

**TRACE ELEMENTS AND Sr-Nd ISOTOPES IN AQUA REGIA
EXTRACTS TO ASSESS POLLUTION IN URBAN
AND FARMLAND SOILS FROM RAVENNA (ITALY)**

**LES ÉLÉMENTS-TRACES ET LES ISOTOPES DE Sr ET Nd
DANS LES EXTRAITS AVEC AQUA REGIA POUR UNE ÉVALUATION
DE LA POLLUTION EN SOLS URBAINS ET AGRICOLES
DE RAVENNE (ITALIE)**

**ELEMENTI IN TRACCIA E ISOTOPI DELLO Sr E DEL Nd
NEGLI ESTRATTI D'AQUA REGIA PER UNA VALUTAZIONE
DELL'INQUINAMENTO IN SUOLI URBANI E AGRICOLI
DI RAVENNA (ITALIA)**

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Abstract

Sr/Ca ratios, and Sr and Nd isotopes, were determined in aqua regia extracts from three urban and agricultural soils from Ravenna. Sr/Ca ratios suggested preferential retention of Sr in the agricultural soils during the weathering of bedrock minerals. Despite of the different land use, the three soils displayed similar isotopic ranges, suggesting common sources for the two elements, likely represented by old marine carbonates and crustal silicates. The Nd isotopes of the urban park topsoil suggest some contamination by the soot of car exhausts.

Key words: *Sr-Nd isotopes; soils; Ravenna; aqua regia; Sr-Nd sources, pollution*

Résumé

Les rapports Sr/Ca et les isotopes du Sr et du Nd ont été déterminés dans les extraits avec aqua regia de trois sols agricoles et résidentiels dans la zone de Ravenne. Les rapports Sr/Ca suggèrent la rétention préférentielle du Sr dans les sols agricoles pendant l'altération des minéraux. Nonobstant leur utilisation différente, les sols ont des valeurs isotopiques semblables, qui suggèrent des sources communes pour les deux éléments, représentées par d'anciens carbonates marins et des silicates de la croûte terrestre. Les horizons, les plus superficiels du sol du parc urbain sont probablement affectés par une pollution de Nd dérivé des émissions de voitures.

Mots-clés: *Isotopes du Sr et Nd; sols; Ravenne; aqua regia; sources de Sr et Nd, pollution*

Riassunto

Sono stati determinati i rapporti Sr/Ca e i rapporti isotopici di Sr e Nd in estratti di aqua regia di tre suoli interessati da uso agricolo e residenziale della zona di Ravenna. I rapporti Sr/Ca suggeriscono la ritenzione preferenziale dello Sr nei suoli agricoli durante l'alterazione dei minerali. Nonostante il differente uso, i suoli hanno rapporti isotopici simili, suggerendo che Sr e Nd derivano da sorgenti comuni, rappresentate da carbonati marini antichi e silicati cristallini. Gli orizzonti più superficiali del suolo del giardino pubblico mostrano una probabile presenza di Nd derivato dalle emissioni di scarico dei veicoli.

Parole chiave: *Isotopi dello Sr e del Nd; suoli; Ravenna; aqua regia; origini di Sr e Nd, inquinamento*

Introduction

This paper illustrates a study of three soils from the Ravenna area applying chemical analysis and the isotopic systematics of Sr and Nd to detect the geochemical processes taking place in those matrices and the potential pollution. In fact, the soils can be affected to variable extent by anthropogenic contamination because of agricultural practices and proximity to Ravenna and its important industrial zone. Therefore, this study has an added value, presenting the first environmental screening survey of the studied area, beside the results of the typical academic scientific investigation.

Since the 90's, it is known that Sr isotopes may provide interesting information about the sources and the processes involving Sr in soils, and in particular the Sr available to plants, i.e. the bio-available fraction (e.g. Aberg, 1995; Capo et al., 1998; Stewart et al., 1998; Négrel et al., 2001). In fact, Sr isotopes can allow for distinguishing among the contributions from the minerals present in the soil bedrock and a variety of anthropogenic and natural sources supplying the element from outside, especially via atmospheric (dry and wet) deposition. These sources are represented by industrial and vehicular emissions, dust from soils, marine aerosol, as well as the waters infiltrated from rivers, drainage canals and coastal lagoons. All these anthropogenic and natural sources are present in the Ravenna area, that is a typical industrial and farming area near the Adriatic coastline. Only three papers have been so far carried out on the Sr isotopic composition of Italian soils (Castorina and Masi 2007, 2008, 2009); in particular, the last paper has been devoted to the study of a typical soil from san Vitale Pinewood, a natural reserve belonging to the Po-river delta National Park, located north of Ravenna. Although of more recent application to soil studies (e.g. Borg and Banner 1996, Martin and McCulloch, 1999), Nd isotopes can also provide interesting information. In fact, Nd, and in general the REE, derive from the minerals of the soil bedrock and/or can be added by anthropogenic activities, such as industrial and vehicular emissions, and particularly some natural fertilizers used in agricultural practices. Therefore, the coupled use of chemical analysis and the isotopic systematics of Sr

and Nd can provide better insight into the geochemical processes taking place in soils and inform about possible environmental risks derived from the pedogenesis.

Setting and sampling

Three soil profiles located in the Ravenna area were selected for this study (Fig. 1). One profile (Gp-1) was open in the urban park of downtown near a major traffic street; a second profile (Per-2) was dug in the northern outskirts of the town at the Perdisa farm, and the third (Pa-4) was open in the farm land, west of the southern edge of san Vitale Pinewood, north of Ravenna. Pa-4 soil is close to the highway leading to Venice, and lay in the range of emissions from the chimneys of the industrial zone. Moreover, the agricultural soils are located in the areas reclaimed in the last century, upfilling former marshlands with the sediments of the Lamone river draining Romagna's sedimentary Apennines.

As a whole, we collected 17 samples from the different horizons of the three soil profiles, that are classified Udifluventic Haplustepts, fine-silty, mixed, mesic (SSS, 2006) according to Buscaroli et al. (2009).

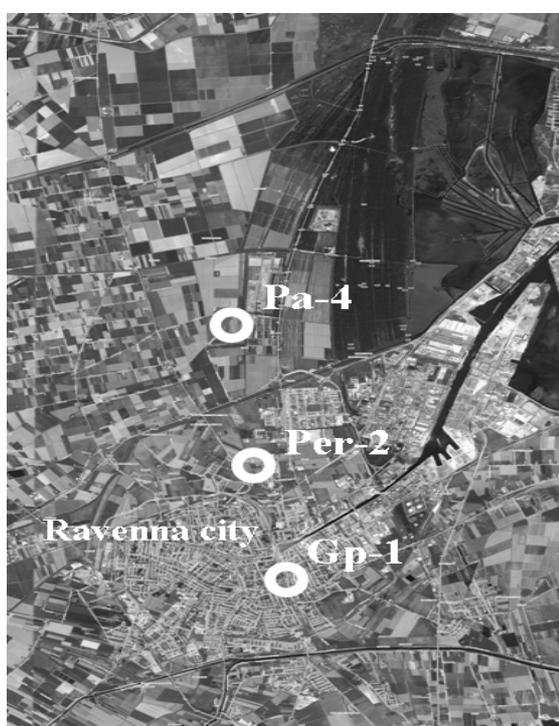


Figure 1

The study area. Geographical location of ITAS "L. Perdisa" farm (Per-2), central urban Park (Gp-1) and agricultural soil (Pa-4).



Profile	WGS84-UTM33	
	E(m)	N(m)
Pa-4	276918	4926335
Per-2	277105	4923765
Gp-1	277768	4921580

Analytical procedure

Trace elements aqua regia digestion (AR). Soil samples were dried at room temperature, then ground in an agate mill and passed through a 2 mm mesh sieve and lastly finely pulverized. A 250 mg aliquot from each homogenized and DOI: 10.6092/issn.2281-4485/3795

powdered sample was mineralized with aqua regia (HCl/HNO₃ 3:1) in a microwave oven (Milestone 1200) in a Teflon vessel and the specific digestion program consisted of four steps: 1) heating at 250 Watt for 3 min; 2) heating at 400 Watt for 2 min; 3) resting at 0 Watt for 2 min; 4) heating at 700 Watt for 2 min. After digestion and cooling, solutions were transferred at a dilution of 20 mL.

Solutions were analyzed for heavy metals and microelements using a Spectro Inductively Coupled Plasma Optical Emission Spectrometer (Circular Optical System CIR.O.S.^{CCD}). For the construction of calibration lines, certified multi-element standard solutions were used (CPI International - Amsterdam). The accuracy of the analytical method and the results obtained were verified by analyzing certified standard specimens of soils (BCR-CRM 141R, 142R, 143R).

Among the 36 elements analyzed, we discuss here only the results for Ba, Cr, Cu, Ni, Pb, Sn, V and Zn which are the most significant and allow for direct comparison with total concentrations.

Sr-Nd isotopes. Each sample was first washed with bi-distilled water to remove soluble salts and then attacked with aqua regia to dissolve carbonates, gypsum, phosphates, and partially both Fe-Mn oxide-hydroxides and organic matter; aqua regia also allows for releasing metals adsorbed onto the various soil matrices. Isotopic analyses were carried out at IGAG-CNR c/o Dipartimento di Scienze della Terra, University of Rome "La Sapienza" using a FINNIGAN MAT 262RPQ multicollector mass spectrometer with Re double filaments in static mode. The internal precision (within-run precision) of a single analytical value is given as two standard error of the mean. Repeated analyses of standards gave averages and errors expressed as two standard deviation (2σ) as follows : NBS 987, $^{87}\text{Sr}/^{86}\text{Sr}=0.710241\pm 13$ (n=20), $^{86}\text{Sr}/^{88}\text{Sr}$ normalized to 0.1194. Sr and Nd isotope ratios are expressed as $\delta^{87}\text{Sr}$, i.e. deviation of the isotopic ratio of the sample from that of seawater standard assumed to be 0 (Richter and De Paolo, 1987), and ϵ_{Nd} , i.e. the isotopic ratio of the sample relative to CHUR standard (De Paolo and Wasserburg, 1976), respectively.

Analytical results

Table 1 reports Sr contents (mg/Kg), Sr/Ca ratios and Sr-Nd isotope ratios of the samples.

The ranges of Sr contents in the A horizons of the three soils overlap; these ranges are lower (210-292 mg/Kg) than those of the B (296-344 mg/Kg) horizons of soils. As concerns the latter, Pa-4 soil displays lower Sr content (296 mg/Kg) than Gp-1 and Per-2 soils exhibiting similar ranges (313-344 mg/Kg). Lastly, relative to C horizons, Pa-4 soil is significantly Sr-poorer (78-124 mg/Kg) than the other soils displaying close values (284 and 303-343 mg/Kg for Gp-1 and Per-2 soils, respectively).

Despite the similar Sr ranges in the epipedon, Pa-4 and Gp-1 soils generally display lower Sr/Ca ratios (4.21 and 3.61-3.66, respectively) than Per-2 soil (7.84) (Fig. 2). In contrast, the Sr/Ca ratios of the B horizons of the three profiles are close (3.72-

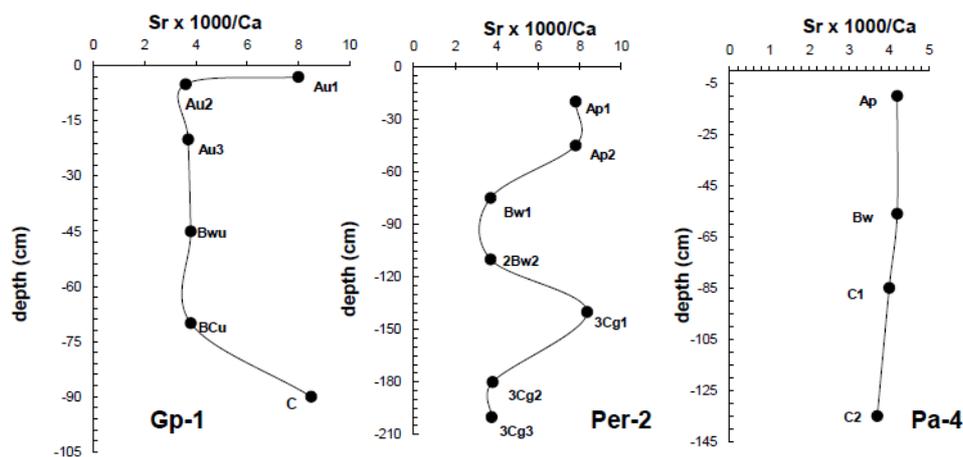
4.17) and the ratios of C horizons are quite variable (3.67-8.52), even in a same soil (Fig. 2).

Soil profile	Horizon	$\delta^{87}\text{Sr}$	ϵ_{Nd}	Sr	Ca	Sr/Ca
Gp-1 urban-park	Apu1	-0.58	-7.49	210	26305	8.0
	Apu2	-0.67	-6.50	272	75317	3.6
	Apu3	-0.61	-7.06	293	79810	3.7
	Bwu	-0.63	-7.55	344	89751	3.8
	BCu	-0.97	-8.23	334	86981	3.8
	C	-0.64	-7.06	284	33314	8.5
Per-2 farmland	Ap1	-0.62	-7.22	254	32365	7.8
	Ap2	-0.50	-8.39	263	33545	7.8
	Bw1	-0.63	-7.74	313	83608	3.7
	2Bw2	-0.49	-9.42	343	92231	3.7
	3Cg1	-0.50	-7.45	303	36282	8.35
	3Cg2	-0.60	-7.49	338	89207	3.8
	3Cg3	-0.66	-8.21	343	91386	3.75
Pa-4 farmland	Ap	-0.56	-8.10	274	65039	4.2
	Bw	-0.57	-7.82	296	70920	4.2
	C1	-0.52	-7.76	78	19710	4.0
	C2	-0.62	-7.69	124	33811	3.7

Table 1

Sr contents (mg/Kg), Sr/Ca (x 1000) ratios and Sr-Nd isotopic ratios of the samples from the studied soils.

Figure 2 – Sr/Ca ratios (x 1000) for the studied soils.



Sr and Nd isotopic ratios display similar ranges for all samples ($\delta^{87}\text{Sr}$ -0.49:-0.97, and ϵ_{Nd} -6.5:-9.42). Figures 3 and 4 show the isotopic variations of Sr and Nd, respectively, with depth for each soil profile.

Lastly, the distribution of some trace elements along the soil profiles is shown in Figure 5. The concentrations of Cu in the Per-2 topsoil, and Pb, Sn, Zn for the Gp-1

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topsoil, are higher corresponding than the limits of Italian Law (D.Lgs 152/2006). Concentrations decrease along the profile.

Figure 3 – $\delta^{87}\text{Sr}$ variations with depth in the studied soils.

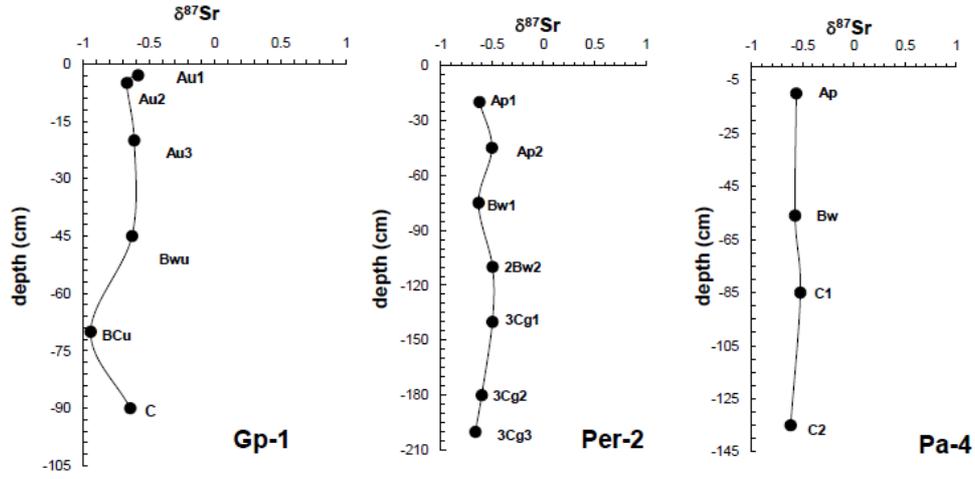


Figure 4 – ϵ_{Nd} variations with depth in the studied soils.

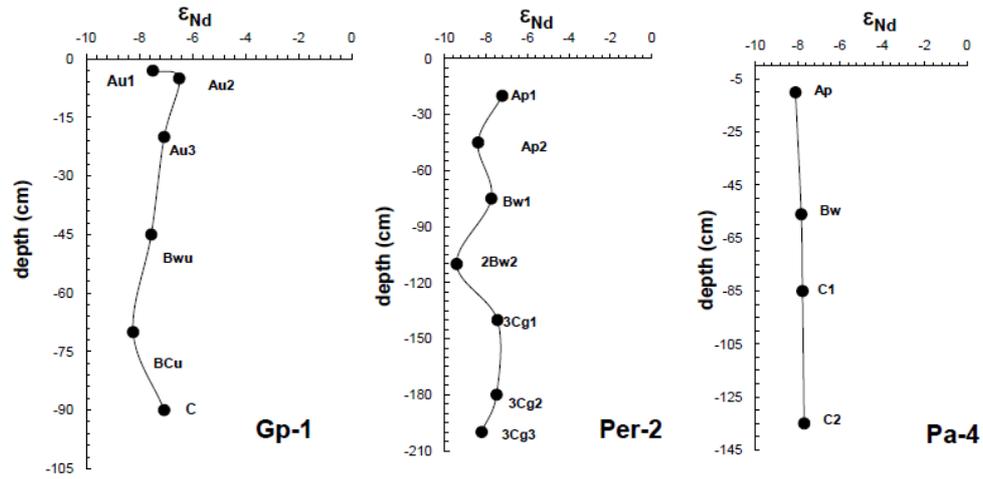
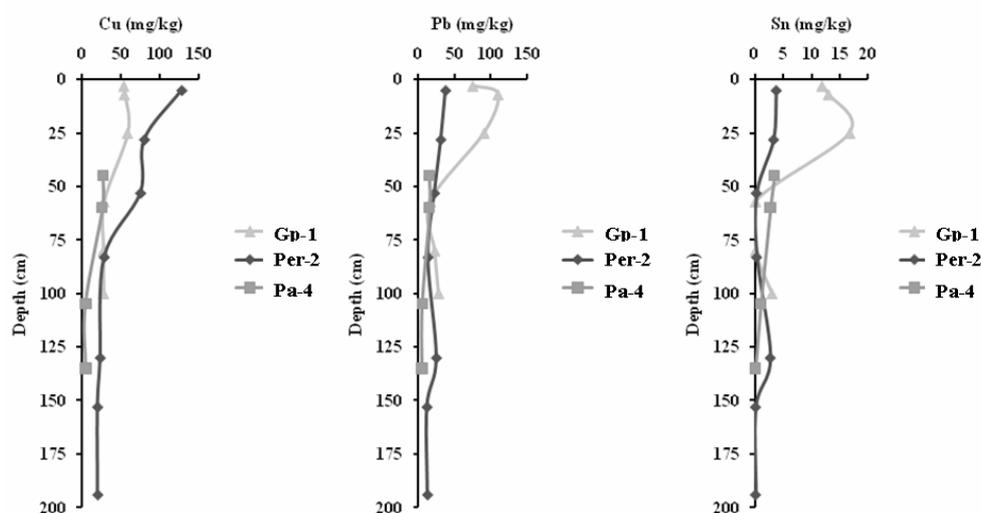


Figure 5 –Distribution of Cu, Pb and Sn along the three soil profiles.

Discussion

As it appears from Table 1, the distribution of Sr contents with depth is different in the three soils. In fact, Sr contents decrease significantly in Pa-4 soil, while they show a trend of increase in the other profiles. The decrease of Sr contents with depth in Pa-4 soil may suggest addition of Sr to upper horizons from an external source. However, this hypothesis finds no support as the Sr contents in upper horizons are comparable with those of the other two soils, with which Pa-4 soil shares similar chemical and mineralogical compositions. Alternatively, it is envisaged that the Sr-bearing minerals in the upper horizons of Pa-4 soil are less abundant than in the bedrock.

This hypothesis may be reasonable assuming that Pa-4 soil is composed of two “layers” of different chemical and mineralogical compositions. Such assumption recalls the fact that Pa-4 soil occurs in a marshland emplaced on the old coastal dune of san Vitale Pinewood and reclaimed by upfilling with the sediments of the Lamone river. Therefore, upper horizons are composed of the sediments from Romagna’s Apennines, while lower horizons are composed of sediments mainly from the Po-river basin encompassing the Alps and northern Apennines. The trend of Sr increase with depth observed in the other two soils may be explained by stronger weathering of bedrock silicates in upper horizons and subsequent removal of Sr by waters and/or the plants growing on the soil. Therefore, upper horizons are Sr-poorer than deeper horizons.

Sr/Ca ratios provide interesting information about the behaviour of the two alkaline earths in the three soils (Fig. 2). In fact, higher Sr/Ca ratios in the A horizons from

Per-2 soil than in the other soils suggest preferential removal of Ca relative to Sr, probably by the plants growing on the soil and/or waters. In contrast, the similar ranges in B and C horizons from the three soils suggest that the two metals are carried by the same phases in those layers.

The overlap of Sr-Nd isotope ranges in the three soils (Tab.1) suggests common sources of the two metals. The negative $\delta^{87}\text{Sr}$ suggest that the Sr source is represented by Cenozoic evaporites (carbonates and/or gypsum) and/or natural phosphate fertilizers (Castorina and Masi, 2010). In this context, the low S contents measured in the soils rule out any significant Sr contribution from gypsum. As concerns phosphates, they can contain both Sr and Nd in large amount and, thus, their addition to soils can characterize Sr-Nd isotopic signatures. However, the low P contents measured in the three soils rule out any significant addition of natural phosphorites to soils.

Therefore, the Sr source is only represented by Cenozoic carbonates, that are widely present in Romagna's Apennines. As concerns Nd isotopes, the low ϵ_{Nd} measured in the three soils suggest that bulk Nd is supplied by the leaching of Fe-Mn oxides (Castorina and Masi, 2010). However, pollution from a vehicular source (soot of car exhausts) may be possible in the Gp-1 topsoil, as the high measured ϵ_{Nd} fall within or close to the characteristic range (Lahd Geagea et al., 2008). In contrast, significant contamination from industrial emissions is not apparent, as Per-2 soil displays comparable Sr-Nd isotope ratios with Pa-4 soil, that is the soil potentially most exposed to contamination being located closer to the industrial zone.

The variations of $\delta^{87}\text{Sr}$ with depth are very little in the two agricultural soils; however, Per-2 soil displays a trend of slightly decreasing values in C horizons (Fig. 3). This fact suggests that there is a minor source supplying Sr of higher $\delta^{87}\text{Sr}$ confined to upper horizons. Such source is likely represented by Fe-Mn oxides (Castorina and Masi, 2010). In Gp-1 soil, the only major variation is observed in the BC horizon; as there is no ready explanation for that, it is remembered that this soil is not natural and thus deeply disturbed by human activities. As concerns the variations of ϵ_{Nd} with depth (Fig. 4), there is systematic slight increase for Pa-4 soil and a trend of decrease for Gp-1 soil. The decrease observed in the latter suggests that the source of higher ϵ_{Nd} is concentrated in the topsoil (traffic pollution?) and becomes less abundant with depth. In contrast, the ϵ_{Nd} increase in Pa-4 soil may be explained by the two-layer structure of this soil. Lastly, Per-2 soil displays a zig-zag pattern, although the values are, as average, rather uniform.

The linear correlations between the analyzed trace elements are shown in table 2.

The high coefficients of correlation obtained for Ba, Pb, Sn and Zn highlight their anthropogenic origin (Gherardi et al., 2009). No correlations have been found between the trace elements and $\delta^{87}\text{Sr}$, in agreement with the different chemical and geochemical behaviour of Sr and heavy metals. Positive linear correlations have been found between Cd, Pb, Sn and Zn and ϵ_{Nd} (0.46, 0.57, 0.54, 0.47, respectively); thus, Nd isotopes can be considered a possible tracer of anthropogenic pollution.

Table 2 - Correlation matrix between trace elements found along the three soil profiles.
* at significance $p < 0.05$, ** at significance $p < 0.01$, ***at significance $p < 0.001$, ns not significant.

	Ba	Cr	Cu	Ni	Pb	Sn	V	Zn
Ba	1							
Cr	ns	1						
Cu	ns	ns	1					
Ni	ns	ns	0.38*	1				
Pb	0.41*	ns	ns	ns	1			
Sn	ns	ns	ns	ns	0.88***	1		
V	ns	ns	ns	0.81***	ns	ns	1	
Zn	0.66**	ns	ns	ns	0.89***	0.76***	ns	1

Conclusions

Although there are some exceptions explained by the fact that the three soils are significantly disturbed by human activities, Sr contents and Sr/Ca ratios can allow for evaluating the different behavior of the two elements. In particular, it has been observed preferential retention of Sr in the two agricultural soils during the weathering of bedrock minerals. Moreover, Sr and Ca contents allow for recognizing Pa-4 soil structure as composed of two “layers”, probably represented by an Apenninian top and a Padan bottom of different chemical and mineralogical compositions.

The aqua regia extracts from the three soils display similar Sr- and Nd-isotope ratios, suggesting that Sr and Nd derive mainly from common sources, likely represented by the old marine carbonates and crustal silicates present in soil bedrocks. Lastly, the Nd isotopes of the uppermost horizons of the urban-park soil suggest the probable Nd contribution from soot of car exhausts, in agreement with the soil location close to a major traffic street.

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References

- ABERG G. (1995) The use of natural strontium isotopes as tracers in environmental studies. *Water Air Soil Pollution* 79: 309–322.
- BORG L.E., BANNER J. L., (1996) Neodymium and strontium constraints on soil sources in Barbados, West Indies. *Geochimica et Cosmochimica Acta*, 60: 4193–4206.
- BUSCAROLI A., GHERARDI M., VIANELLO G., VITTORI ANTISARI L., ZANNONI D. (2009) Soil survey and classification in a complex territorial system: Ravenna (Italy). DOI: 10.6092/issn.2281-4485/3795

- EQA Environmental quality 3: 115-128.
- CAPO R.C., STEWART B.W., CHADWICK O.A. (1998) Strontium isotopes as tracers of ecosystem processes: theory and methods. *Geoderma* 82: 197–225.
- CASTORINA F., MASI U. (2007) Use of Sr isotopes to constrain Sr (and Ca) sources in a Mediterranean soil profile near Muravera (SE Sardinia). *Acta Vulcanologia* 19: 103-108.
- CASTORINA F., MASI U. (2008) The Sr-isotope composition of soils: a case study from Muravera (SE Sardinia, Italy). *Journal of Geochemical Exploration* 96: 86-93.
- CASTORINA F., MASI U. (2009) Sr isotopic evidence for studying the salinization of soils: an example from the san Vitale Pinewood (Ravenna). *EQA Environmental quality* 3: 143-147.
- CASTORINA F., MASI U. (2010) Comparison of Sr isotopic ratios in aqua regia and two-step sequential extracts from two soils at Ravenna (Italy). *EQA Environmental quality* 4: this volume.
- DE PAOLO D. J., WASSERBURG G. J. (1976) Nd isotopic variations and petrogenetic models. *Geophysical Research Letters* 3: 249-252.
- GHERARDI M., PONTALTI F., VIANELLO G., VITTORI ANTISARI L. (2009) Heavy metals in the soil plant system: monitoring urban and extra-urban parks in the Emilia Romagna Region (Italy). *Agrochimica*, LIII, 3: 196-208.
- LAHD GEAGEA M.L., STILLE P., GAUTHIER-LAFAYE F., PERRONE TH., AUBERT D. (2008) Baseline determination of the atmospheric Pb, Sr and Nd isotopic compositions in the Rhine valley, Vosges mountains (France) and the Central Swiss Alps. *Applied Geochemistry* 23: 1703-1714.
- MARTIN C.E., McCULLOCH M.T. (1999) Nd-Sr isotopic and trace element geochemistry of river sediments and soils in a fertilized catchment, New South Wales, Australia. *Geochimica et Cosmochimica Acta*, 63: 287–305.
- NEGREL P., CASANOVA J., ARANYOSSY J.F. (2001) Strontium isotope systematics used to decipher the origin of groundwaters sampled from granitoids: the Vienne case (France). *Chemical Geology*, 177: 287–308.
- RICHTER F.M., DE PAOLO D.J. (1987) Numerical models of diagenesis: application to DSDP 590B and the Neogene Sr isotopic evolution of seawater. *Earth Planetary Science Letters*, 83: 27-38.
- SOIL SURVEY STAFF (2006) *Keys to Soil Taxonomy*, 10th edition, USDA - NRCS, Washington D.C., USA.
- STEWART B.W., CAPO R.C., CHADWICK O.A. (1998) Quantitative strontium isotope models for weathering, pedogenesis and biogeochemical cycling. *Geoderma* 82: 173–195.