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REY and Sr-Nd isotopic ratios of aqua regia extracts to assess pedogenic processes and pollution in soils from Ravenna (north Italy)

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Abstract

Sr, Ca and REY (REE+Y) concentrations along with Sr-Nd isotopic ratios have been determined in 17 aqua regia extracts from three soils of different land use, located in the area near the industrial town of Ravenna, in northern Italy, to test what information can be obtained about the pedogenesis, Sr and REY provenance and soil pollution. 6 samples of selected parts of horticultural plants from the agricultural soil, have also been analyzed for Sr isotopic composition. The Sr and Ca concentrations in the extracts generally increase with depth in each soil profile, reflecting selective mineral weathering in upper horizons and removal of the two elements by the soil solution. In this context, the decrease of the Sr/Ca ratios with depth in each profile suggests preferential removal of Ca, due to resistance of non-carbonate Sr-bearing minerals to weathering and preferential Ca uptake by plants as a nutrient. The PAAS-normalized REY patterns of the extracts from two out of the three studied soils, are similar, displaying middle REE enrichment with a Gd peak and, generally, a positive Y anomaly. These characteristics suggest the contribution of marine carbonates and phosphates.

The aqua regia extracts of the two soils perturbated by plowing and gardening practices, exhibit narrower ranges of δ^{87}Sr (from -0.49 to -0.97) than the natural soil (from -1.03 to +0.37). However, excluding decarbonated upper horizons, the natural soil displays a δ^{87}Sr range (from -0.47 to -1.03) similar to the other two soils. These overlapping ranges indicate that labile Sr mainly derives from a common source, represented by marine carbonates and phosphates of the bedrocks. In the geological context of the study area, Miocene sedimentary formations of Romagna's Apennines may be the likely sources of those phases. In contrast, the more positive δ^{87}Sr (from -0.21 to +0.37) of decarbonated upper horizons of the natural soil, likely reflect the contribution of radiogenic Sr from silicates of old crustal rocks from either the bedrock and/or atmospheric deposition (Saharan dust). The three soils display overlapping and relatively narrow ranges of ε_{Nd} (from -6.5 to -9.4), indicating a common source of Nd, mainly represented by phosphates. The contribution from silicates of old crustal rocks appears to be very subordinate. The Sr-Nd isotopic overlap of the soil extracts with the corresponding ranges of anthropogenic (i.e. industry, traffic) sources, prevents from ascertaining potential pollution from the study area. Compared with the isotopic values of the soil extracts, the higher δ^{87}Sr (from -0.32 to -0.07) of selected parts of horticultural plants grown on the agricultural soil, indicate the soil solution from which the plants uptake Sr, contains more radiogenic Sr. The comparison with the δ^{87}Sr of the ammonium acetate extracts from the same soil samples, indicates that the milder extraction than that carried out with aqua regia, leaves non-radiogenic Sr-bearing phosphates undissolved and, thus, more radiogenic Sr in the solution. As a whole, the aqua regia extraction of soil samples can provide significant information on the behavior of Sr and REY in the pedogenesis as well as in recognizing the sources of these elements with respect to the soluble soil phases and their possible references in the geological context of the study area. In contrast, the aqua regia extraction is not a suitable procedure for studying the soil-plant relationship, providing less information than the ammonium acetate extraction.

Key words: Sr-Nd isotopes; REY; Ca and Sr; soils; horticultural plants; aqua regia extracts; REY-Sr sources; Ravenna; Italy.

Introduction

The rare earth elements (REE) are a coherent group of elements, to which Y is commonly associated to form the REY; they can fractionate due to slight variations of physical-chemical conditions in natural processes (e.g. Henderson, 1986; Wood, 1990). As a result of the studies on REY behavior during weathering, particularly of granites, and soil formation under the temperate climate, it has been ascertained that, unlike light rare earth elements (LREE), middle and heavy rare earth elements (MREE and HREE, respectively) are progressively leached out (e.g. Scheepers and Rozendaal, 1993; Aubert et al., 2001). The factors responsible for LREE retention in soils are not yet well understood, but they may be related to preferential sorption onto Fe oxides (Köppenkastrop and De Carlo, 1992; White, 2000) and clay minerals (Coppin et al., 2002). According to Compton et al., (2003), the fate of REE in soils under the Mediterranean climate depends on different factors such as the climate regime, hydrology and carbonate precipitation.

Since the 90's, Sr isotopes can provide basic information about the sources and processes involving this element in the pedogenesis and the soil fraction available to plants (e.g. Åberg and Hamilton, 1989; Åberg, 1995; Blum and Erel, 1997; Bullen et al., 1997; Capo et. al., 1998; Stewart et al., 1998; Vitousek et al., 1999; Dia et al., 2000; Négrel et al., 2001; Green et al., 2004; Poszwa et al., 2004; Drouet et al., 2005; Pett-Ridge et al., 2009; Reynolds et al., 2012). In fact, Sr isotopes allow for distinguishing among the contributions from the different phases present in the soil bedrock and a variety of natural and anthropogenic sources supplying Sr from outside the soil, especially via atmospheric deposition. These external sources are mainly represented by marine aerosol, runoff, dust, industrial and vehicular emissions, and fertilizers. Nd isotopes have also been applied to soil studies either by alone (e.g. Öhlander et al., 2000; Viers and Wasserburg, 2004; Roig et al., 2006) and, more frequently, in combination with Sr isotopes (e.g. Borg and Banner, 1996; Steinmann and Stille, 1997; Martin and McCulloch, 1999; Dia et al., 2006). As Sr, Nd and in general the REY, can provide information about their sources and, thus, allow for evaluating their roles in the pedogenesis and soil pollution. In particular, as the phases providing Sr may not be the same ones supplying Nd, the coupled application of the two isotopic systematics can provide more exhaustive information.

Although there is widespread international concern about the applications of Sr and Nd isotopic systematics to soils, there are only a few studies on Italian soils (e.g. Castorina and Masi, 2007, 2008, 2009, 2010; Castorina et al., 2010), and likewise, on REY distribution in these materials (e.g. Genova et al., 2001; Fedele et al., 2008; Cidu et al., 2013). Therefore, this paper provides a contribution to reduce the gap, presenting REY distribution and isotopic compositions of Sr and Nd in the aqua regia extracts from three soils of the Ravenna area, a town located amid important factories from cement to steel production, chemical manufacturing and oil refinery, an oil-fed power station, and farmlands, in northern Italy (Figure 1). In this context, the studied soils are potentially prone to any environmental hazard. While the REY concentrations here presented are the first data available for aqua regia extracts from Italian soils, the Sr-Nd isotopic ratios are in part after Castorina and Masi (2010) and Castorina et al. (2010), and in part new complementary measurements, aimed at providing a comprehensive review of the whole data set for testing the reliability of three main goals. One goal is to evaluate what information Sr-Nd isotopes and REY can provide for studies of pedogenesis and soil pollution using the aqua regia extraction. This latter is the procedure requested by Italian law (Legislative Decree 152/2006) to assess pollution in the leachable fraction of the soil. In this context, being critical the possibility of distinguishing between geogenic and anthropogenic sources of the studied elements, here is the second goal of this paper: testing whether the aqua regia extraction allows for recognizing the origin of Sr and REY with respect to the soluble phases of the soil and, possibly, within the geological background of the study area. Lastly, as aqua regia extracts may approach, to some extent, the soil solution through which chemical elements enter plants, REY concentrations and Sr-Nd isotopic ratios of such extracts, could provide information about the bio-available fraction, i.e. the third goal. Therefore, this paper presents the Sr isotopic composition of selected parts of horticultural plants grown on the agricultural soil among the three studied, investigating, although in a preliminary way, the soil-plant relationship.

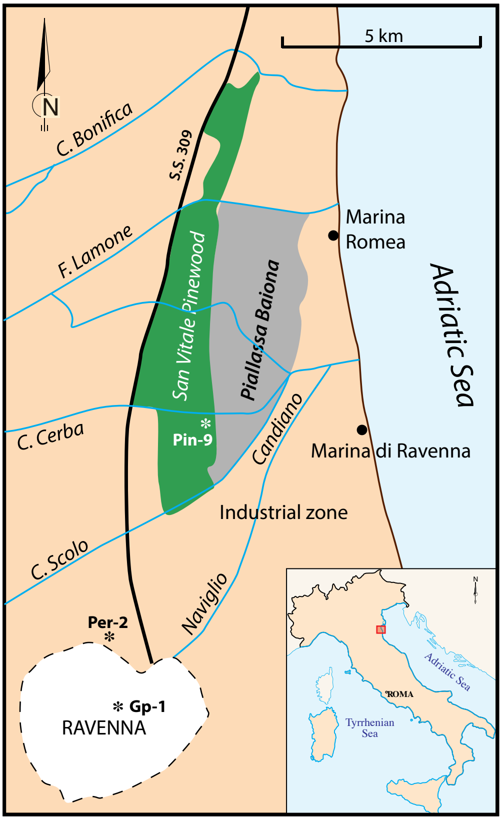

Figure 1. Location map of the three studied soils. The inlet map shows the Ravenna area.

The setting, characteristics and sampling of the soils

The three soil profiles, named Pin-9, Per-2 and Gp-1, have developed on sedimentary terrains of Holocene age (e.g. Amorosi et al., 2005 and references therein) located in the Ravenna area, near the Adriatic coastline (Figure 1). In particular, the Pin-9 soil profile was dug in the interdune lowland of the south-eastern edge of the San Vitale Pinewood, a protected area of the Po-river delta Park facing the industrial zone of Ravenna. It has developed on an ancient coastal dune system, formed by sediments of the Po river, and is classified as mixed, calcareous, mesic Sodic Psammaquent (Buscaroli et al., 2009, 2011b). It shows the water table at depth of about 0.5 m or less according to seasonal fluctuations, and presents diffuse salinity throughout the profile, likely related to the intrusion of saline water from the adjacent coastal lagoon. It displays coarse texture and A-Cg pattern of evolution. It is weakly calcareous at surface and more calcareous at depth, indicating significant surficial decarbonation favored by the coarse texture. The Per-2 soil profile was dug in the Perdisa farm, in the northern outskirt of Ravenna, and has developed on alluvia of the Lamone and Montone rivers (e.g. Mazzotti, 2003). These latter flow down from Romagna's Apennines through turbidites, marine clays and sands, encompassing the whole Cenozoic. This soil, that is relatively deep and fine-silty, displays the typically developed A-B-C profile. In particular, the uppermost horizons are more clayish than the lower ones that are more silty. Lastly, the Gp-1 soil profile was dug in the urban park of downtown Ravenna near a major traffic street, and is composed of coarse-loamy sediments mainly from the Montone river, mixed with some debris from the ancient port of Ravenna (Regione Emilia-Romagna, 1999). The Gp-1 and Per-2 soils, that are significantly perturbated by man's activity, are classified as mixed, mesic, Udifluventic Haplustepts (Buscaroli et al., 2009, 2011b).

As other main physical-chemical parameters of the studied soils were reported by Buscaroli et al. (2011b), therefore, here only a summary is given. All the soils exhibit overlapping ranges of pH (7.7-9.1); in particular, pH increases systematically from 7.7 to 8.6 with depth in the Gp-1 soil, while it shows less systematic increase in the Pin-9 soil, and partial increase as down as the Cg1 horizon in the Per-2 soil. Organic C, that decreases systematically with depth in all the soils, displays larger ranges in the Gp-1 and Pin-9 soils (from 73.1 to 0 and from 49.3 to 2 g/kg, respectively) than in the Per-2 soil (from 11.3 to 2.5 g/kg). $CaCO_3$ contents, that generally increase with depth in all the soils, are lower (from 11 to 147 g/kg) in the Pin-9 soil than in the Per-2 and Gp-1 soils exhibiting similar ranges (from 203 to 241, and from 141 to 232 g/kg, respectively). Lastly, the mineralogical composition of the three soils is similar, although the mineral abundance may be different, even through a same profile. Quartz and silicates are the most abundant minerals; the latter are represented in order of decreasing abundance by plagioclase, K-feldspar, muscovite and chlorite. Among carbonates, calcite is always dominant over dolomite; it is much more abundant in deeper horizons.

As a whole, we have analyzed 17 samples from the three soil profiles; these samples were provided by the colleagues of the University of Bologna within the frame of the project 20077A9XJA Prin 2007 (Buscaroli et al., 2011b). Each sample is representative of a given horizon of the soils; in particular, 5 samples refer to the 5 different horizons of the Pin-9 soil, 7 samples to the corresponding horizons of the Per-2 soil, and 6 samples to those of the Gp-1 soil. Lastly, we have analyzed for Sr isotopic composition 6 samples of selected parts from horticultural plants grown on the Per-2 soil.

Analytical procedure

Each soil sample was first sieved to remove the fraction > 2 mm that was not analyzed; then the finer fraction was washed with bi-distilled water to eliminate soluble salts and, lastly, treated with aqua regia. This method is based on the extraction protocol proposed as the standard method by ISO 11466 (1995). 2 g of the fine soil sample were digested with a mixture of ultrapure HCl (37%) and HNO_3 (65%) in the ratio of 3:1 (v/v) at room temperature for 16 h and, then, at 130 °C for 2 h under reflux conditions. Each suspension was filtered, evaporated and converted in conventional solution elemental determinations. Lastly, Sr and Ca were determined in the solutions of the three soils by ICP-AES; in contrast, REY were measured only in the extracts from the Pin-9 and Per-2 soils by ICP-MS.

The samples of selected parts of horticultural plants were acid-digested in a mixture of 6 ml of ultrapure HNO_3 (65%) and 1 ml ultrapure H_2O_2 (30%). The solutions were then evaporated to near dryness and residuals were dissolved in 2 ml of ultrapure HNO_3 4N. After total evaporation, the samples were converted in hydrochloric form before of Sr separation from the matrix.

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. Sr and Nd isotopic fractionations were corrected against $^{86}Sr/^{88}Sr = 0.1194$ and $^{146}Nd/^{144}Nd = 0.7219$, respectively. During the period of data acquisition, the measured isotopic ratios for NBS 987 Sr and La Jolla Nd standards were $^{87}Sr/^{86}Sr = 0.710264 \pm 0.000007$ (2σ; n = 27) and $^{143}Nd/^{144}Nd = 0.511885 \pm 0.000010$ (2σ; n = 10), respectively. Within-run precision, expressed as 2se (2 standard errors), is better than 0.000012 for Sr and 0.000010 for Nd. Measured Sr isotopic ratios are expressed as $\delta^{87}Sr$, i.e. deviation of the isotopic ratio of the sample from seawater standard assumed to be 0 (or $^{87}Sr/^{86}Sr = 0.709175$, Richter and DePaolo, 1987). The $^{87}Sr/^{86}Sr$ ratio measured in Adriatic seawater collected from the coast facing Ravenna, have given a value of 0.70917 ± 0.00001 (2σ; n = 3). Lastly, measured Nd isotopic ratios are expressed as ε_{Nd}, i.e. the isotopic ratio of the sample relative to CHUR (DePaolo and Wasserburg, 1976).

Results

Table 1 reports the Sr and Ca concentrations along with the Sr-Nd isotopic ratios of the soil extracts, while Figure 2 illustrates the variation of these parameters with depth in each profile. Table 2 yields the REY concentrations in the extracts from the Pin-9 and Per-2 soils, of which Figure 3 shows the Nd variations with depth, and Figure 4 depicts the REY patterns of the extracts normalized against PAAS (Post-Archean Australian Shale, Taylor and McLennan, 1985). Lastly, Table 3 exhibits the $\delta^{87}Sr$ of selected parts of horticultural plants grown on the Per-2 soil.

The Pin-9 soil extracts display lower ranges of Sr (51-192 mg/k except for the Cg3 horizon showing 358 mg/kg) and Ca (3.6-25 g/kg) than the extracts from the Per-2 and Gp-1 soils exhibiting overlapping values (Sr = 254-343 mg/kg; Ca = 32.4-92.2 g/kg, and Sr = 210-344 mg/kg; Ca = 26.3-89.7 g/kg, respectively). The Sr and Ca concentrations generally increase with depth in the extracts of the three soils (Figure 2). The extracts of the Per-2 and Gp-1 soils exhibit lower (7.8-7.9, and 3.6-8, respectively) Sr/Ca ratios in A horizons than the extracts from the Pin-9 soil (10.3-14.2). In contrast, the Sr/Ca ratios of the extracts from B horizons of the two man-perturbated soils are similar (3.7-3.8). Lastly, the Sr/Ca ratios are quite variable in the extracts from C horizons of the Pin-9, Per-2 and Gp-1 soils (7.7-15.9, 3.8-8.3, and 8.5, respectively), even along the same profile. From Figure 3, it appears the Nd concentrations range

Table 1. Concentrations of Sr and Nd (mg/kg) and Ca (g/kg), along with Sr/Ca (x 1000) ratios and Sr-Nd isotopic ratios of the aqua regia extracts from the studied soils. The isotopic data of the Per-2 and Gp-1 soil samples are after Castorina et al. (2010), while the δ^{87}Sr of the Pin-9 soil after Castorina and Masi (2010).

Horizon	Depth (cm)	Sr mg/kg	Ca g/kg	Nd mg/kg	Sr/Ca	^{87}Sr/^{86}Sr± 2se*	δ^{87}Sr ± 2se*°	^{143}Nd/^{144}Nd ± 2se*	εNd
Pin-9 soil									
A	0-5	51	3.6	4.21	14.2	0.709434± 5	0.37± 0.007	0.512186±14	-8.85
Ag	5-10	60	5.8	5.06	10.3	0.709067± 6	-0.21± 0.008	0.512278±14	-7.06
Cg1	10-30	146	19.0	5.24	7.7	0.708838±10	-0.47± 0.014	0.512183± 6	-8.91
Cg2	30-80	192	25.0	4.42	7.7	0.708697± 8	-0.67± 0.011	0.512193± 8	-8.71
Cg3	80-100+	358	22.5	4.15	15.9	0.708437±22	-1.03± 0.031	0.512258±11	-7.45
Per-2 soil									
Ap1	0-28	254	32.4	9.19	7.8	0.708728±11	-0.62± 0.016	0.512270±10	-7.22
Ap2	28-53	263	33.5	10.32	7.9	0.708814±8	-0.50± 0.011	0.512210±7	-8.39
Bw1	53-83	313	83.6	9.86	3.7	0.708722±6	-0.63± 0.008	0.512243±10	-7.74
Bw2	83-130	343	92.2	11.04	3.7	0.708819±9	-0.49± 0.013	0.512157±10	-9.42
Cg1	130-153	303	36.3	8.77	8.3	0.708818±20	-0.50± 0.028	0.512258±11	-7.45
Cg2	153-194	338	89.2	7.85	3.8	0.708744±14	-0.60± 0.020	0.512256±8	-7.49
Cg3	194-210+	343	91.4	8.80	3.8	0.708700±7	-0.66± 0.010	0.512219±8	-8.21
Gp-1 soil									
Au1	0-3	210	26.3	nd	8.0	0.708757±9	-0.58± 0.013	0.512256±12	-7.49
Au2	3-7	272	75.3	nd	3.6	0.708697±13	-0.67± 0.018	0.512307±11	-6.50
Au3	7-25	293	79.8	nd	3.7	0.708736±4	-0.61± 0.006	0.512278±11	-7.06
Bwu	25-57	344	89.7	nd	3.8	0.708724±8	-0.63± 0.011	0.512253±10	-7.55
BCu	57-80	334	87.0	nd	3.8	0.708501±14	-0.97± 0.020	0.512218±27	-8.23
C	80-100+	284	33.3	nd	8.5	0.708715±12	-0.64± 0.017	0.512278±7	-7.06

*Uncertainties correspond to last digits. °We use an ^{87}Sr/^{86}Sr value of 0.70917 for Modern Seawater

from 4.15 to 5.24 mg/kg in the Pin-9 soil extracts, increasing with depth down to the Cg1 horizon and, then, decreasing. In contrast, the Nd concentrations range from 7.85 to 11.04 mg/kg in the Per-2 soil extracts, swinging with depth and showing the least value in the Cg2 horizon. Y, that is the second most abundant REY after Ce in the extracts of the Pin-9 and Per-2 soils,

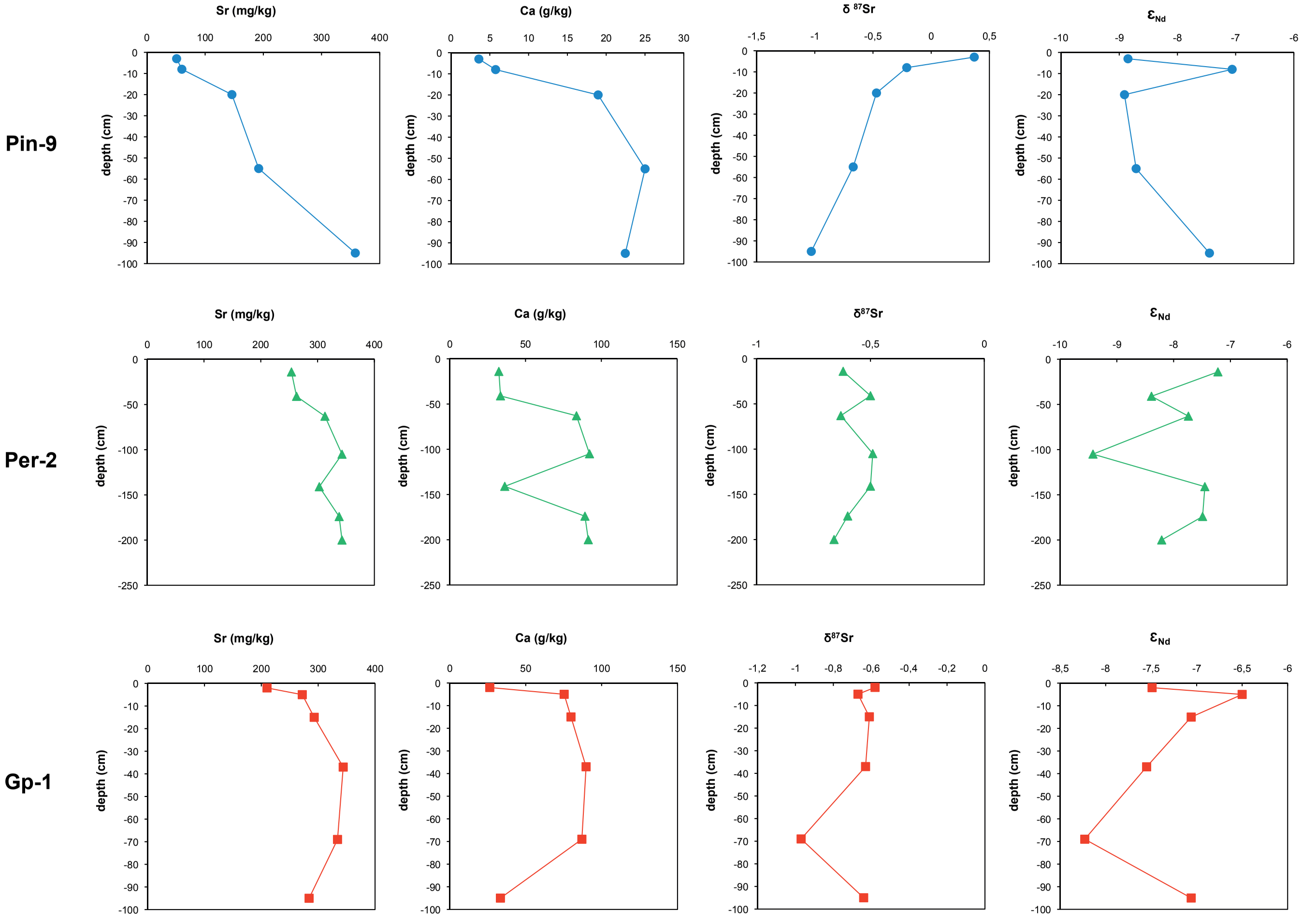

Figure 2. Variations of the Sr and Ca concentrations, δ^{87}Sr and ε_{Nd} with depth in the aqua regia extracts from the studied soils.

Table 2. REY concentrations (mg/l) in the aqua regia extracts from the Pin-9 and Perd-2 soils.

Pin-9 soil

Horizon	Depth (cm)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	ΣREE	ΣREY	Y/Ho	Gd/Gd*
A	0-3	3.92	8.52	1.09	4.21	1.17	0.25	1.20	0.18	1.03	5.60	0.19	0.49	0.06	0.39	0.05	22.76	28.36	29.47	1.14
Ag	3-7	4.71	10.14	1.30	5.06	1.40	0.31	1.45	0.22	1.25	6.71	0.23	0.59	0.08	0.47	0.06	27.26	33.97	29.43	1.14
Cg1	7-15	4.79	10.95	1.36	5.24	1.45	0.32	1.49	0.22	1.28	8.11	0.24	0.61	0.08	0.48	0.06	28.57	36.68	34.51	1.14
Cg2	15-50	4.24	9.25	1.13	4.42	1.25	0.28	1.32	0.20	1.16	6.92	0.22	0.56	0.07	0.45	0.06	24.60	31.52	32.04	1.15
Cg3	50-100	4.05	8.90	1.08	4.15	1.14	0.25	1.19	0.18	1.03	6.13	0.19	0.50	0.07	0.39	0.05	23.16	29.29	32.26	1.15

Per-2 soil

Horizon	Depth (cm)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	ΣREE	ΣREY	Y/Ho	Gd/Gd*
Ap1	0-28	9.39	19.93	2.44	9.19	2.32	0.48	2.24	0.32	1.84	10.94	0.34	0.88	0.12	0.70	0.10	50.28	61.22	32.46	1.15
Ap2	28-53	10.60	22.40	2.75	10.32	2.60	0.54	2.47	0.36	2.02	12.13	0.37	0.97	0.13	0.77	0.11	56.40	68.53	32.61	1.14
Bw1	53-83	10.08	21.31	2.63	9.86	2.49	0.51	2.34	0.33	1.89	11.55	0.34	0.90	0.12	0.70	0.10	53.61	65.16	33.58	1.14
Bw2	83-130	11.10	23.74	2.93	11.04	2.82	0.59	2.67	0.38	2.16	13.15	0.40	1.03	0.13	0.80	0.11	59.90	73.05	33.21	1.15
Cg1	130-153	8.62	18.99	2.30	8.77	2.27	0.47	2.19	0.32	1.82	10.94	0.33	0.86	0.11	0.66	0.09	47.81	58.75	32.95	1.14
Cg2	153-194	7.72	17.19	2.07	7.85	2.04	0.43	1.97	0.29	1.63	9.86	0.30	0.78	0.10	0.60	0.08	43.03	52.89	33.09	1.14
Cg3	194-210+	8.53	18.88	2.31	8.80	2.28	0.48	2.19	0.32	1.83	10.99	0.33	0.87	0.11	0.67	0.09	47.68	58.67	33.00	1.14

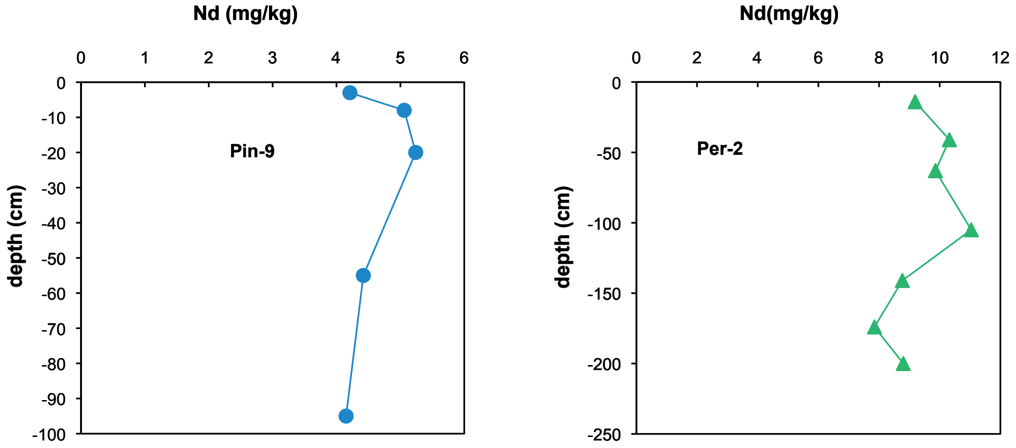

Figure 3. Variations of the Nd concentrations in the aqua regia extracts from the Pin-9 and Per-2 soils.

Table 3. Sr isotopic composition of selected parts of horticultural plants grown on the Per-2 soil.

Sample	Species	Plant Parts	$^{87}Sr/^{86}Sr \pm 2se$*	$\delta^{87}Sr \pm 2se$*
V1	Lettuce	leaves	0.709120 ± 6	-0.07± 0.008
V2	Tomato	leaves	0.709027 ± 5	-0.20± 0.008
F5	Tomato	trunk	0.709030 ±23	-0.20± 0.032
R8	Lettuce	root	0.709103 ± 6	-0.09± 0.008
R9	Tomato	root	0.709034 ± 5	-0.20± 0.007
B-13	Peach	fruit skin	0.708943 ±13	-0.32± 0.018

*Uncertainties correspond to last digits.

shows vertical patterns of abundance quite coherent with Nd. ΣREE range 22.76-28.57 and 43.03-59.90 mg/kg for the extracts from the Pin-9 and Per-2 soils, respectively. Both soils display similar PAAS-normalized REY patterns, characterized by MREE enrichment with a Gd peak, a negative Nd anomaly and a positive Y anomaly; this latter lacks in decarbonated A horizons of the Pin-9 soil. Lastly, the extract from the Cg2 horizon of the Per-2 soil exhibits a negative Eu anomaly (Figure 4).

The extracts from the Gp-1 and Per-2 soils share similar $\delta^{87}Sr$ ranges (from -0.5 to -0.7, but the BCu horizon of the Gp-1 soil displays -1), narrower than the range of the Pin-9 soil extracts (from -1.03 to +0.37). The $\delta^{87}Sr$ decrease systematically with depth in the Pin-9 soil, while they swing in the other two soils (Figure 2). The ranges of ε_{Nd} of all the extracts overlap (from -6.5 to -9.4), displaying swinging vertical patterns (Figure 2).

Lastly, the samples of selected parts of horticultural plants grown on the Per-2 soil exhibit a narrow range of δ^{87}Sr, from -0.32 to -0.07 (Table 3). In particular, lettuce displays higher δ^{87}Sr than tomato and peach, this latter showing the lowermost value. No significant isotopic fractionation between root and leaf of the same plant species has been observed. The plants exhibit higher δ^{87}Sr than the Per-2 soil extracts.

Sources of Sr and REY in the studied soils

The potential sources of these elements can be either natural and/or anthropogenic. Among natural sources, there are bedrock, runoff, groundwater, atmospheric dry and wet depositions, while among anthropogenic sources, there are fertilizers, soot emissions from car exhausts, and smoke stacks from industrial plants.

Among the main Sr-bearing minerals of the Pin-9 soil bedrock, muscovite and K-feldspar releases radiogenic Sr by weathering, while Rb-free carbonates and plagioclase yield non-radiogenic Sr. Nd and in general REY, are mainly hosted by K-minerals, as carbonates contain only very low concentrations (e.g. Tanaka et al., 2009 and reference therein). Among REY, Eu^{2+} is generally enriched in plagioclase and secondary products as clay minerals relative to the other common minerals, but sedimentary rocks rarely display chondrite-normalized negative Eu

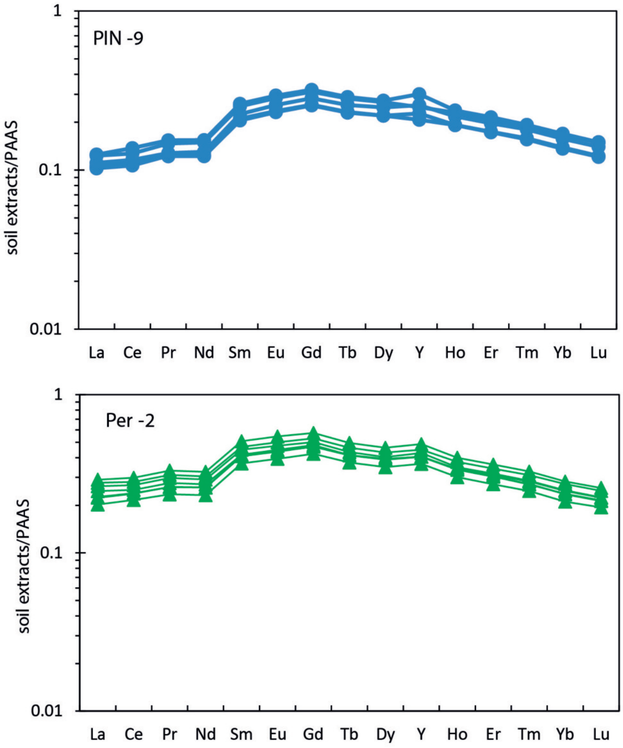

Figure 4. REY patterns of the aqua regia extracts from the Pin-9 and Per-2 soils, normalized to PAAS (Post-Archean Australian Shale, Taylor and McLennan, 1985).

anomaly (e.g. Rengarajan and Sarin, 2004). Moreover, both Sr and Nd are hosted, to larger extent, in accessory minerals such as apatite and other phosphates (e.g. Wright et al., 1987), all common in acidic igneous and metamorphic rocks. Although phosphates have not been detected by XRD analysis in the studied soils, likely because of their low abundance, however, their presence is indicated by chemical analysis of the soils (Cidu et al., 2013). Apatite, that is a Rb-free mineral and, thus, has no radiogenic Sr, is commonly enriched in MREE (e.g. Weber et al., 1998) and particularly Sm relative to Nd. In contrast, monazite (Andrehs and Heinrich, 1998), muscovite, plagioclase and chlorite display reverse Sm-Nd patterns (e.g. Scarciglia et al., 2008; Stille et al., 2009). As the abundance and the patterns of REY are generally preserved during rock weathering, being these elements little mobile during sedimentary processes, the Nd isotopic composition of phosphates can be preserved during diagenesis. In contrast, the preservation of Sr isotopes may be only partial, as phosphate recrystallization can occur with more radiogenic Sr-rich waters (e.g. Martin and Scher, 2004). As concerns Y, marine carbonates display lower concentrations than clay minerals (e.g. Tanaka et al., 2009 and references therein), and a positive Y anomaly in the PAAS-normalized pattern (Taylor and McLennan, 1985).The balance of the different contributions of Sr and Nd from all the phases yield the δ^{87}Sr and ε_{Nd} of the bulk soil sample. In this context, to represent approximately the large spectrum of sediments carried by the Po river and, thus, the composition of the Pin-9 soil bedrock, we consider lithogenic sediments from the Adriatic sea, of which the Po river is the main supplier. Therefore, the isotopic characteristics of the Pin-9 bedrock can be assimilated to those of the latter sediments: average δ^{87}Sr = 12.4 and ε_{Nd} = -11 (Weldeab et al., 2002). As there are no data of Sr-isotopic composition of the carbonate fraction of these sediments, considering that this fraction is generally represented by marine limestones, it is inferred isotopic range between -3 and 0 in the Phanerozoic (McArthur et al., 2001). For Nd isotopic ratios, it is proposed ε_{Nd} range from -5.1 to -9.4 (Castorina, unpublished data of Italian limestones). Lastly, the main formations of Romagna's Apennines, that likely represent the sediment source of the Per-2 and Gp-1 soils, exhibit δ^{87}Sr between -0.1 and +6.3 (Table A of the Appendix), but the carbonate fraction likely shows δ^{87}Sr < 0 (McArthur et al., 2001).

Surficial waters, that periodically inundate the depression of the Pin-9 soil from the canals draining Ravenna's floodplain, display δ^{87}Sr between -0.16 and -0.2 (Cidu et al., 2011) and, presumably, ε_{Nd} by -10 (Frost et al., 1986). Unlike brackish groundwater of this soil exhibiting δ^{87}Sr close to present-day Adriatic seawater, groundwater from the Pinewood area shows δ^{87}Sr ranges between -0.56 and +0.25, reflecting potential exchange processes among water, sediments and soils (Cidu et al., 2011). Lastly, there are no isotopic data of groundwater used to irrigate the man-perturbated soils.

Wet and dry atmospheric depositions are represented by marine aerosol and dust, respectively. However, salt deposition by marine aerosol can be ruled out because all the samples were rinsed with water before being processed for isotopic analyses. As concerns dust, it can be derived from Ravenna's floodplain and, thus, is likely composed of aerosols from sedimentary rocks of Romagna's Apennines. So, it brings no significant impact on the isotopic composition of the Per-2 and Gp-1 soils, but it may be eventually significant for the Pin-9 soil mainly developed on the Po river sediments. Another source of dust is the Sahara desert (e.g. Le-Bolloch et al., 1996; Rognon et al., 1996; Moulin et al., 1997; Yaalon, 1997; Grousset et al., 1998; Grousset and Biscaye, 2005; Erel and Torrent, 2010; Scheuvens et al., 2012; Thevenon et al., 2012), as Italy lay on wind trajectories from North Africa to the Alps and central Europe. Saharan dust exhibits relatively large ranges (Grousset et al., 1998; Grousset and Biscaye, 2005; Scheuvens et al., 2012) of δ^{87}Sr (5.36-25.1, average = 17.8) and ε_{Nd} (from -8 to -17, average = -13).

Lastly, among anthropogenic sources, natural fertilizers may contain Sr and REY-rich phosphate. This source might be important only for the agricultural Per-2 soil. Actually, the commonly used fertilizer in Romagna is synthetic (N-P-K); nevertheless, it contains some Sr (e.g. Senesi et al., 1983). Soot emissions of car exhausts might affect all the soils and particularly the Gp-1 soil located near a heavy-trafficked street. However, as the pollution rate generally decreases esponentially with increasing distance from the road, being negligible at some tens of meters, this potential source is unlikely except for the Gp-1 soil. In fact, the other two soils are located at > 500 m far away the roads. As we do not know the isotopic signatures of the particulate matter from traffic pollution, we take into account the data available from the literature (δ^{87}Sr about -0.66 and ε_{Nd} between -6 and -6.9, Lahd Geagea et al., 2008a). Smoke stacks from industrial plants may affect the Pin-9 soil and, subordinately, the farther Per-2 soil. To characterize the isotopic signatures of the stacks, we take into account ranges after Lahd Geagea et al. (2007, 2008a, b): from -1.69 to +1.13, and from -5 to -13, for δ^{87}Sr and $\varepsilon_{Nd,}$ respectively.

Discussion

The aqua regia extracts from the soils

Element relationships and REY patterns. The general increase of Sr and Ca with depth in the extracts from the three soils (Figure 2) may be explained by mineral weathering in upper horizons and consequent removal of the two elements by the soil solution and/or uptake by plants. In particular, the higher Sr/Ca ratios in the extracts from A horizons, are explained by the decarbonation of those horizons and resistance of K-(Sr-rich) minerals to weathering. The lower ranges of Sr and Ca in the extracts from the Pin-9 soil relative to those from the man-perturbated soils, may be consistent with the lower abundance of carbonates in the former soil (Table 1). The similar concentrations of Sr and Ca in the extracts from B horizons of the two man-perturbated soils, indicate a common source of these elements, while the large variation of the Sr/Ca ratios in the extracts from C horizons of the three soils suggests quite variable conditions in those layers. Figure 5 summarizes the Sr-Ca relationship in all the extracts. It appears a general positive correlation between the two elements, suggestive of a common source of Sr and Ca in the three soils. Moreover, looking at the detail, within the general positive correlation, two subparallel lines can be distinguished: one for the extracts of the Pin-9 soil and some of the man-perturbated soils, and the other for the remainder extracts, outlining likely how man's activity can alter natural pedogenesis.

The Per-2 soil extracts display concentrations of Nd and the other REY roughly twice than the Pin-9 soil extracts. This might reflect the inferred different sediment sources of the two soils: Apenninian and Padan, respectively (e.g. Buscaroli et al., 2011a and references therein) and/or the different pedogenic evolution. The vertical trend of increasing Nd and ΣREY as down as the Cg1 horizon in the Pin-9 soil extracts, is consistent with selective mineral weathering in upper horizons and subsequent REY mobilization downward. This pattern was also observed in other natural soils (e.g. Harlavan et al., 2009 and references therein). In contrast, the swinging vertical pattern of the Per-2 soil, may reflect the combined effect of natural and agricultural processes in the context of more advanced pedogenesis. Lastly, in the Pin-9 soil, the concentrations of Nd and ΣREY do not distinguish between A and lowermost Cg horizons, while in the man-perturbated Per-2 soil, the concentrations

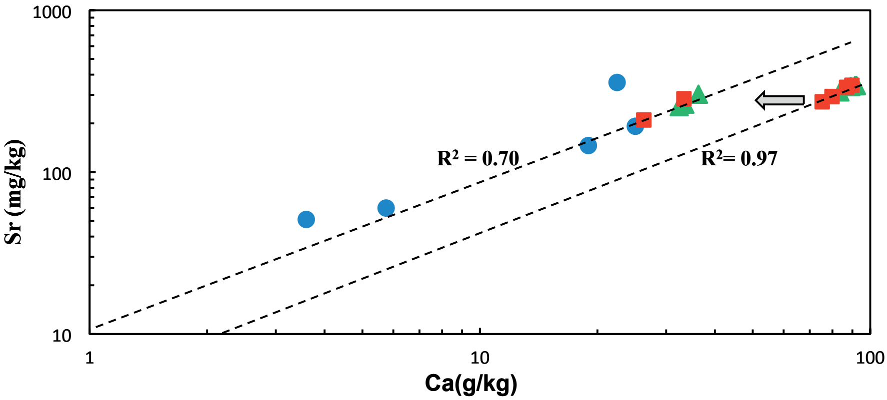

Figure 5. Diagram showing the Sr-Ca relationship in the aqua regia extracts from the studied soils. Symbols as in Figure 2.

in upper horizons are higher than in Cg horizons. As concerns the Pin-9 soil, upper horizons are more altered than lower horizons, but in these latter, however, the much higher proportion of REY-poor carbonates "dilute" ΣREY concentrations, thus rendering lower horizons comparable with A horizons. In contrast, agricultural practices may have perturbated the natural trend of mobilization of REY by weathering in upper horizons of the Per-2 soil.

The similar PAAS-normalized patterns of REY of the extracts from the Pin-9 and Per-2 soils, are accounted for by their broadly similar mineralogical compositions. MREE enrichment, although typical of the contribution from phosphates (Weber et al., 1998), may also indicate REY complexation with soil organic matter in upper horizons (Davranche et al., 2011). Similar patterns of MREE enrichment were recorded in the carbonate, oxide and organic fractions of other soils from the San Vitale Pinewood (Cidu et al., 2013). These authors suggest calcite and phosphate dissolution as possible mechanism to release REY to the soil water. The Gd peak observed in all the patterns of the Pin-9 and Per-2 soils, could mean a positive Gd anomaly [$Gd/Gd^* = Gd_N/(0.67Tb_N + 0.33Sm_N)$], accounted for by anthropogenic Gd addition to the soils (e.g. Bau and Duski, 1996). The calculated value of this anomaly ranges between 1.14 and 1.15 (Table 2), overlapping the range of the Gd anomaly in seawater (e.g. Knappe et al., 1999) and being < 2, it is lower than the least value observed in river waters from populated and industrialized regions (e.g. Bau and Duski, 1996; Nozaki et al., 2000; Elbaz-Poulichet et al., 2002; Rengarajan and Sarin, 2004; Ogata and Terakado, 2006). Therefore, the small positive Gd anomaly measured in the extracts cannot be ascribed to anthropogenic pollution, but it results from the dissolution of marine carbonates of the soils. It may also be in part referred to interaction of the soil sediments with seawater, but this is true only for the Pin-9 soil. This conclusion is supported by the Y/Ho (unnormalized) values, that ranging between 29.4 and 34.5, and between 32.5 and 33.6 in the Pin-9 and Per-2 soils, respectively (Table 2), are intermediate between those of seawater-marine carbonates (44-74) and terrigenous sediments (27, Nagarajan et al., 2011). In this context, the Y/Ho ratios of the extracts provide evidence that the latter also contain a contribution leached from the non-carbonate fraction of the soils, in addition to that from the dissolution of carbonates. The positive Y anomaly present in all the patterns except for those of decarbonated A horizons of the Pin-9 soil, suggests this element is mainly associated with carbonates (e.g. Nagarajan et al., 2011). The negative Nd anomaly of all the extracts envisages Nd retention in the less soluble fractions, probably the clay fraction (e.g. Prudêncio et al., 1995). Lastly, the negative Eu anomaly shown by the sample from the lowermost horizon of the Per-2 soil, is consistent with Eu release from clay minerals derived from plagioclase alteration (Rengarajan and Sarin, 2004).

Strontium isotopes. The relatively narrow and overlapping ranges of negative δ^{87}Sr of the Per-2 and Gp-1 soil extracts (Table 1 and Figure 2), indicate a single source of Sr, that is mainly represented by bedrock minerals such as marine carbonates and phosphates, likely from the Cenozoic formations of Romagna's Apennines. In particular, the measured δ^{87}Sr of the two soils, fall within the isotopic range of marine carbonates of the Miocene (δ^{87}Sr from -1.3 to -0.2, McArthur et al., 2001). In the studied context, the widespread Marnoso-Arenacea formation may probably be responsible for this isotopic signature. As for the element concentrations, the relatively narrow isotopic ranges may also result from soil homogenization by agricultural/gardening practices. In contrast, the comparatively larger range in the Pin-9 soil extracts, straddling the value (0) of seawater, along with the significant vertical decrease of δ^{87}Sr (Figure 2), suggest that the Sr isotopic composition is controlled by two groups of minerals. In particular, the source characterized by negative δ^{87}Sr, is mainly located in deeper horizons and represented, for isotopic composition similar to that of the other two soils, by Miocene marine carbonates and phosphates. This may suggest a significant contribution of Sr from the Apenninian source to the Pin-9 soil. At first glance, this suggestion appears in contrast with the Padan origin of the Pin-9 soil sediments (Buscaroli et al., 2011a and references therein). However, although the Po river carries sediments to the Adriatic sea from a vast area encompassing the central-western Alps and the northern Apennines, it is envisaged that the proportion of sediments discharged by the rivers draining Romagna's Apennines, i.e. the closest mountain range to the Po delta area, was comparatively relevant in the final (about 150 km) leg of the Po river course up to a few centuries ago (e.g. Bondesan, 1985; Mazzotti, 2003). In fact, these rivers were then the only tributaries to the Po river before being diverted from merging it by reclamation works, that made them independent waterways. Unlike the source of negative δ^{87}Sr, the source of positive δ^{87}Sr located mainly in upper horizons of the Pin-9 soil, can be either internal and/or external to the soil. Anyway, this latter source is represented by silicates, particularly K-silicates from old crustal rocks, releasing radiogenic Sr by weathering. These silicates are likely either those of the bedrock and thus similar, to some extent, to lithogenic sediments of the Adriatic (average δ^{87}Sr = 12.4, Weldeab et al., 2002), and those added to upper horizons from atmospheric deposition, for instance Saharan dust (average δ^{87}Sr = 17.8, Grousset et al., 1998, Grousset and Biscaye, 2005, Scheuvens et al., 2012). Decarbonation of upper horizons of this soil, has increased the proportion of silicates relative to the other minerals, thus explaining why these horizons display higher δ^{87}Sr than deeper horizons. An additional aeolic contribution could come from the particulate of industrial smoke stacks (δ^{87}Sr from -1.69 to +1.13, Lahd Geagea et al., 2007, 2008b). However, the isotopic overlap of this anthropogenic source and the above geogenic sources, makes it not possible to distinguish between the two different contributions. Lastly, surficial waters can also provide subordinate Sr of suitable isotopic ratio

(δ^{87}Sr from -0.16 to +0.2, Cidu et al., 2011), mainly to upper horizons.

Neodymium isotopes. The relatively narrow and overlapping ranges of ε_{Nd} measured in the extracts from the three soils, suggest that Nd is supplied by a single source, i.e. likely bedrock minerals. Among the latter, dismissing marine carbonates because of their negligible REE contents (e.g. Parekh et al., 1977; Palmer, 1985) and no relationship between ε_{Nd} or Nd, and $CaCO_3$ in the extracts (Figures not shown for brevity sake), marine phosphates are suitable phases to provide the most of the contribution, as indicated by MREE enrichment in the PAAS-normalized patterns of the Pin-9 and Per-2 soils (Figure 4). In this context, lacking Nd isotopic data of phosphates from Italian sedimentary rocks, and minding that these phases, particularly of the Cenozoic, preserve their original isotopic composition similar to seawater (Martin and Scher, 2004), this can explain why the ε_{Nd} of the extracts are similar to the values of marine carbonates (ε_{Nd} from -5.1 to -9.4, Italian limestones Castorina unpublished; from about -4 to -10, Holser, 1997). Any contribution from the leaching of silicates, although possible, is likely very subordinate. Lastly, as already noted for the δ^{87}Sr, the overlap of the ε_{Nd} ranges of the soil extracts and industrial (ε_{Nd} from -5 to -13, Lahd Geagea et al., 2007, 2008b) or traffic (ε_{Nd} = -6 to -6.9, Lahd Geagea et al., 2007; 2008a) sources, makes it uncertain to assess the real contribution of anthropogenic pollution. This is particularly true for the extracts from A horizons of the Gp-1 soil, although the ε_{Nd} fall within the isotopic range for soot of car exhausts. In fact, this soil displays comparable ε_{Nd} with the Pin-9 soil located remote from traffic ways. Moreover, Angelone et al. (2007) demonstrated that traffic pollution is still insignificant in Rome's soils, i.e. in a much larger and trafficked area than Ravenna's.

Lastly, the swinging vertical patterns of the Per-2 and Pin-9 soils (Figure 2), likely reflect selective mineral weathering through the profiles. In particular, the higher ε_{Nd} of the Ag and Cg3 horizons of the Pin-9 soil may suggest that REE-bearing minerals of lower ε_{Nd} have been more weathered than the others, thus favoring increase of the isotopic value of those horizons after Nd release to the soil solution.

Sr isotopic composition of selected parts of horticultural plants grown on the Per-2 soil

The higher δ^{87}Sr of selected parts of the three vegetal species relative to the corresponding values of the soil extracts, indicate that the soil solution from which these plants uptake Sr, contains comparatively more radiogenic Sr. In this context, we have also carried out extractions with ammonium acetate from the same soil samples, obtaining a range of δ^{87}Sr from -0.33 to -0.08. Therefore, it appears that the soil solution displays closer isotopic composition to the latter extracts than to the aqua regia extracts. This is because the milder acetate extraction leaves the most of phosphates of lower δ^{87}Sr undissolved and, unlike the aqua regia extraction, provides the contribution of exchangeable Sr.

Concluding remarks

The Sr and Ca concentrations in the extracts generally increase with depth in each soil profile, suggesting selective mineral weathering in upper soil horizons and removal of the two elements by the soil solution. The Nd concentrations show increase with depth in the Pin-9 soil as down as the Cg1 horizon, then they decrease, while they exhibit a swinging vertical pattern in the Per-2 soil extracts. These different patterns can be explained by the different processes affecting the natural and man-perturbated soil, respectively. The PAAS-normalized REY patterns of the extracts from both soils indicate the dominant contribution from marine phosphates and carbonates, proven by

MREE enrichment and the positive Y anomaly, respectively. The small positive Gd anomaly also measured in all the extracts supports the contribution from marine carbonates, ruling out any anthropogenic pollution. Moreover, the patterns display a negative Nd anomaly, suggestive of Nd retention in the less soluble clay fraction. The persistence of these features downward in the two soils, is consistent with the mineralogical homogeneity of horizons.

Figure 6 summarizes the δ^{87}Sr-ε_{Nd} relationship in the extracts from the three soils. It appears isotopic overlap, apart from decarbonated A horizons of the Pin-9 soil exhibiting higher δ^{87}Sr because of the contribution of silicates from old crustal rocks. Moreover, as the ranges of the extracts overlap the field of Miocene marine carbonates and coeval phosphates, there is evidence that labile Sr and Nd derive mainly from the dissolution of these minerals. In particular, the Nd isotopic composition of the extracts suggests the main Nd contribution comes from phosphates. In the geological context of the studied soils, in particular for those composed of Apenninian sediments, the Sr isotopic composition suggests the carbonate fraction mainly derives from the Marnoso-Arenacea formation of Romagna. Any contribution from anthropogenic sources external to the soils, such as industry and traffic, appears to be not distinguishable from that of bedrock minerals because of overlapping isotopic ranges with those of geogenic sources.

Lastly, the analyzed selected parts of the three vegetal species grown on the agricultural Per-2 soil, display higher Sr isotopic composition than the aqua regia soil extracts, indicating the soil solution from which the plants uptake Sr, contains comparatively more radiogenic Sr. Extractions from the same soil samples carried out for comparison with ammonium acetate, commonly used to determine labile Sr in the soil, have yielded δ^{87}Sr close to the values of the plants, indicating that the milder extraction than that carried out with aqua regia, leaves non-radiogenic Sr-bearing phosphates undissolved. Therefore, the

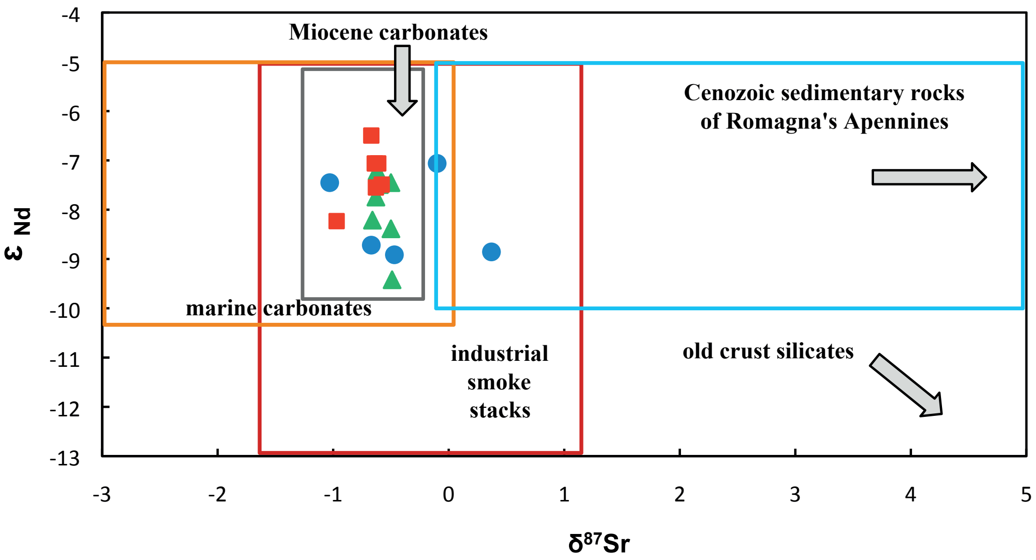

Figure 6. Plot of δ^{87}Sr vs ε_{Nd} variations in the studied soils and reference Sr-Nd sources (see text). Symbols as in Figure 2.

proportion of radiogenic Sr in the ammonium acetate extracts, is comparatively larger.

As a whole, although the aqua regia extraction cannot be the best analytical procedure to investigate the pedogenesis and soil pollution, however, it can provide significant information about the behavior of Sr and REY in soils similar to those here studied. With respect to the sources of Sr and Nd, the application of their isotopic systematics can allow for recognizing the contribution of these elements from the soluble phases of the soil, and suggesting the provenance of the latter in the geological context of the study area. Lastly, the aqua regia extracts is not the suitable procedure for evaluating the bio-availability of Sr, as soil leaching with ammonium acetate fits better the natural soil-plant exchange.

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Appendix

Table A. The isotopic composition of the main formations from Romagna’s Apennines.

Sample	Formation	δ^{87}Sr
PV-4	Marnoso-arenacea (loc. Firenzuola)	6.34
PV-10	Marnoso-arenacea (loc. via Modiglianese , SR302)	5.74
PV-2	Marnoso-arenacea (carbonate fraction - loc. Firenzuola)	-0.05
PV-3	Marnoso-arenacea (carbonate fraction- loc. Rifredi)	-0.08
PV-8	Messinian Gypsum (Morticini Quarry - loc. Brisighella)	-0.37
PV-11	Pliocene clay and sand (loc. Brisighella)	-0.09