soils from Southern Brazil (mg kg⁻¹)

	Sr	Zn	V	Ce	U	La	Ni	Zr	Cu	Pb	Nb	Th	Co
Mean	62	38	12	15	1.1	7.8	2.3	33	8.6	7.3	4.5	1.7	1.4
Median	41	19	11	10	0.5	5.3	1.6	37	5.9	6.7	2.1	1.1	1.2
RSD (%)	83	132	53	120	131	115	74	18	76	58	136	92	74
Minimum	27	9	5.0	2.9	0.32	2.2	0.79	25	2.0	3.5	1.2	0.47	0.51
Maximum	168	151	23	57	4.3	28	5.0	39	18	15	18	5.0	3.3

The spatial distribution of P (Figure 2a) along the sampled transect on the peninsula shows the highest concentration of 5225 mg kg⁻¹ in the top soil close to the production site (km 0). From here decreasing concentrations with increasing distance to the P fertilizer factory were found. In the distance of -1.1 and 1 km the concentration of P is still strongly elevated (1188 and 496 mg kg⁻¹, respectively) when compared to the top soil in the distance of 9.3 km at the end of the peninsula with 148 mg kg⁻¹. A slight increase in top soil concentration at the sampling point at km 6.3 is a possible effect of P fertilization of pasture land used for cattle grazing.

Calcium concentrations (Figure 2b) along the transect have also their maximum (15035 mg kg⁻¹) at the factory site, where apatite rocks (CaPO₄) are extracted by H₂SO₄ for P fertilizer production. The lowest concentration (1200 mg kg⁻¹) was found in a distance of 1.9 km. The increasing influence of brackish groundwater causes an increasing Ca concentration in top and sub soils with increasing distance from the sampling point km 5.1 towards the southern end of the peninsula (km 9.3).

The Mg concentration (Figure 2c) in the top soil is elevated at the factory site (774 mg kg⁻¹), but the maximum concentration (1121 mg kg⁻¹) can be found at the northernmost sampling point (km -1.1). The elevated concentrations of Mg and Fe (Figure 2f) at the sampling km -1.1 are probably an effect of urban dust immission. Temporal water logged conditions cause a higher groundwater level at the southern end of the peninsula (km 6.3 and 9.3) which yields anoxic conditions and Fe oxidation along O₂

gradients at plant roots and other macropores up to the top soil. The spatial distribution of K and Na (Figure 2d and 2e) along the sampled transect on the peninsula also shows enrichment at the factory site (7532 mg K kg⁻¹ and 4095 mg Na kg⁻¹, respectively), but has the highest top soil concentrations (8675 mg K kg⁻¹ and 5911 mg Na kg⁻¹, respectively) at the outermost sampling point (km 9.3) at the southern end of the peninsula, due to the brackish groundwater influence.

The high concentrations of P and Ca (Figure 2a and 2b) in the top soil (0 to 10 cm) in comparison to the deeper soil layers at 10 to 40 cm and 40 to 100 cm at the factory site (km 0) demonstrate the high P and Ca input to the soils by the P fertilizer production compared to the natural background concentration. The high load of P to the top soil and the acidic pH values of 4.7 enabled slight P leaching to deeper soil horizons as indicated by the small P peak at the factory site in the 10 to 40 cm soil layer. Potassium and Na (Figure 2c and 2d) show a different distribution in top and sub soils at the factory site compared to P. The higher mobility of the monovalent cations K and Na in comparison to the bivalent Ca and Mg in the soil column is reflected in the mostly equal distribution of the elements in top (0 to 10 cm) and sub soil (10 to 40 cm and 40 to 100 cm) horizons. However, the sub soil concentrations of all major elements and P are elevated in the soil layer between 10 to 40 cm at the factory site in comparison to the surrounding sub soils. The dislocated elements are sorbed to the iron-rich Go horizon, which is influenced by changing groundwater levels.

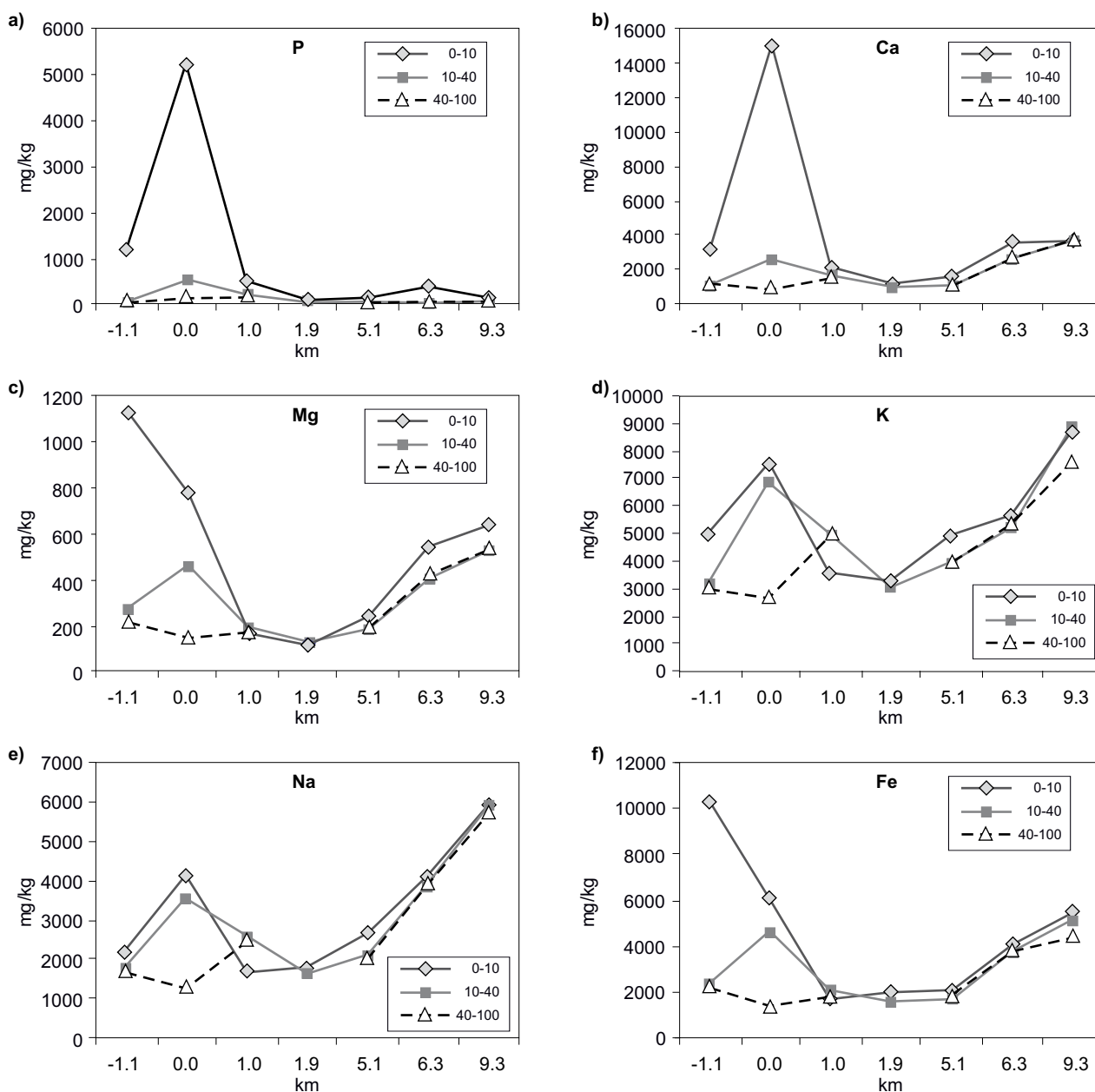


Figure 2:

Spatial distribution of P (a), Ca (b), Mg (c), K (d), Na (e), and Fe (f) in top (0 to 10 cm) – and sub (10 to 40 cm and 40 to 100 cm) – soils (mg kg⁻¹) in relation to the distance from a fertilizer factory (0 km corresponds to the factory position).

The spatial distribution of U (Figure 3a) along the sampled transect on the peninsula shows the highest concentration of 4.3 mg kg⁻¹ in the top soil close to the production site (km 0). With increasing distance to the P fertilizer factory decreasing concentrations were found. In the distance of 1 km the concentration of U is still elevated (0.9 mg kg⁻¹) in comparison to the top soil in the distance of 9.3 km at the end of the peninsula (0.5 mg kg⁻¹). The lowest U concentration is found in 5.1 km distance (0.3 mg kg⁻¹). The spatial distributions of Nb, La, Zn, and Pb (Figure 3b, 3c, 3d, and 3e) resemble that of U. The comparison of top soil

and sub soil concentrations of trace elements demonstrate the enrichment in the uppermost horizon at the fertilizer factory. Niobium as a refractory element, which is considered extremely immobile in soils (Kurtz et al., 2000), shows the strongest enrichment of the top soil in comparison to the sub soil at km 0 (Figure 3b) of all analysed trace elements. In comparison to Nb, elevated concentrations of U, Ni, Zn, Pb, and V are found in the iron-rich Go horizon (10 to 40 cm) at the fertilizer factory (km 0), which points to the vertical dislocation of these trace elements at this site. Lead can be found in slightly higher concentration in

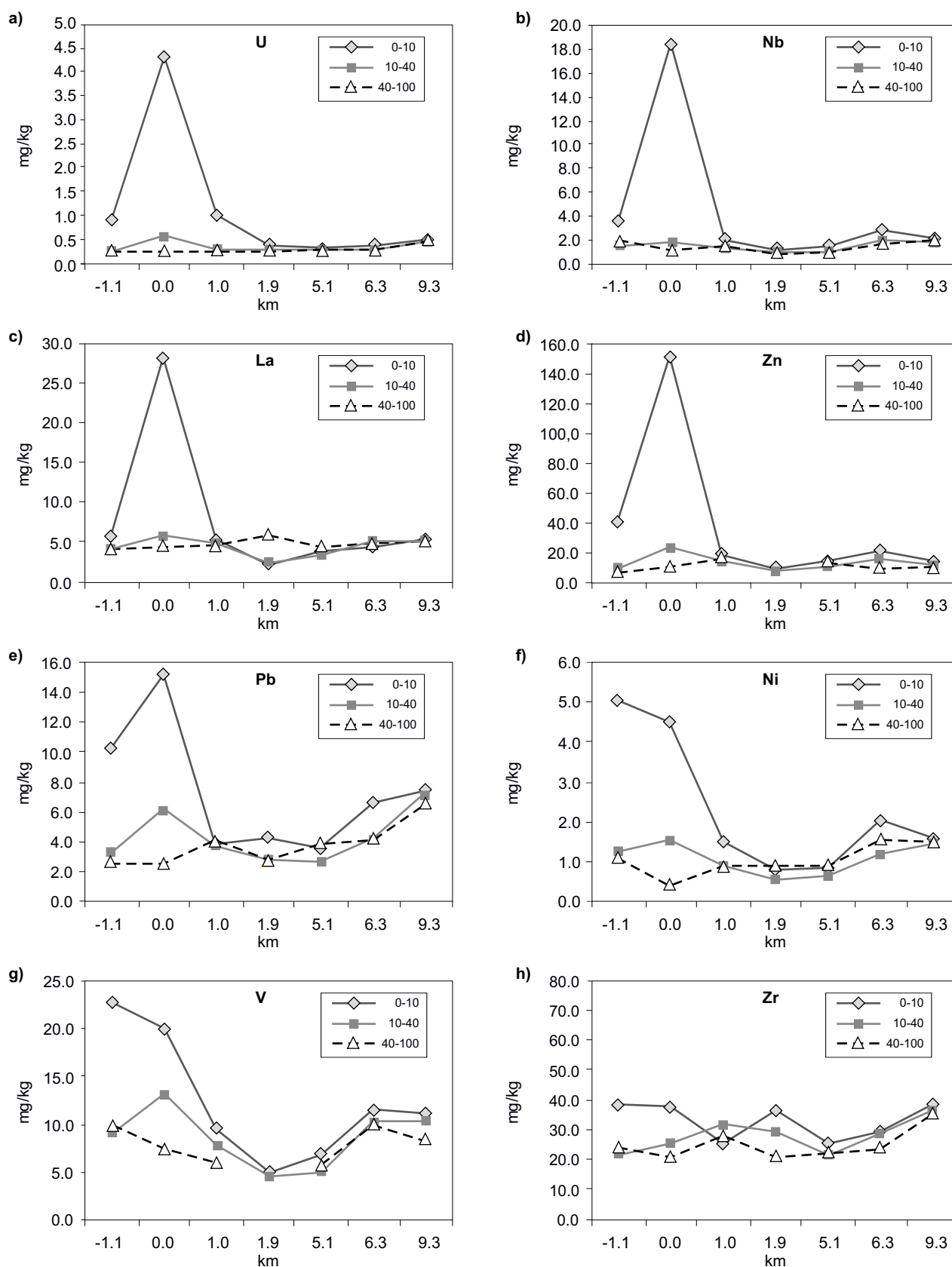


Figure 3: Spatial distribution of U (a), Nb (b), La (c), Zn (d), Pb (e), Ni (f), V (g), and Zr (h) in top (0 to 10 cm)- and sub (10 to 40 cm and 40 to 100 cm) – soils (mg kg⁻¹) in relation to the distance from a fertilizer factory (0 km corresponds to the factory position).

the top soils along the whole transect in comparison to the sub soils, which possibly originates from the emission of leaded gasoline exhaust from cars until the 1990s. This pollution source may also have affected the increased top soil concentration of Pb (Figure 3e) at the northern end (km -1.1) of the peninsula in the close vicinity to the city of Rio Grande. Copper was found to be increased in top soils at two sampling points along the transect. The potential sources are discussed in the following section. Due to analytical uncertainties the spatial distribution of Cd is not shown, but Mirlean and Roisenberg (2006) found elevated Cd concentrations in topsoils (9.3 mg kg⁻¹) in the vicinity of the P fertilizer factory in comparison to the local background (0.03 mg kg⁻¹).

3.3 Variations of element enrichment factors

Zirkonium (Zr) was chosen as the conservative element for normalization of the trace element enrichment factors (EF_{TE}), since the concentration in the soil transect is practically exclusively influenced by geogenic sources. The mean concentration of Zr is 33.1 ± 6.1 mg kg⁻¹ in top soils and 27.7 ± 5.5 mg kg⁻¹ in sub soils and its spatial distribution does not show any trend (Figure 3h). The sampling point at 5.1 km distance from the P factory is chosen as the control site. This location in the intermediate location between factory and ocean showed the lowest concentration for most of the observed trace elements. Only Cu is normalized against another control site (km 1.9), because Cu is assumed to have another pollution source besides the P fertilizer factory. A wood preservative factory is located at the southern end of the peninsula.

While an EF_{TE} value around 1 indicates no trace element enrichment in the top soil, values higher than 1.5 show a clear enrichment of trace elements by either anthropogenic activities or geological sources. Uranium (9.3), Nb (8.3), Zn (7.3), Ce (5.6), La (5.1), and Th (3.4) show high EF_{TE} only at the factory site (Table 5), which indicates the fertilizer

factory to be a one point pollution source for these elements. The EF_{TE} of Pb (2.9), Ni (3.7), Co (1.7), and V (2.0) also reflect an emission by the fertilizer factory, but the EF_{TE} at the sampling point km -1.1 (1.9, 4.0, 3.8, and 2.2, respectively) give indications for other emission sources from the city of Rio Grande. A petrochemical refinery is located in 2 km linear distance of the sampling point km -1.1 (Figure 1). Nickel and V are known to be emitted by oil refineries and a recent study conducted in the vicinity of the local production site showed four times higher Ni and V concentrations in the top soils close to the emission source in comparison to the local background (Garcia et al., 2010). Another source of pollution of Ni and V could be the combustion of heavy residual fuel oils which typically contain 1 to 1000 mg kg⁻¹ V and 3 to 345 mg kg⁻¹ Ni (Russell et al., 2010). Heavy residual fuel oils also contain Co, but the concentration level is lower (7 to 3300 µg kg⁻¹) in comparison to Ni and V (Russell et al., 2010). The elevated EF_{TE} of Co, Zn, and Pb at the northern end of the transect are possibly derived from other industrial sources in the city of Rio Grande. The spatial distribution of EF_{TE} for Cu shows two points of enrichment in the top soil on the peninsula. One is located at the fertilizer factory (8.9), the second one is located at the sampling point km 5.1 (11.6) and km 6.3 (6.4). At this sampling point a wood factory is located in approximately 500 m distance (Figure 1), possibly using chromated-copper-arsenates (CCA) for wood preservation. The elevated concentrations of As in top soils reported by Mirlean and Roisenberg (2006) are most likely related to this contamination source, too.

3.4 Elemental composition of groundwater

The analyses of groundwater did not show any significantly elevated trace element concentrations at the sampling points close to the fertilizer factory (km -1.1 and km 1). However, the results of anion analyzes show high nitrate, phosphate, fluoride, and sulfate concentrations

Table 5:

Element enrichment factors (EF_{TE}) of trace elements in top soils from Southern Brazil in relation to the distance from a fertilizer factory (TE concentration normalized to background and Zr concentration in top soils at km 5.3 (background for Cu at km 1.9))

Distance (km)	Sr	Zn	V	Ce	U	Nb	La	Ni	Cu	Pb	Th	Co
-1.1	0.9	1.9	2.2	1.2	1.9	1.6	1.0	4.0	2.8	1.9	1.2	3.8
0.0	3.9	7.3	2.0	5.6	9.3	8.3	5.1	3.7	8.9	2.9	3.4	1.7
1.0	1.0	1.3	1.4	1.5	3.2	1.4	1.4	1.8	3.5	1.1	0.9	0.9
1.9	0.7	0.5	0.5	0.3	0.8	0.6	0.4	0.7	1.0	0.8	0.3	0.7
5.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	11.6	1.0	1.0	1.0
6.3	1.7	1.3	1.5	1.1	1.0	1.7	1.0	2.1	6.4	1.6	1.0	1.7
9.3	1.9	0.7	1.1	1.0	1.0	0.9	0.9	1.3	1.2	1.4	0.9	2.0

Table 6:

Concentrations of selected compounds (F, NO_3^- , PO_4^{3-} , SO_4^{2-} , Cl, Na, and Sr) and pH values in four groundwater samples along a transect across the P fertilizer factory (km 0) in Southern Brazil (mg L^{-1}), (Groundwater could not be sampled at sites km 0, km 1.9, km 5.1 since the groundwater table was lower than 100 cm).

Distance (km)	F	NO_3^-	PO_4^{3-}	SO_4^{2-}	Cl	Na	Sr	pH
-1.1	1.7	32.7	0.69	36	48	22	0.15	6.6
1.0	7.6	11.5	15.8	143	8.1	6.5	0.16	5.0
6.3	0.26	1.5	< LLD	0.36	38	21	0.16	5.9
9.3	0.39	0.06	< LLD	0.61	112	57	0.43	6.5

LLD = lower limit of detection

(Table 6) at the sampling point at km +1. The highest NO_3^- concentration was found at the northern sampling point at km -1.1, which is influenced by a rural settlement not connected to the urban waste water treatment system. The high Na, Sr, and Cl concentrations at the sampling points at km -1.1, 6.3, and 9.3 indicate the influence of brackish groundwater at these sites. A previous study conducted by Mirlean and Roisenberg (2006) on groundwater of the peninsula showed high concentrations of these anions in the vicinity of the fertilizer production site, too. Here, Cd was found in correlation with ortho-phosphate and nitrate with maximum concentration of $3.06 \mu\text{g L}^{-1}$ (background $0.06 \mu\text{g L}^{-1}$) in groundwater in the vicinity to the factory.

3.5 Rare earth elements in soils and fertilizers

The determination of rare earth elements and yttrium (REY) and the normalization of the REY_{SN} concentrations against Post Achaean Australian Shale (sub-script 'SN' refers to shale (PAAS) normalized REE concentrations, Taylor and McLennan, 1989) enabled to identify the marine sedimentary or the igneous deposit source of the P rock used for the production of the P fertilizers used in Brazil. Of our 39 fertilizer samples, 5 could be identified as igneous P rock derived, while the remaining 34 were of marine sedimentary origin. This distribution ratio is consistent with the value of 87 % given in literature for a marine sedimentary origin of P fertilizers (Kratz et al., 2006). Fig-

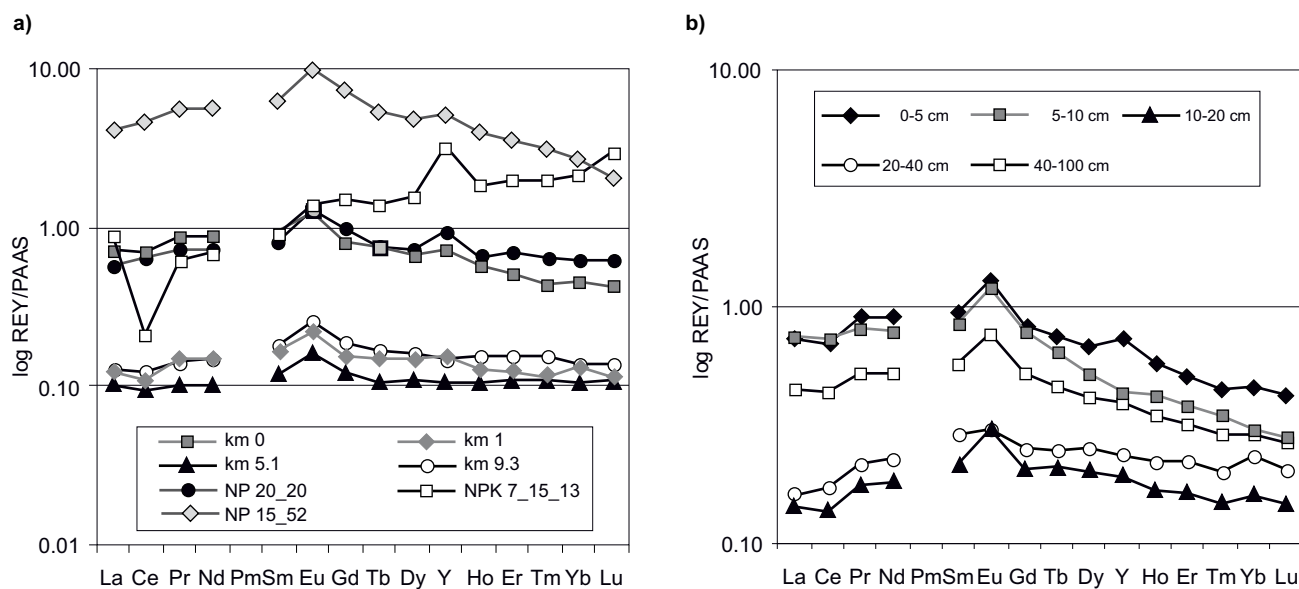


Figure 4a:

REY_{SN} patterns in four top soil samples (0 to 5 cm) from the Rio Grande peninsula (km 0, km 1, km 5.1, and km 9.3) and three fertilizer samples traded in Southern Brazil (NP 20_20, NPK 7_15_13 and NP 15_52)

Figure 4b:

REY_{SN} patterns in five different soil horizon samples (0 to 5, 5 to 10, 10 to 20, 20 to 40, and 40 to 100 cm) from the P fertilizer factory (km 0)

ure 2 shows shale normalized REY patterns of three selected fertilizer samples from the analysed set of 39 samples. The sedimentary origin of fertilizer sample NPK 7_15_32 is indicated through the negative Ce and the positive Y anomaly, which are typical seawater features. The samples NP 15_52 and NP 20_20 both show the typical distribution patterns for igneous P rock deposits, indicated by a positive Eu and a slight positive Y anomaly.

The REY_{SN} pattern of the top soil sample at km 0 (Figure 4a and 4b) shows enrichment in REY elements, which confirms the results of the enrichment factor that the P fertilizer factory (km 0) is obviously the source of high REY emission. This also indicates that the factory has predominantly been processing rock phosphates of sedimentary origin. Nevertheless, high Nb concentration found at km 0 also gives indication for processing of rock phosphates of igneous origin. Igneous phosphate rock deposits are used in Brazil for Nb mining providing 85 % of the worldwide Nb supply (Oliveira et al., 2011). Igneous P fertilizers show also significantly higher Nb contents than fertilizers of sedimentary origin (Table 2). Since the factory has been processing fertilizers for 40 years (Mirlean and Roisenberg, 2006), it can be assumed that the rock phosphate sources fluctuate. Figure 4b shows the vertical REY_{SN} patterns of the different soil horizons at the sampling point km 0. The positive europium (Eu) anomaly found in all analyzed top and sub soil samples along the transect originates probably from feldspar mineral content in the dune sand with arkosic composition (Tomazelli et al., 2000; Martins, 2003).

4 Conclusion

The study provides evidence for the release of numerous trace elements from a P fertilizer factory in Rio Grande (Southern Brazil) by analyzing soil samples at different depth and at different distances to the factory and a set of typical fertilizer samples from the region. As P fertilizers contain high concentrations of elements with potential toxicity (U, Cd, Zn, Pb, Ni, Co, and F) the risk of environmental contamination due to the uncontrolled particulate release of these elements is high at such production sites. The multi trace element analyzes of soils conducted in this study identified various industrial pollution sources emitting different trace elements which are spatially distributed along a north-south transect of the peninsula. Beside the P fertilizer factory, a refinery could be identified to emit Ni and V at the northern end of the peninsula. Furthermore, a wood factory possibly using chromate-copper-arsenates is assumed to be the source of elevated Cu (and As) concentration in top soils at the southern end of the peninsula. REY_{SN} patterns of fertilizers in comparison to top soils allowed to distinguish between marine sedimentary or igneous rock sources used as raw material for the fertilizer

production and are yet another manifestation of fertilizer factory-derived pollution of top soils at the investigated site.

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