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ORIGINAL ARTICLE

Geochemical features of rocks, stream sediments, and soils of the Fiume Grande Valley (Calabria, Italy)

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Abstract The role of both natural weathering and anthropogenic pollution in controlling the distribution of major oxides and several trace elements in soils, stream sediments, and rocks of the Fiume Grande catchment was evaluated. The contents of major oxides and trace elements in soils appear to be governed by weathering and pedogenetic processes, although the use of fertilizers in agriculture could also partly affect K_2O and P_2O_5 contents. Stream sediments have concentrations of major oxides (except CaO) very similar to soils, as relevant amounts of soil materials are supplied to the stream channels by erosive phenomena. In contrast, stream sediments have concentrations of Cr, Co, Ni, Zn, As, and Pb significantly higher than those of soils, probably due to different conditions and rates of mobility of these elements within the three considered matrices and/or disposal of wastes in the drainage network. Comparison of the concentrations of PHEs in soils with the maximum admissible contents established by the Italian law shows that these limits are too restrictive in some cases and too permissive in other ones. The approach of setting these limits with no consideration for the local geological–geochemical framework may lead to improper management of the territory and its resources.

Keywords Geochemical survey · Stream sediments · Soils · Rocks

Introduction

Today, many efforts of applied geochemists are aimed to establish geochemical baselines for different geo-environmental matrices, such as soils, stream sediments, surface waters, groundwaters, etc., with special emphasis on potentially hazardous elements (PHEs).

In the framework of a recent research project sponsored by ANPA (The National Environmental Protection Agency of Italy) and CNR (The National Research Council of Italy), available geochemical data on stream sediments, mostly collected during several

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mining exploration surveys, have been processed and mapped for establishing natural backgrounds or geochemical baselines (Ottonello and Serva 2003). This review of the available geochemical data for the Calabria Region led to select the Fiume Grande catchment for further detailed investigations on different geo-environmental matrices (Apollaro et al. 2003; Apollaro 2005).

Suitable numbers of stream sediment, soil, and rock samples were, therefore, collected in the study area and analyzed for major oxides and relevant trace elements. Obtained data were processes by using univariate and bivariate statistics to investigate the role of natural weathering and pedogenetic processes in controlling the abundance, distribution and behaviour of the considered chemical elements in the different geo-environmental matrices of the study area. The effects of anthropogenic pollution, if any, were also emphasized.

This paper intends to present the results of this geochemical research. The chemistry of stream waters and groundwaters was discussed in a separate contribution (Apollaro et al. 2006a). The characteristics of soils will be presented in other communications (e.g., Apollaro et al. 2006b).

Study area and geological background

The study area is located along the western coast of Calabria (Italy) close to the town of Nocera Terinese (CZ) and covers an area of approximately 37 km^2. In this area the Lower Ophiolite Unit, the Upper Ophiolite Unit, the Bagni Unit, the Castagna Unit and Neogene-Quaternary sediments crop out (Piluso et al. 2000).

The Lower Ophiolite Unit is represented by metabasalts and metahyaloclastites with a sedimentary cover, which is mainly made up of calcschists of early Cretaceous age.

The Upper Ophiolite Unit is characterized by metabasalts, locally with well-preserved pillow, and metahyaloclastites, topped by a metasedimentary cover, which is made up of calcschists and metaradiolarites associated to minor phyllites and metarenites. A Tithonian–Neocomian age has been proposed for the cover.

The Bagni Unit consists of alternating greenschist-facies, metamorphosed phyllites and metarenites derived from the metamorphism of the siliciclastic and pelitic deposits.

The Castagna Unit is formed of micaschists, paragneiss and orthogneiss, metagranites and subordinate marbles and amphibolites, partly affected by mylonitic deformation.

Five different phyllitic lithotypes belonging to the Bagni Unit, namely phyllites, quartz–phyllites, chlorite–phyllites, carbonate–phyllites, and chloritoid–schists (Piccarretta and Zirpoli 1970) crop out over most of the Fiume Grande valley (Fig. 1). The prevailing lithotype is a phyllite composed by alternating mica-rich beds and quartz-rich beds, which is expected to dominate the geochemistry of the different geo-environmental matrices of the study area.

The main mineralogic constituents of these rocks are: quartz, muscovite (sericite), chlorite, albite, and locally carbonate minerals. The latter ones are chiefly represented by calcite and are present as either granoblasts (where they are scarce) or monomineralic layers (where they are abundant). Accessory minerals are ilmenite, rutile, pyrite, garnet, epidote, tourmaline, and apatite.

Sampling and analytical methods

A total of 37 stream sediments and 90 soil samples from 37 soil profiles were collected in the Fiume Grande catchment, with an average density of either 1 sample/km^2 for stream sediments or 1 profile/km^2 for soils (Fig. 1). In addition, nine rock samples were also collected for comparative purposes. Major and trace elements in rocks, stream sediments, and soil samples were determined by X-ray fluorescence spectroscopy (XRF) by using a XRF spectrometer Philips PW 1480. X-ray counts were converted into concentrations by a computer program based on the matrix correction method (Franzini et al. 1975). The certified international reference materials AGV-1, BCR-1, BR, DR-N, GA, GSP-1, and NIM-G (see http://www.georem.mpch-mainz.gwdg.de/ for chemical composition) were used as monitors of data quality. Quartering and pulverization procedures were applied to stream sediments, and soil samples before XRF analysis. All the chemical data are reported as electronic supplement. The main statistical indices of stream sediments, top soils and bottom soils are given in Table 1.

Stream sediments

Sampling sites were selected through a preliminary analysis of the hydrographic network, which was carried out by superimposing a grid composed by rectangular cells with surface area of ~1 km^2 onto the 1:10,000 topographic maps of the study area. The sampling procedures recommended by IGCP and FOREGS were followed. In particular: (i) sampling points situated at least 100 m upstream of roads and

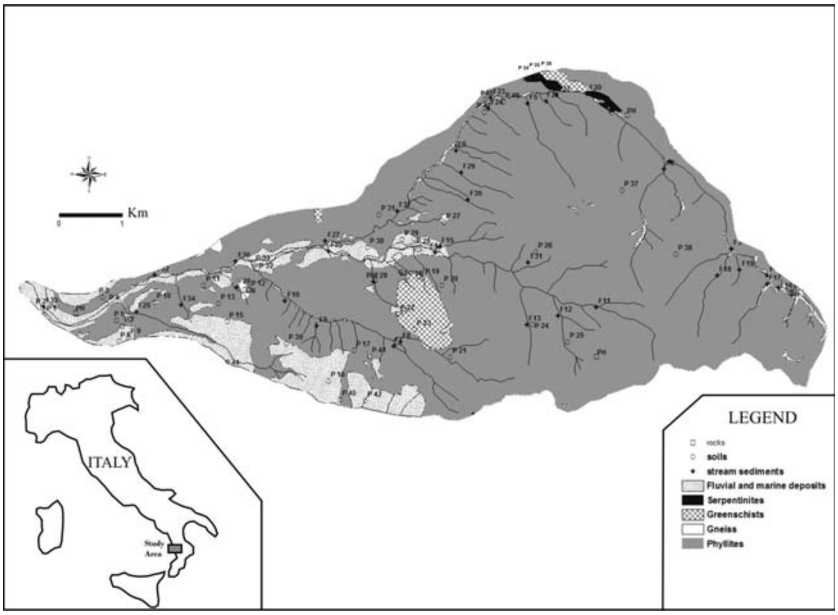

Fig. 1 Geological sketch map of the Fiume Grande catchment. The location of soil, stream sediment and rock samples is also shown

villages were selected; (ii) contact with metals was avoided to prevent sample contamination, (iii) oxidized materials and organic substances, if any, were eliminated, (iv) three to four sub-samples were collected in distinct points of the stream bed over a linear distance of 50–100 m, approximately, (v) wet-sieving was carried out in situ by using sieves made up of a wood frame and a teflon net; (v) the <0.15 mm fraction was finally collected in polyethylene bags.

Rocks

Five samples of phyllitic rocks were collected in order to evaluate their average composition. These samples are representative of the prevailing rock type of the study area (i.e., the phyllites of the Bagni Unit), constituting the parent rock of most soil samples. Two samples of greenschists, and one sample for both serpentinites and gneiss were also acquired. Each rock sample represents a composite sample from a single outcrop.

Soils

The map of landscape units (homogeneous zones based on both lithological and morphological characteristics as well as on land use) was used to select soil sampling sites. This map was obtained through photointerpretation, study of the slope of the hillsides and field controls.

Samples for laboratory analyses were collected from each horizon recognized in the field and stored in polyethylene bags. Samples were then air dried at room temperature and the <2 mm fraction was separated by sieving. The chemical composition of the <2 mm fraction was determined by X-ray fluorescence.

The description of soil profiles and the results of other analyses carried out on soil samples (particle size distribution, pH(H_2O), organic matter, cation exchange capacity, exchangeable bases, etc.) are presented and discussed in separate contributions (e.g., Apollaro et al. 2006b).

Chemical characteristics of soils, stream sediments, and rocks

The distribution of major oxides and trace elements in soils and stream sediments is conveniently investigated through a series of correlation plots in which the concentration of Al_2O_3, taken as the reference variable, is displayed on the abscissa, and the average composition of local rocks (phyllites, serpentinites, greenschists, and gneiss) is reported for comparison. It must be recalled once more that phyllites represent by far the prevailing lithotype, cropping out over most of the Fiume Grande catchment, whereas the other considered rocks are present only in small areas.

Al_2O_3, total Fe_2O_3 and total MnO

In the total Fe_2O_3 versus Al_2O_3 diagram (Fig. 2a), most soil samples plot together into a well defined trend, which departs from the average composition of phyllites and extends towards higher contents of both

Table 1 Main statistical indices of stream sediment, top soil and bottom soil samples (concentrations of major oxides in wt%, concentrations of trace elements in mg/kg)

Oxide/element	Mean	Median	Min value	Max value	25° percentile	75° percentile
Stream sediment samples						
SiO_2	57.62	57.42	51.42	63.79	56.12	58.85
TiO_2	1.30	1.30	0.80	1.61	1.25	1.38
Al_2O_3	21.15	21.25	18.33	23.95	20.06	21.99
Fe_2O_3,tot	9.62	9.58	5.80	16.50	9.14	10.18
MgO	3.63	3.61	1.72	5.93	3.05	3.91
CaO	1.44	1.35	0.51	2.45	1.20	1.63
MnO	0.21	0.21	0.11	0.35	0.17	0.24
Na_2O	1.07	1.00	0.69	2.44	0.90	1.17
K_2O	3.72	3.81	2.02	4.82	3.39	4.12
P_2O_5	0.24	0.23	0.12	0.41	0.20	0.26
As	59	54	14	134	36	80
Ba	550	552	274	740	485	633
Ce	106	106	23	160	94	120
Co	31	32	15	37	29	34
Cr	189	174	71	323	156	217
La	57	56	10	82	49	65
Nb	30	28	16	42	25	35
Ni	107	100	38	225	83	122
Pb	47	42	11	79	35	59
Rb	159	160	66	278	146	175
Sr	127	118	86	237	109	133
V	172	172	98	224	163	182
Y	56	55	26	82	50	60
Zn	163	154	72	302	134	195
Zr	407	376	257	818	329	450
Top soil samples						
SiO_2	59.37	58.81	48.52	68.93	57.24	61.40
TiO_2	1.14	1.16	0.55	1.46	1.05	1.28
Al_2O_3	20.82	21.52	9.89	26.67	19.43	23.02
Fe_2O_3,tot	9.26	9.18	4.71	17.87	8.43	9.84
MgO	3.76	2.73	1.27	26.78	2.09	3.66
CaO	1.00	0.66	0.12	9.08	0.44	0.79
MnO	0.22	0.20	0.08	0.46	0.14	0.29
Na_2O	0.84	0.80	0.27	1.61	0.64	0.98
K_2O	3.39	3.35	0.55	5.78	2.92	3.95
P_2O_5	0.21	0.17	0.08	0.63	0.12	0.26
As	27	20	7	90	15	31
Ba	525	520	172	793	478	593
Ce	102	96	38	199	80	114
Co	28	26	13	86	22	31
Cr	202	124	43	1884	100	165
La	54	49	24	106	42	63
Nb	26	26	9	56	19	31
Ni	98	54	19	794	39	82
Pb	39	39	8	77	29	49
Rb	154	157	32	245	141	175
Sr	97	94	35	207	74	113
V	160	157	84	242	145	179
Zn	100	102	17	156	88	115
Zr	250	247	92	420	208	291
Y	29	29	10	46	25	33
Bottom soil samples						
SiO_2	59.43	58.62	46.62	68.89	56.32	63.75
TiO_2	1.13	1.20	0.19	1.53	1.03	1.28
Al_2O_3	21.63	22.40	4.51	28.26	19.63	23.76
Fe_2O_3,tot	9.22	9.36	4.55	18.01	7.87	10.15
MgO	3.57	2.48	1.20	37.46	2.03	3.04
CaO	0.60	0.39	0.02	6.39	0.25	0.57
MnO	0.18	0.16	0.06	0.45	0.10	0.21

Table 1 continued

Oxide/element	Mean	Median	Min value	Max value	25° percentile	75° percentile
Na_2O	0.79	0.70	0.05	1.48	0.61	1.01
K_2O	3.30	3.31	0.10	5.35	2.88	3.83
P_2O_5	0.14	0.14	0.02	0.42	0.08	0.21
As	27	22	3	138	17	31
Ba	539	557	26	889	446	628
Ce	109	103	12	251	76	125
Co	28	25	11	109	22	27
Cr	187	121	41	2009	102	149
La	52	52	5	107	38	65
Nb	27	28	1	48	20	35
Ni	93	52	17	1343	38	62
Pb	33	36	0	71	24	45
Rb	156	162	11	242	143	176
Sr	90	88	17	212	73	107
V	168	172	81	248	153	184
Y	28	30	1	45	24	33
Zn	100	103	49	140	86	115
Zr	255	259	19	412	209	301

chemical components. This picture is consistent with the geochemical behavior of both Al and Fe during weathering, as both chemical components are preferentially incorporated in secondary solid phases such as Al-oxyhydroxides (e.g., gibbsite), Al-silicates (chiefly clay minerals), Fe(III)-oxyhydroxides, and organic molecules. Besides, both Al and Fe may be adsorbed on the negatively charged surfaces of clay minerals and/or organic matter (exchangeable complex). In particular, a hydroxide solid mixture rich in $Fe(OH)_3$ and at least one Al-bearing solid phase (either gibbsite or kaolinite or beidellite or illite) persist throughout the weathering process affecting the Fiume Grande phyllites, according to reaction path modeling predictions (Apollaro et al. 2006a). Consequently, progressive weathering is expected to cause a gradual increase in both Al_2O_3 and Fe_2O_3 contents in soils, with respect to the initial concentrations of both components, which coincide with those of the underlying bedrock, usually phyllites. Only few samples do not belong to the general trend, owing to the presence of either a different protolith (e.g., the serpentinites for the soil samples P35 and P34, and the gneiss for sample P12) or a local excess of Fe(III)-oxyhydroxides, as is the case of the soil sample P42 which appears intensely rubified.

Figure 2a also shows that most stream sediments belong to the same general trend of the soils, suggesting that the chemistry of the former ones is heavily affected by the composition of the latter ones, evidently because the erosive processes conveying solid materials into the drainage network act chiefly on soils rather than on the underlying bedrocks. This coincidence between soil- and stream sediment-compositions is observed for most chemical constituents (see below) and is in line with the morphology of the Fiume Grande catchment, which is mostly characterized by gentle slopes.

The spread of points in the total MnO versus Al_2O_3 diagram (Fig. 2b) is quite similar to that of Fig. 2a. Again, most soil samples plot together into a trend departing from the phyllites' box and moving towards higher concentrations of both MnO and Al_2O_3. However, the trend is less tight than in Fig. 2a, and the bottom soil samples have, in general, MnO contents somewhat lower than the top soil samples, as suggested by the different lines of regression (B and T, respectively). This picture probably reflects the dependence of the geochemical behavior of Mn on the redox state. Under the relatively oxidizing conditions of top soils, tetravalent Mn prevails and Mn is rather immobile as it is fixed in insoluble Mn(IV)-oxides. In contrast, under the relatively reducing conditions of bottom soil horizons, probably promoted by higher clay percentages and/or seasonally fluctuating water table, sometimes clearly indicated by graysh mottles and tongues, divalent Mn dominates and Mn becomes rather mobile due to the relatively high solubility of Mn(II) compounds. Under these redox potentials, Mn may become immobile upon attainment of saturation with respect to a rhodochrosite-containing solid mixture of trigonal carbonates, but this is a comparatively late step during the weathering process of the Fiume Grande phyllites, according to the results of geochemical modeling (Apollaro et al. 2006a).

As already observed in Fig. 2a, the stream sediment samples plot together with the soil samples in Fig. 2b as well. Moreover, the regression line of the stream sediment samples (line SS) is very close to that fitted by the top soil samples (line T), suggesting that these (rather than the bottom soils) are preferentially transported into the stream channels by erosion. This might seem a rather obvious conclusion, but this preferential link between top soils and stream sediments, which is evident only for a few chemical components (such as MnO and P_2O_5, see below), helps to elucidate the processes controlling the chemistry of the solid geo-environmental matrices in the study area.

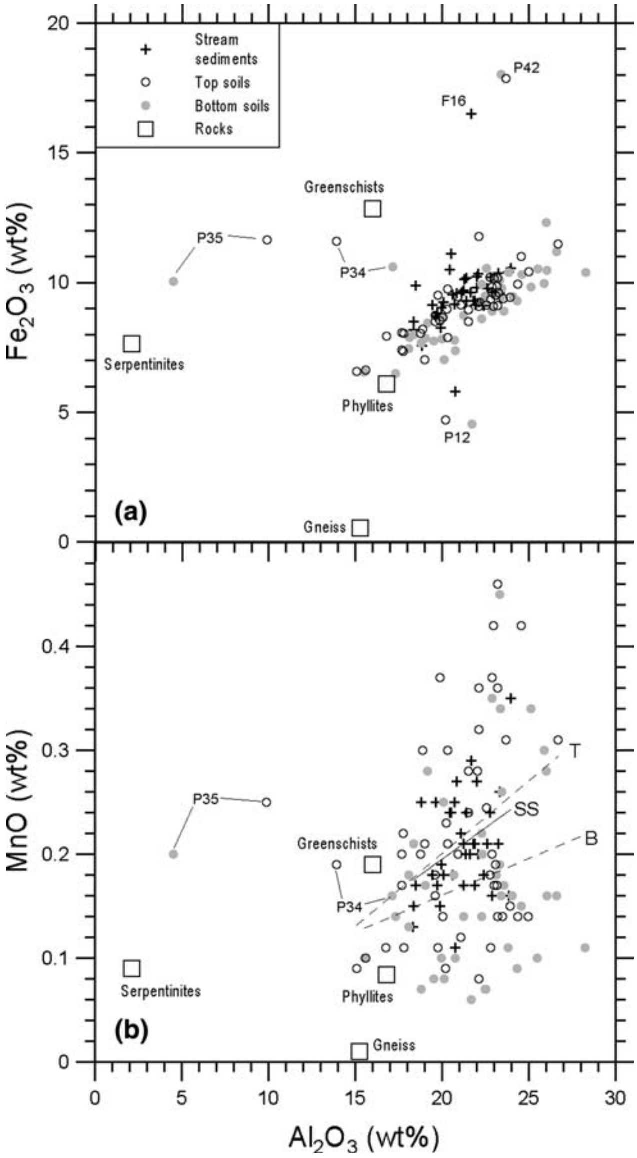

Fig. 2 Correlation diagrams of **a** total Fe_2O_3 versus Al_2O_3 and **b** total MnO versus Al_2O_3 for the soils, stream sediments, and rocks of the Fiume Grande catchment. The *lines* labeled *SS*, *T*, and *B* are the regression lines fitted by stream sediments, top soils, and bottom soils related to phyllitic protoliths, respectively

SiO_2, Na_2O, MgO, and CaO

Taking into account the numerous soil samples related to phyllitic rocks, SiO_2, Na_2O, MgO, and CaO appear to be inversely correlated with Al_2O_3 (Fig. 3a–d), in contrast to what observed in Fig. 2. In other words, the increase in the Al_2O_3 concentrations of soils, upon progressive weathering of phyllites, is accompanied by a gradual depletion in SiO_2, Na_2O, MgO, and CaO with respect to the initial, protolith concentrations. In fact, Si, Na, Mg, and Ca are preferentially leached by the meteoric waters percolating through the soils, in agreement with the general knowledge on the geochemical behavior of these elements in soils.

The few soil samples developed on serpentinites (P35 and P34) occupy peculiar positions reflecting the high MgO and the low SiO_2, Na_2O, and CaO of these lithotypes.

As expected on the basis of previous discussion, stream sediment samples are situated together with the soil samples in the plots of Al_2O_3 versus SiO_2, Na_2O, and MgO, whereas they are generally enriched in CaO with respect to the soils. This might reflect precipitation of calcite from the stream waters of the Fiume Grande catchment, which are generally close to saturation or slightly oversaturated with respect to a calcite-rich solid mixture of trigonal carbonates (Apollaro et al. 2006a). Precipitation of this solid phase could be favored by evaporation of the stream waters during the dry periods. Local precipitation of calcite in soils could also explain the high CaO concentrations of some soil samples (P45, P36, P34 and P35).

K_2O and P_2O_5

Based on the general knowledge on the geochemical behavior of K_2O, soils are expected to be depleted in K_2O with respect to the parent lithotype, owing to preferential removal of K by the aqueous solutions draining the soils. In contrast to these expectations, the soils of the Fiume Grande catchment are generally enriched in K_2O with respect to the underlying bedrocks (Fig. 4a), possibly due to the presence of illite components (where K^+ is the main cation occupying the lattice interlayer) among the neoformed clay minerals in soil samples, as they represent typical alteration products of mica- and feldspar-bearing parent rocks under temperate humid climates (e.g., Sequeira Braga et al. 2002; Scarciglia et al. 2005). Indeed, illite is expected to be produced during weathering of the Fiume Grande phyllites, according to reaction path modeling predictions (Apollaro et al. 2006a). Also the effect of fertilization in agricultural lands, which is a very common practice not only in the study area (e.g., Griffioen 2001), cannot to be excluded. No significant difference occurs between the abundance of K_2O in top and bottom soils.

The geochemical behavior of P_2O_5 in soils is expected to be governed by incorporation of phosphate in secondary Fe(III)-oxyhydroxides (Gunnars et al. 2002) or iron phosphate phases (Luedecke et al. 1989), owing to the relatively low durability of apatite (Valsami-Jones et al. 1998), the main P-bearing primary mineral in the lithotypes of the study area. Consequently, the increase in the P_2O_5 concentrations of soils, with respect to the parent lithotype, is not surprising (Fig. 4b). The plot of P_2O_5 versus Al_2O_3 also shows that the P_2O_5 contents of top soil samples are generally higher than those of bottom soil samples, as indicated by the different regression lines, T and B, respectively. Moreover, the regression line fitted by the stream sediment samples (line SS) is very close to line T, similarly to what observed for MnO (see above), evidently because of preferential erosion and introduction in the stream channels of top soils rather than bottom soil horizons. This obvious fact confirms that the different P_2O_5 contents of top soils and bottom soils is not an artifact. The ultimate cause for this difference is probably due to the occurrence of high amounts of organic phosphorous forms that are usually well correlated to the soil organic matter content, which is higher, in turn, in surface soil horizons. Moreover, the use of inorganic fertilizers or animal manure cannot be excluded in agricultural lands, in line with what suggested for K_2O.

TiO_2 and conservative trace elements

As already recalled, rutile and ilmenite are the main Ti-bearing primary minerals in the rocks of the study area. Their high durability (White et al. 1994) explains the enrichment in TiO_2 in soils with respect to the local protoliths, chiefly phyllites (Fig. 5a). Figure 5a also confirms the links between stream sediments and soils in the study area.

Similar inferences can be drawn from the correlation plots between conservative trace elements such as Y, Zr, Nb, and rare earth elements (e.g., the La vs. Nb diagram, Fig. 5b), although the relative mobility of

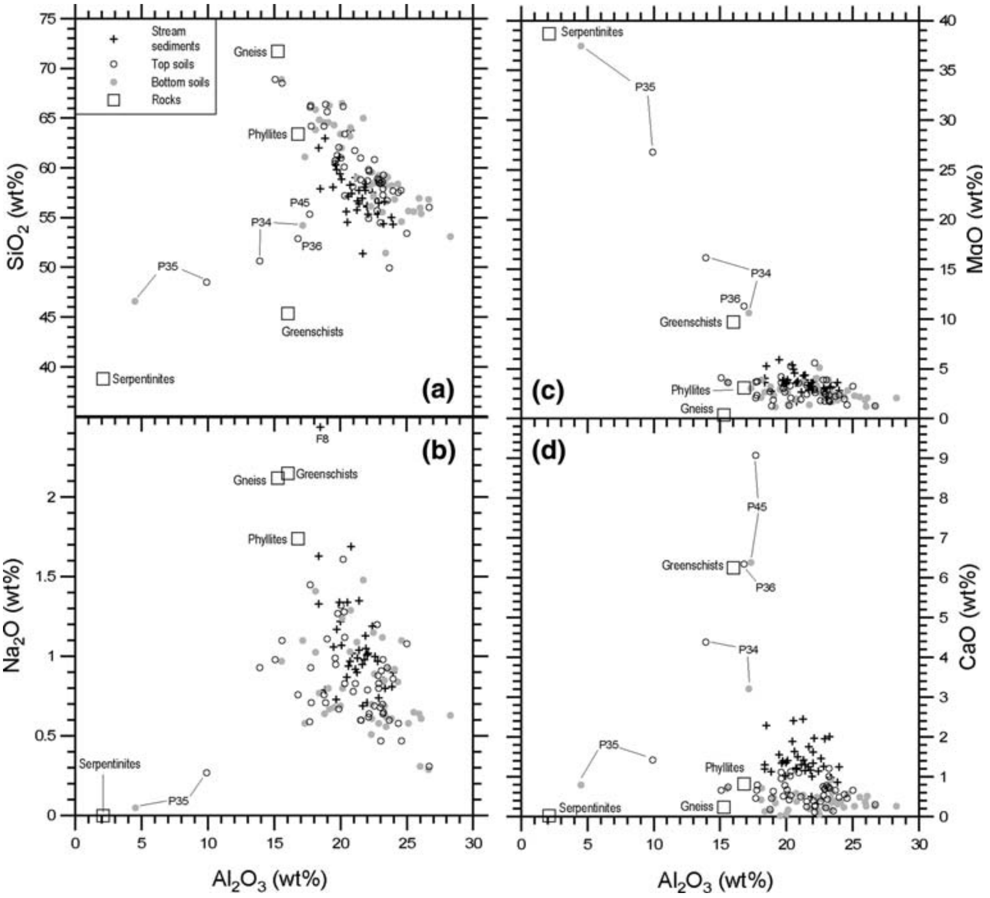

Fig. 3 Correlation diagrams of **a** SiO_2 versus Al_2O_3, **b** Na_2O versus Al_2O_3, **c** MgO versus Al_2O_3, and **d** CaO versus Al_2O_3 for the soils, stream sediments, and rocks of the Fiume Grande catchment

these elements in different weathering environments has been a matter of considerable disagreement in the geochemical literature (White 1995).

The potentially harmful elements V, Cr, Co, Ni, Zn, As, and Pb

Seven PHEs were analysed in the geo-environmental solid matrices collected in the Fiume Grande catchment, namely V, Cr, Co, Ni, Zn, As, and Pb.

As expected, Cr, Ni, and Co contents result to be the highest in serpentinitic rocks and related soil samples (Fig. 6a–c), especially sample P35, with 1,884–2,009 mg/kg Cr, 794–1,343 mg/kg Ni, and 86–109 mg/kg Co (and contents in the bottom soil samples always greater than in the top soil). These concentrations are entirely ascribable to natural weathering processes, but they are much higher than the maximum admissible contents in soils for residential uses (150 mg/kg Cr, 120 mg/kg Ni, and 20 mg/kg Co) according to the Italian law (e.g., D.M. 25 October 1999, N. 471) and even above the maximum allowable contents in soils for industrial uses (800 mg/kg Cr, 500 mg/kg Ni).

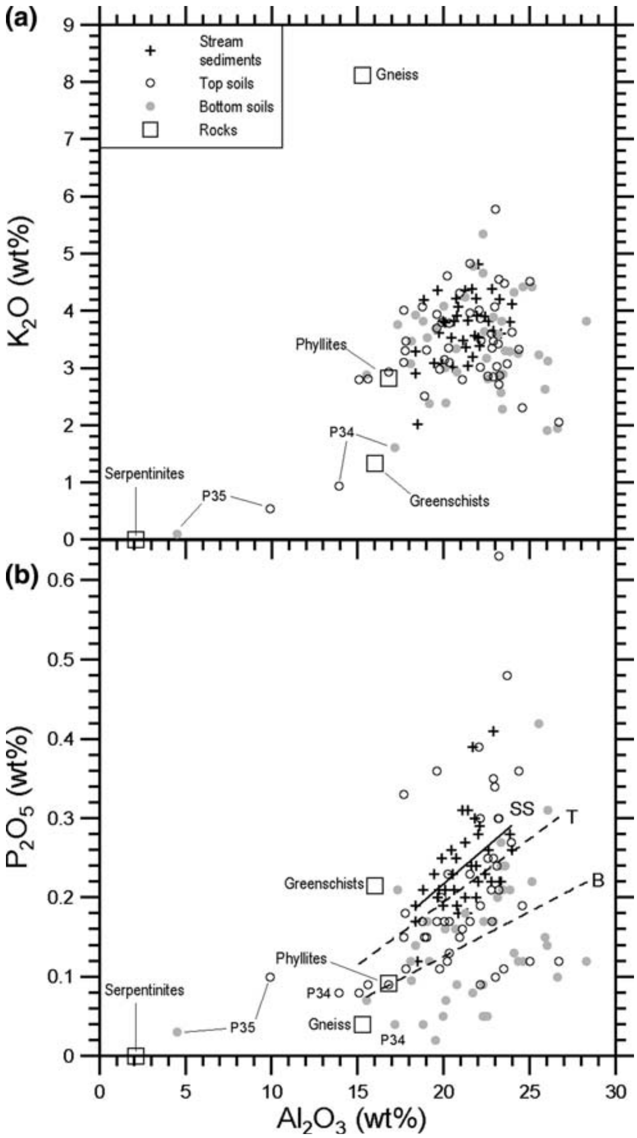

Fig. 4 Correlation diagrams of **a** K_2O versus Al_2O_3 and **b** P_2O_5 versus Al_2O_3 for the soils, stream sediments, and rocks of the Fiume Grande catchment. The *lines* labeled *SS*, *T*, and *B* are the regression lines fitted by stream sediments, top soils, and bottom soils related to phyllitic protoliths, respectively

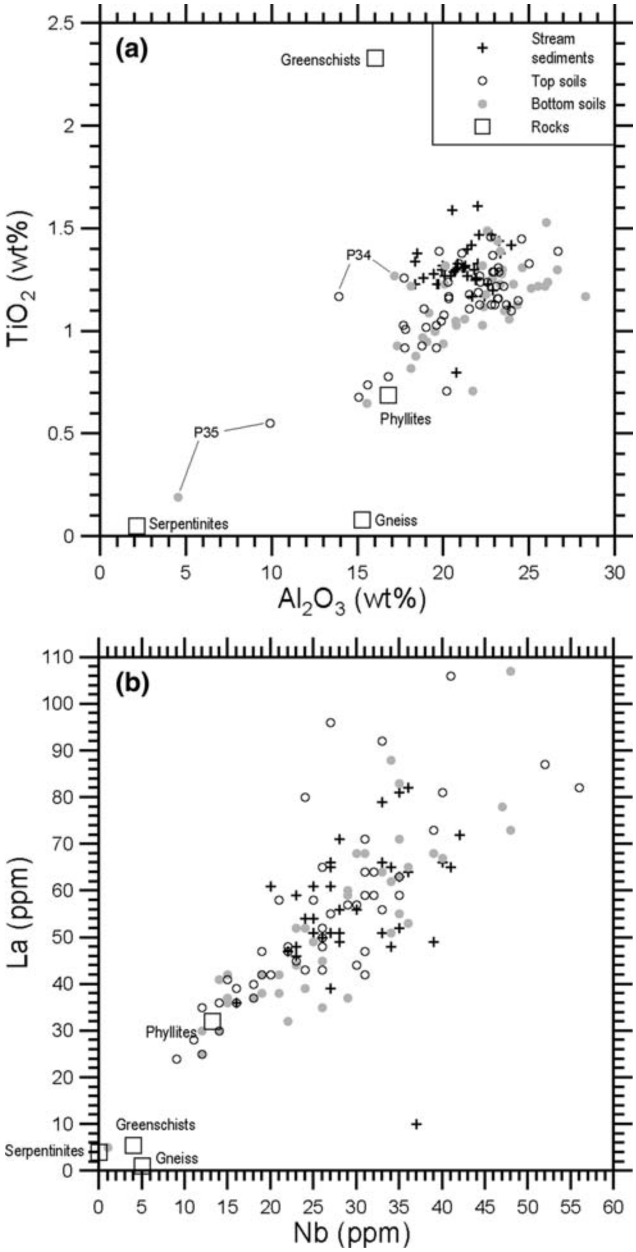

Fig. 5 Correlation diagrams of **a** TiO_2 versus Al_2O_3 and **b** La versus Nb for the soils, stream sediments, and rocks of the Fiume Grande catchment

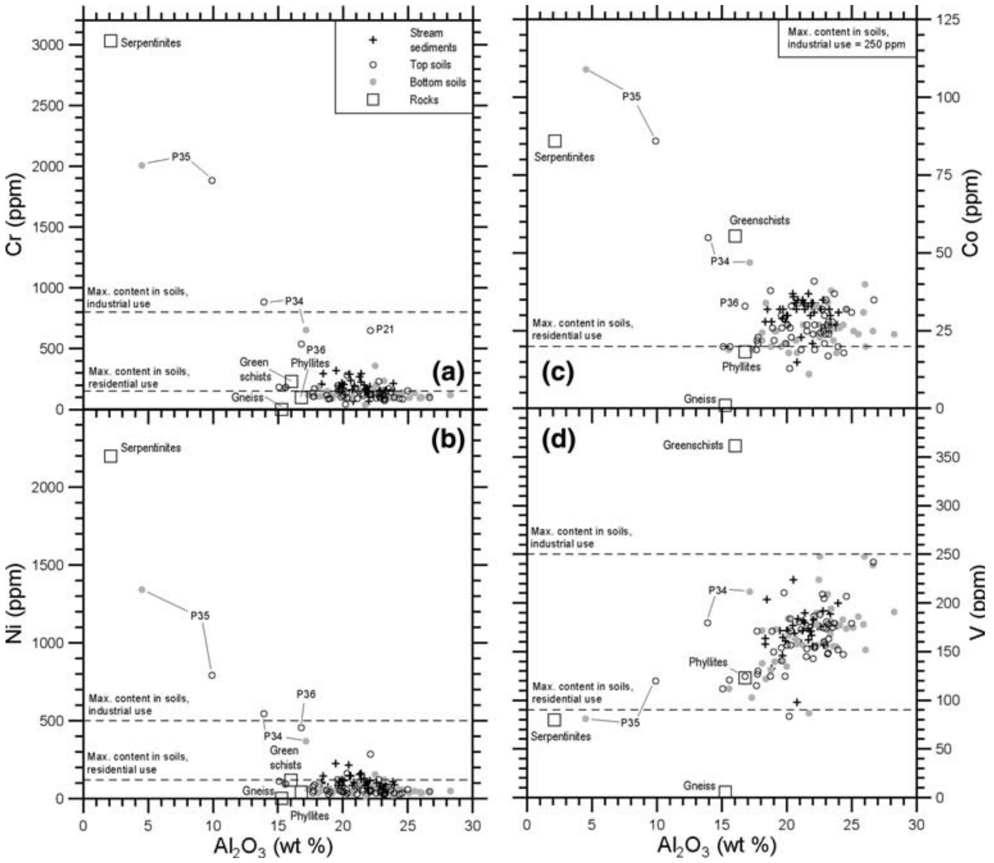

Fig. 6 Correlation diagrams of **a** Cr versus Al_2O_3, **b** Ni versus Al_2O_3, **c** Co versus Al_2O_3, and **d** V versus Al_2O_3 for the soils, stream sediments, and rocks of the Fiume Grande catchment

Restricting the attention to the soils related to weathering of phyllitic protoliths, it turns out that top soils have Cr, Ni, and Co contents similar to bottom soils, whereas stream sediments results to be significantly enriched in Cr and Ni and slightly enriched in Co with respect to soils.

All these phyllitic-derived soil samples have Cr, Ni, and Co contents significantly lower than those of sample P35. Accordingly, Cr and Ni concentrations of most soil samples (72% and 90.1% of the total, respectively) are below the residential-use threshold, but Co contents of most samples (83.5% of the total) are above it. Stream sediments are somewhat richer in Cr, Ni, and Co than soils and, consequently, the residential-use limit is exceeded by 79% of the samples for Cr, 27% of the samples for Ni, and 97% of the samples for Co.

Also V concentrations in soils (Fig. 6d) are ascribable to weathering of either phyllites, in most cases, or serpentinites, for samples P35 and P34. Stream sediments have V contents essentially comparable with those of soils. In spite of the natural origin of V, 97.5% of soil samples and all the stream sediment samples have V contents higher than the maximum admissible content for residential uses (90 mg/kg), whereas neither soil samples nor stream sediment samples exceed the limit for industrial uses (250 mg/kg).

Zinc concentrations in top soils developed over phyllitic protoliths are similar to those in bottom soils related to the same lithotypes, as indicated by the similarities in the regression lines fitted by the two batches of samples, which are labeled T and B, respectively (Fig. 7a). It must be underscored that, in spite of the relatively large scatter of soil samples, both regression lines begin close to the point representative of the average Zn and Al_2O_3 contents in phyllitic rocks and extend towards higher Zn and Al_2O_3 concentrations, as expected for natural weathering. In contrast, the regression line fitted by the stream sediment samples (SS) is situated well above the two regression lines for soils (T and B), suggesting the presence of excess Zn in stream sediments. Zinc could have been relatively enriched in stream sediments as they have partly lost other chemical components (more mobile than zinc) in response to the progressive degradation of parent rocks leading to sediment production; conversely, both top and bottom soil samples could have undergone further depletion in Zn, because of more intense leaching processes due to a prolonged time span of weathering and

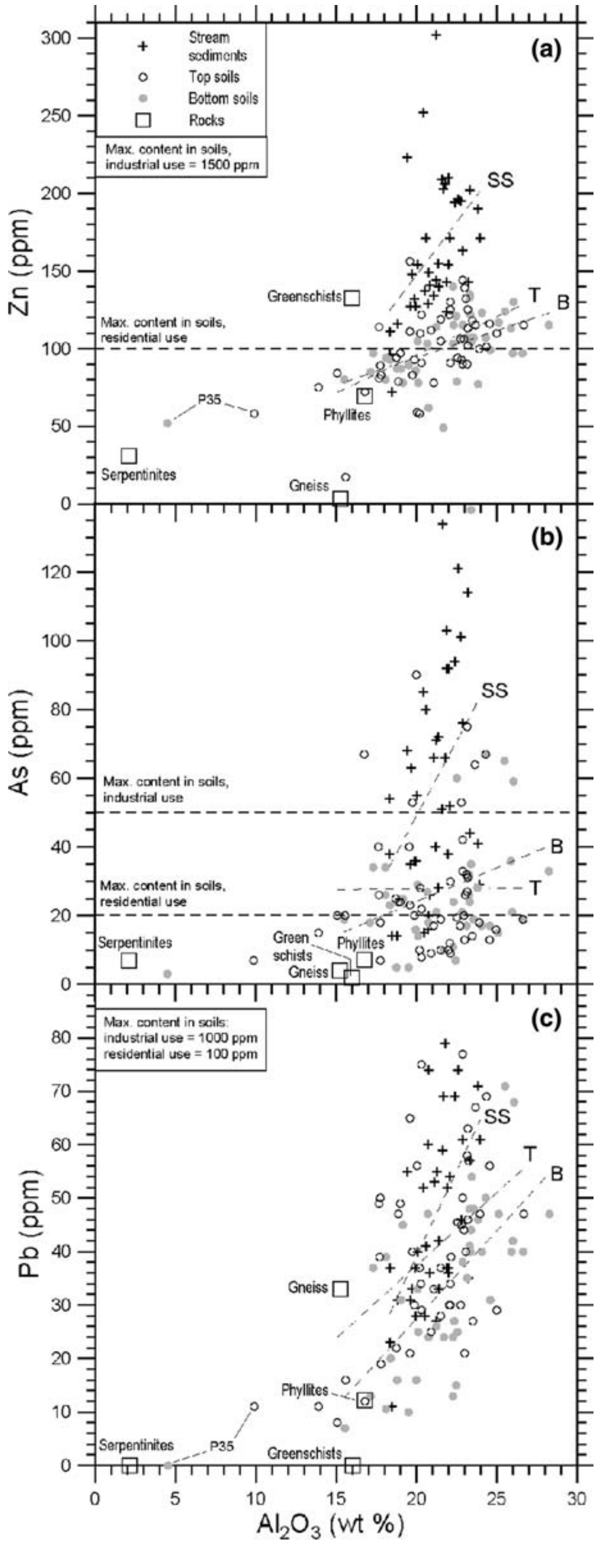

Fig. 7 Correlation diagrams of **a** Zn versus Al_2O_3, **b** As versus Al_2O_3, and **c** Pb versus Al_2O_3 for the soils, stream sediments, and rocks of the Fiume Grande catchment. The *lines* labeled *SS*, *T*, and *B* are the regression lines fitted by stream sediments, top soils, and bottom soils related to phyllitic protoliths, respectively

pedogenesis and possibly to the acidic pH conditions (mean value 6.1) measured in the studied soils. Alternatively, an anthropogenic origin of Zn surplus could be supposed, possibly related to the discharge of Zn-plated iron wastes in the drainage network. Most stream sediment samples (95%) and about half soil samples (52%) have Zn contents higher than the maximum admissible concentration in soils for residential use (100 mg/kg) but all are lower than the industrial-use threshold (1,500 mg/kg).

The spread of points in the diagram of As versus Al_2O_3 (Fig. 7b) is similar to that of Fig. 7a, with the regression line fitted by the stream sediment samples (SS) situated well above the regression lines of top soils (T) and bottom soil horizons (B). As long as weathering and pedogenetic processes go on, a relative enrichment in As is promoted in stream sediments and soils in respect of the protoliths, but at a lesser extent in the soil samples, where lower pH values and persistence of leaching processes enhance its progressive depletion. Again, an anthropogenic derivation for the excess As in stream sediments is not to be excluded, but the involved As-compounds cannot be defined based on the available data. A large number of stream sediment samples (87%) and about half soil samples (51%) have As contents greater than the maximum allowable content in soils for residential use (20 mg/kg). The limit for industrial uses (50 mg/kg) is exceeded by 57% of the stream sediment samples and 12% of the soil samples.

Also the diagram of Pb versus Al_2O_3 (Fig. 7c) shows a distribution of points quite similar to those of Fig. 7a, b, although the differences between soils and stream sediments are less evident. Similarly to the interpretation of Zn and As, such differences in Pb contents among parent rocks, soil samples and stream sediments are consistent with different degrees and rates of mobility of Pb in these different matrices and/or with an anthropogenic pollution but, again, the Pb-containing compounds responsible for this excess Pb cannot be specified based on the present knowledge. All the soil and stream sediment samples have Pb concentrations lower than the residential-use limit (100 mg/kg) and much lower than the industrial-use threshold (1,000 mg/kg).

Conclusions

This geochemical study of soils, stream sediments, and rocks in the Fiume Grande catchment allowed us to evaluate the role of both natural weathering and anthropogenic pollution in controlling the distribution of major oxides and several trace elements, including seven PHEs (V, Cr, Co, Ni, Zn, As, and Pb), in the considered geo-environmental matrices.

Most phyllites-related soils are enriched in Al_2O_3, total Fe_2O_3, total MnO, TiO_2, and conservative trace elements (Y, Zr, Nb, La and Ce) and depleted in SiO_2, Na_2O, MgO, and CaO with respect to the protolith composition. These chemical changes are essentially governed by weathering and pedogenesis, whereas the influence of anthropogenic pollution is nil. Also the contents of the considered PHEs in soils appear to be chiefly controlled by weathering, although the use of fertilizers in agriculture could also affect, at least partly, the K_2O and P_2O_5 contents of the soils in the study area.

Stream sediments have concentrations of major oxides very similar to soils, as relevant amounts of soil materials are supplied to the drainage network by erosive phenomena. The only exception is represented by the anomalously high CaO contents which are probably caused by precipitation of a calcite-rich solid mixture of trigonal carbonates, especially during the dry periods. In contrast, stream sediments have concentrations of Cr, Co, Ni, Zn, As, and Pb significantly higher than those of soils, probably due to either different conditions and rates of mobility of these elements within the three different matrices considered or the blamable but common practice of disposing wastes in the stream channels. Consequently, use of stream sediments for establishing the natural background of these PHEs in soils is not recommendable, at least in the study area.

Comparison of the concentrations of PHEs in soils with the maximum admissible contents established by the Italian law shows that these limits are too restrictive for some elements (e.g., Co) and too permissive in other cases (e.g., Pb). Besides, much higher background concentrations of Cr, Ni, and Co and lower baselines of Zn and Pb are expected for soils developed over serpentinites with respect to those related to phyllitic protoliths. Consequently, the approach of establishing general thresholds, neglecting completely the local geological-geochemical framework, is highly questionable and may lead to improper management of the territory and its resources. Moreover, the speciation of PHEs could be even more useful than elemental abundances for defining the mobility and bioavailability of chemical species, that is their environmental fate. This will represent the subject of further investigations.

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