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Sources of major and trace elements in the stream sediments of the Arno river catchment (northern Tuscany, Italy)

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The source of major and trace elements has been studied in the Arno river catchments, with repeated sampling of stream sediments in 73 stations within the basin. The study was performed for the inventory, survey, assessment and monitoring of metal pollution, and for geochemical mapping of the most representative elements. Chemical data displayed a wide dispersion, greater in the tributaries than in the Arno river, but in general, there was a good overlap between the stream sediments and the major geological units. SiO_2 (32–75 wt%) was high in the main portion of the Arno river and in the northern tributaries, whereas CaO (1.5–27 wt%) was enriched in the southern ones. High MgO values (up to 5.7 wt%) were related to the presence of ophiolitic masses and/or to the ultramafic fraction of Macigno and Cervarola geological formations, which affected the distribution of Ni and Cr. However, in the highly industrialized areas northwest of Florence, high Cr values were associated to Cu, Zn and Pb anomalies. Copper (and sulphur) anomalies also occurred where agricultural practices were widespread. Organic matter content was variable (Corg 0.19–8.97 wt%) with an average C/N ratio of 8.7 (range 3.2–12.4), which is consistent with other C/N ratios of river sediments in the world. The relationships between Corg and N, S, P_2O_5 and heavy metals indicated that the organic matter had a mixed origin (industrial, agricultural, urban) and that both natural and anthropogenic metals entered the Arno river catchment.

Keywords: stream sediments, geochemistry, pollution, Arno river

INTRODUCTION

Investigations of the chemical composition of stream and river sediments have been used as a prospecting tool for mineral deposits (Levinson, 1974; Rose *et al*., 1979; Plant and Hale, 1994) but the same principles and techniques can be extended to more environmentally-related studies (Howarth and Thornton, 1983; Förstner, 1983; Förstner *et al*., 1991).

In general, the chemical composition of stream sediments depends on several factors, such as the lithology, morphology and structural setting of the catchment, and on the effect of climate, which controls weathering rates and hydrological features as well as the density and type of vegetation cover (e.g., Salomon and Förstner, 1984). In addition, human activity can sometimes strongly influence fluvial dynamics and the environmental quality of the fluvial systems (e.g., Mantei and Foster, 1991).

Fluvial sediments, both bed-load and suspended, can act as sink and/or carriers for a large number of pollutants that can either be transported away from source areas according to fluvial dynamics or be stored in the solid fraction of the bed sediments. In such case, sediments can become a source of pollution if the environmental conditions change within the sedimentary column or in the river course, and if the solids are removed and resuspended. In some cases, "natural pollution" can overprint the anthropogenic pollution, the former being related to the weathering of ore deposits or to the occurrence of peculiar types of rocks.

The present work focuses on the bulk chemistry of active bedload sediments from the Arno river catchment in northern Tuscany (Italy). The samples were collected both from the main river and from its principal tributaries during low flow conditions in November 1996 and June–July 1997, and in July 2000, for some selected tributaries (Elsa, Era and Usciana). The analyses were performed for the inventory, survey, assessment and monitoring of metal pollution, and for geochemical mapping to delineate the spatial distribution of chemical elements. The results are compared to available geological data in order to evaluate the effects of lithology on sediment com-

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position and to suggest background values. The role of organic matter in controlling heavy metal distribution is also discussed.

BACKGROUND

Catchment lithology

The Arno river is 242 km long and its catchment covers an area of 8228 km^2. The river flows into the Tyrrhenian Sea about 10 km downstream from Pisa (Fig. 1). Florence, the biggest town of Tuscany, is situated about 135 km from the headwaters of the Arno river. Other towns include Arezzo, located in the upper section of the river, and Pistoia and Prato, located north of Florence in the catchment area of the Ombrone river and Bisenzio river, respectively, both right-hand tributaries of the Arno river.

Sedimentary rocks dominate the Arno river catchment (Fig. 2). Sandstones (Cervarola and Macigno Formations) are widespread in the headwaters of the Arno river and near the northern tributaries in the upper catchment, such as Salutio and Sieve. Marls, clays and minor sandstones (Pliocene and Pleistocene marine, continental and lacustrine deposits) occur in the Chiana valley, the most important tributary of the Arno river in its upper section. Sandstones, shales and calcareous turbidites interbedded with chaotic clays along with scattered ophiolitic blocks are the prevailing terrains in the central part of the basin around Florence. Clastic deposits occur in the plain area between Florence and Pistoia, which consisted of a lacustrine basin during the late Pleistocene (Capecchi *et al*., 1975; Bossio *et al*., 1993). Downstream from Florence, the right-hand tributaries (Bisenzio, Ombrone and Usciana) drain an area composed of sandstones belonging to the Macigno Formation and limestones and cherty limestones. The left-hand tributaries (Greve, Egola, Pesa, Elsa and Era) flow over Plio-Quaternary fine-grained marine and lacustrine clayey and sandy deposits. Triassic limestone and gypsum-anhydrite along with Messinian gypsarenite occur in the headwaters of Elsa and Era rivers which are also characterized by the occurrence of ophiolitic rocks, mainly serpentinites. At the end of the basin, north of Pisa, metamorphic rocks (marbles and metapelites) occur in the Monti Pisani area, on the right-side of the Arno river. The coastal plain around Pisa is composed of a graben filled by alluvia.

Hydrochemistry and human activity

In the Arno river catchment, the water discharge variations follow those of the precipitations, although with a slight delay, since the majority of the basin is composed of low-permeability rocks. Historical records of discharge indicate a distribution with two maxima (December and March), with a major minimum in August.

As reported by the Consorzio Pisa Ricerche (1998), major anthropogenic inputs in the Arno river occur downstream from Florence. They originate from:

(1) The direct discharge of the whole Florence city domestic black and white water system, with a pollution load equivalent to 10^6 inhabitants. This increases COD from 10 to 30 mg/l, N-NH_4 from trace to 8 mg/l and phosphates from 0.1 to 1 mg/l.

(2) The Bisenzio and Ombrone tributaries carry waste waters from industrial settlements and nurseries around Pistoia and Prato. Pollution load due to waste waters (about 80% depurated) from textiles in the Prato area is

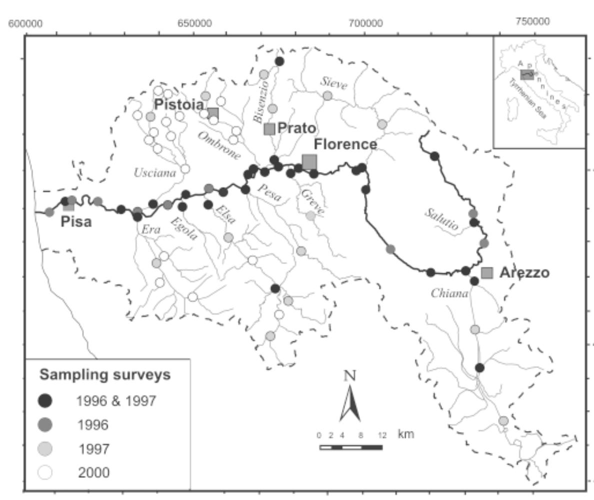

Fig. 1. Map showing the Arno river catchment and its major tributaries, the largest towns, and the sampling stations subdivided according to the sampling year. Coordinates refer to UTM32T (ED50) system.

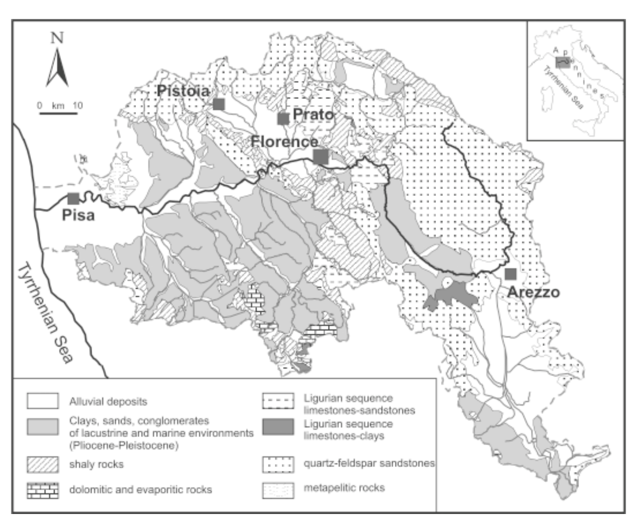

Fig. 2. Schematic lithologic map of the Arno catchment (modified from Bortolotti et al., 1987).

Table 1. Sampling sites and year of survey for 73 stations in the Arno river catchment. Tributaries are listed from West to East in the upper portion of the Arno basin, and from east to west in the southern portion. Coordinates refer to UTM32T (ED50) system.

River	Sample	Locality	East	North	1996	1997	2000
Arno	A01	Cant. La Vallentina	607192	4837405	+		
	A02	Pisa Ovest	611696	4840498	+	+	
	A03	Pisa Est (Porta Fiorentina)	613626	4840838	+		
	A04	Caprona	621041	4840453	+	+	
	A05	S. Giovanni alla Vena	627702	4838184	+		
	A06	Ponte alla Navetta	632389	4837560	+		
	A07	Monte Calvo	641023	4839476	+		
	A08	S. Croce sull'Arno	646091	4842473	+	+	
	A09	Fucecchio	646091	4842473	+		
	A10	Empoli	656894	4843148	+	+	
	A11	Camaioni	664004	4848209	+	+	
	A12	Ponte a Signa	668761	4848897	+	+	
	A13	Nave di Badia	672667	4850399	+	+	
	A14	Firenze Ovest	678452	4849977	+	+	
	A15	Firenze Est	682801	4848353	+	+	
	A16	Rosano	694928	4849301	+	+	
	A17	Rignano sull'Arno	697644	4843819	+	+	
	A18	S. Giovanni Valdarno	704728	4826811	+	+	
	A19	Laterina	716230	4820156	+	+	
	A20	Ponte a Buriano	726240	4820629	+	+	
	A21	Subbiano	731498	4828512	+		
	A22	Rassina	728365	4836978	+		
	A23	Stia	717344	4853388	+	+	
Usciana	II	loc. Cateratte	636829	4839725	+	+	
	II-1	3 km N Pescia	636103	4864706		+	
	USC01	Serravalle pistoiese	643317	4864650			+
	USC02	Chiesina Uzzanese	636345	4859986			+
	USC03	Villa Basilica Collodi	632605	4865278			+
	USC04	San Salvatore	635815	4856827			+
	USC05	Ponte Buggianese	638383	4856245			+
	USC06	Massa-Cozzile	640642	4863037			+
	USC07	Albinatico Montecatini	641984	4859350			+
	USC08	Pescia	635726	4866326			+
	USC09	Ponte di Castelvecchio	637016	4870898			+
	USC10	Ponte di Sorana	637918	4869586			+
	USC11	Pescia	636106	4865647			+
	USC12	Massarella Ponte a Cappiano	644809	4850148			+

River	Sample	Locality	Est	North	1996	1997	2000
Ombrone	VI	Carmignano	665532	4849761	+	+	
	VI-1	P.te S. Felice	651852	4870613		+	
	32	p.te Stella a N di Quarrata	659800	4858700			
	34	p.te dei Baldi loc. Ferriccia	660640	4860620			
	45	p.te loc. Candegli (NE Pistoia)	656240	4869100			
	38	p.te a S di Bonelle	654160	4863680			
	40	S. Pietro in Vincio (O Pistoia)	651414	4865563			
Bisenzio	VII	Valico	671474	4852368	+	+	
	VII-1	Cantagallo	668526	4876753		+	
	VII-2	Le Briglie	671005	4866994		+	
	27	R. Meo - S.Quirico	672980	4880540			
Sieve	IX	Pescaia di S. Francesco	696570	4850142	+	+	
	IX-1	San Piero a Sieve	686710	4870671		+	
	IX-2	Dicomano	702329	4862513		+	
Salutio	XI	Tulliano/La Montanina	728587	4834451	+	+	
Chiana	X	Pratanico/S. Leo	728727	4817703	+	+	
	X bis	Pratanico/S. Leo	728727	4817703		+	
	X-1	S. Adele	737047	4777741		+	
	X-2	Foiano della Chiana	730235	4792914		+	
	X-3	Montagnano	728896	4803852		+	
Greve	VIII	Ponte a Greve	676183	4848536	+	+	
	VIII-1	Il Ferrone	681903	4836367		+	
Pesa	V	Montelupo Fiorentino	662832	4844303	+	+	
	V-1	Sambuca	679176	4826272		+	
Elsa	IV	Ponte a Elsa	652590	4839544	+	+	+
	IV-1	Castellina in Chianti	675487	4812042		+	+
	IV-2	Collalto	670366	4801982		+	+
	IV-3	Ulignano	658374	4830161		+	+
	IV-4	Certaldo	665284	4823668			+
	IV-5	Poggibonsi	671753	4815568			+
	IV-6	Gracciano	672874	4808128			+
Egola	III	Ponte a Egola	645217	4838966	+	+	
Era	I	Pontedera	632388	4836031	+	+	+
	I-1	bivio per Peccioli	638534	4822840		+	+
	I-2	Vicarello	648173	4813162			+
	I-3	Sterza	638758	4817283			+
	I-4	Roglio	639947	4824817			+

the equivalent of 1.4×10^6 inhabitants. In addition, the Bisenzio river receives domestic untreated waste waters from the Vaiano locality and those from the northern part of Florence through the Macinante Canal. All the domestic water contributions to the Ombrone river are treated. On the whole, TDS values increase downstream from 290 to 499 mg/l in the Bisenzio river and from 332 to 1057 mg/l in the Ombrone river (Cortecci *et al*., 2002).

(3) The Usciana river and some minor tributaries receive discharges (95% depurated) from many tanneries in the Santa Croce and Pisa areas, which corresponds to a pollution load of 3.2×10^6 inhabitants. In this same area, there are also numerous paper-mills which release their depurated waste waters to the Usciana tributary. TDS values in the Usciana river increase from 309 mg/l to 2179 mg/l roughly 40 km before the confluence with the Arno river (Cortecci *et al*., 2002).

Upstream from Florence, pollution in the Arno river is basically related to contributions from the Chiana river, which receives waste water from galvanic plants processing gold in the Arezzo district and untreated effluents from intensive agricultural-zootechnic activities along the Val di Chiana. The galvanic plant caused a mercury anomaly in the stream sediments in the area, as reported by Dall'Aglio (1971). At about 30 km from the confluence, TDS values increase (from 552 to 736 mg/l) and then slightly decrease (684 mg/l).

The main conclusions of the hydrogeochemical surveys of the waters from the Arno catchment performed by Bencini and Malesani (1993) and Cortecci *et al*. (2002) are (1) Chiana, Bisenzio, Ombrone and Usciana tributaries considerably influence the chemical composition of the Arno river, contributing valuable amounts of Na (±K) chloride and sulphate of anthropogenic origin, (2) Sieve, Pesa, Elsa, Egola and Era tributaries dilute Na and Cl into the Arno river by adding waters rich in Ca (±Mg) and HCO_3 (Sieve, Egola and Pesa) and SO_4 (Elsa and Era). The chemical composition of the latter tributaries appears to be basically determined by the lithology of the feeding sub-basins.

Sediment features

The mineralogy and heavy metal content of the suspended and bedload sediments from the main river Arno and its tributaries were investigated by Bencini and Malesani (1993). The mineralogy mainly consists of quartz (9 to 44%), feldspars (7 to 32%), calcite (1 to 38%) and clay minerals (11 to 80%), the latter being represented by vermiculite, chlorite, illite, kaolinite. Analysed metals in these sediments (Cu, Pb, Zn, Ni, Cr, Mn) should be predominantly trapped within the mineral structures (92 to 99%), especially in the clay minerals, and to a lesser extent, in metal-organic complexes (0.6 to 8%) and adsorbed on clay particles (0.1 to 0.4%).

Sampling and Analytical Procedures

Sampling campaigns were conducted during low-flow conditions, to ensure maximum recovery of the sediments. Most of the bed sediments were sampled by dredging the centre of the rivers. When cobbles and boulders were present on the river bed, sediments were directly collected by hand in the active channel. Sediments were wet-sieved in the field to <80 mesh (177 μm), according to the method of Rose *et al*. (1979). 500 grams of sediments were collected and analyzed for each site. The location of the sampling sites is reported in Fig. 1 and Table 1, subdivided according to the period of sampling. Major and trace elements were determined by X-ray fluorescence spectrometry on pressed powered pellets using a Philips PW 1480 automated spectrometer following the methods of Franzini *et al*. (1972, 1975), Leoni and Saitta (1976) and Leoni *et al*. (1982) for matrix corrections. Long term reproducibility for major elements was generally better than 7%, whereas for trace elements, it was on average better than 10%. Absolute accuracy relative to certified values or International Reference Material was generally within the reproducibility range (e.g., Dinelli *et al*., 1996). Analytical homogeneity between batches was checked by duplicate analysis of selected samples and found to be better than 5%.

Mineralogical analyses were performed with a Philips PW 1130 (Cu Kα radiation Ni filtered) by pressing powders into alumina holders in order to avoid preferential orientation of sheet-silicates. Corrections for differential intensity response were made according to the methods proposed by Cook *et al*. (1975) to provide a semi-quantitative estimation of mineral abundances based on XRD scans. The analyses were performed on the samples collected during the 1997 survey, using the same powders prepared for the chemical analysis.

Organic carbon and nitrogen were determined in the specimens collected in 1997 using a Carlo Erba EA 1110 CHNS analyser, with a reproducibility better than ±0.1%. Carbonate was removed from the sediments with hydrochloric acid within a Ag-capsule and then heated at 70°C.

The relationships among the various chemical elements were investigated through hierarchical cluster analysis (complete linkage as cluster method, Pearson correlation as similarity measure) using a SPSS® statistical package.

Results and Discussion

The range of composition of the stream sediments sampled in November 1996 and June–July 1997 for the Arno river and its tributaries is reported in Table 2, along with the chemical composition of additional sediments from selected tributaries (Elsa, Era, Ombrone and Bisenzio)

Table 2. *Range of chemical composition of the stream sediments sampled in the Arno river catchment between 1996 and 2000*

	Arno river				Tributaries					
	1996		1997		1996 trib		1997 trib		2000 trib	
(wt%)	min	max	min	max	min	max	min	max	min	max
SiO_2	46.51	67.47	46.37	75.03	37.87	60.95	36.25	75.03	32.36	58.31
TiO_2	0.48	0.97	0.39	0.63	0.48	0.73	0.33	0.73	0.42	0.78
Al_2O_3	10.65	17.19	10.11	16.81	10.88	17.54	7.97	19.13	9.11	18.53
Fe_2O_3	3.31	6.15	2.47	5.92	3.80	6.63	2.78	6.76	3.49	7.12
MnO	0.08	0.16	0.07	0.12	0.08	0.42	0.07	0.42	0.09	0.25
MgO	2.13	4.14	1.44	4.03	2.14	3.39	1.90	5.71	2.29	5.68
CaO	2.31	10.61	2.13	10.11	2.63	19.87	1.46	19.87	1.97	27.20
Na_2O	0.93	2.90	1.00	4.24	0.43	1.41	0.46	4.24	0.23	1.28
K_2O	1.48	2.16	1.64	2.16	1.19	1.99	1.05	2.25	1.09	2.61
P_2O_5	0.14	0.36	0.10	0.31	0.09	1.09	0.07	1.09	0.09	0.78
LOI	6.08	17.28	3.98	17.43	9.57	26.22	7.76	28.46	11.37	24.18
(ppm)										
Sc	12	22	9	23	15	30	12	30	10	28
V	63	133	45	118	66	123	57	154	64	150
Cr	121	787	102	195	104	430	69	592	99	300
Co	7	21	<3	21	5	24	<3	31	52	5
Ni	23	117	40	110	55	99	50	298	60	237
Cu	21	98	3	88	25	213	14	213	25	100
Zn	55	224	41	250	79	949	88	1054	61	480
Ga	8	19	4	14	9	18	5	18	6	25
As	<3	9	<3	7	<3	13	<3	13	<3	16
Rb	63	150	66	144	76	139	63	168	58	154
Sr	121	274	118	238	112	328	99	358	104	696
Y	17	57	15	31	20	30	15	32	143	1
Zr	118	4236	120	439	114	258	91	439	82	279
Nb	7	14	6	16	7	15	7	16	10	18
Ba	311	498	280	525	307	582	190	949	188	1318
La	22	76	12	36	22	44	17	44	19	40
Ce	35	152	39	74	41	69	35	75	27	86
Pb	21	56	16	55	21	82	13	82	10	98
Th	5	35	<3	9	<3	15	<3	15	<3	15
S	110	1330	60	1480	200	4090	180	4090	640	4420

sampled in July 2000 (the complete data set is available upon request from the authors).

Element distribution in stream sediments is expected to show slight seasonal variations (Chork, 1977), and this can be evaluated through the relative standard deviation of the mean of the measurements (Birch *et al*., 2001a, b). The repeated sampling at the same station in the Arno catchment allowed the recognition of systematic variations of the chemical composition for only six stations (A17, A15 and A11, Arno; IX, Sieve; V, Pesa; II, Usciana). The differences were ascribed to marked textural difference, as indicated by the large relative standard deviations of SiO_2 (up to 12%), Al_2O_3 (up to 16.5%) and Zr/Rb (up to 56%), despite the fact that the sediments had been sieved to reduce the uncertainty related to grain size (see Birch *et al*., 2001b, for a discussion of the problem). Textural differences are related to different hydrological conditions during the sampling periods, namely the reduction of flow discharge particularly evident in the summer 1997 survey, which produced a relative enrichment in the fine-grained fraction of the sediments in some stations. However, in the following discussion of the spatial distribution of the elements, mean values from repeated sampling will be used.

General mineralogy of the sediments

The main mineral phases in the sediments were mica, chlorite, sheet-silicates, quartz, feldspars, plagioclases and calcite (Table 3). In some samples, smectite, kaolinite, dolomite were also present, whereas halite was only observed in the sample A02 at Pisa. According to the lithological distribution in the drainage basin, sheet silicates are abundant in the tributaries of the southern flank: Era, Egola, Elsa all contribute to relatively large quantities of these minerals, but the largest contributor is the Chiana. In addition, Ombrone and Sieve, two northern

Table 3. Semi-quantitative estimation of mineral abundances based on XRD analysis performed on the samples collected during the 1997 survey

	mica	chl	clay	sm	kaol	qz	kfeld	cc	plg	dol	hal
A02	*	*	**	—	—	***	*	*	*	—	**
A05	tr	tr	tr	tr	—	****	**	*	***	—	—
A08	*	tr	tr	—	—	****	*	*	***	—	—
A10	tr	tr	*	—	—	****	—	*	***	—	—
A11	*	tr	*	tr	—	****	**	*	***	—	—
A12	tr	tr	**	tr	—	****	—	**	**	—	—
A13	*	tr	tr	tr	tr	***	*	*	***	—	—
A14	*	*	*	—	—	***	*	*	**	—	—
A15	tr	tr	*	—	—	****	—	**	**	—	—
A16	tr	tr	*	—	—	****	—	*	**	—	—
A17	na	na	na	na	na	na	na	na	na	na	na
A19	tr	tr	**	—	—	*****	—	*	*	—	—
A20	*	tr	tr	—	—	***	*	*	***	—	—
A23	**	*	*	—	—	****	—	*	**	—	—
I	*	tr	*	—	—	***	*	**	*	tr	—
I-1	tr	tr	*	—	—	**	—	***	*	**	—
II	tr	tr	*	—	tr	****	*	tr	***	—	—
II-1	tr	tr	*	tr	—	*****	tr	tr	**	—	—
III	*	tr	*	—	tr	****	—	*	**	—	—
IV	tr	tr	*	—	—	****	tr	**	**	tr	—
IV-1	tr	tr	*	—	—	****	tr	***	*	—	—
IV-2	tr	tr	**	—	—	*****	—	**	*	—	—
IV-3	tr	tr	*	—	—	****	tr	**	*	—	—
V	tr	tr	*	tr	tr	***	*	***	*	tr	—
V-1	tr	tr	*	—	—	***	*	***	**	—	—
VI	*	tr	**	—	—	****	—	*	**	—	—
VI-1	*	tr	*	—	—	**	—	*****	*	—	—
VII	*	tr	*	—	—	**	*	**	**	—	—
VII-1	*	tr	*	—	—	****	*	tr	***	—	—
VII-2	*	tr	**	—	—	***	tr	**	*	—	—
VIII	tr	tr	*	—	—	*****	tr	*	*	—	—
VIII-1	tr	tr	*	tr	—	*****	—	**	**	—	—
IX	tr	tr	**	—	—	***	—	**	**	—	—
IX-1	*	tr	*	—	—	*****	—	tr	**	—	—
IX-2	na	na	na	na	na	na	na	na	na	na	na
X	*	tr	*	—	—	***	**	*	**	—	—
X bis	tr	tr	*	—	—	****	—	**	*	—	—
X-1	*	tr	**	—	—	****	—	**	tr	—	—
X-2	*	tr	***	—	—	****	—	tr	*	—	—
X-3	tr	tr	*	—	—	****	—	*	**	—	—
XI	*	tr	*	—	—	*****	—	*	**	—	—

—: not found; na: not analysed.
*tr: traces; *: detected; **: present ***: significant; ****: abundant; *****: dominant.*
mica: micas; chl: chlorites; clay: sheet silicates; sm: smectite; kaol: kaolinite; qz: quartz; kfeld: K-feldspars; cc: calcite; plg: plagioclases; dol: dolomite; hal: halite.

tributaries, transport large amounts of sheet silicates. The Arno river does not seem to be greatly influenced by all these inputs, but sheet silicates were observed in the sediments at station A19 (Laterina), which is located upstream of a dam, at station A12 (Ponte a Signa) and at station A02 (Pisa W).

Sediment geochemistry: general considerations

A schematic picture of the main geochemical features of the stream sediments of the Arno catchment can be obtained by the inspection of the R-mode cluster analysis dendrogram of the whole data set (Fig. 3a). The analysis outlined five main groups of elements:

Group I - includes Na_2O, SiO_2, Zr and to a lower degree Ba. It reflects the abundance of quartz, plagioclases, and some heavy minerals, such as zircon. According to the grain size of the samples, this chemical association can be related to the fine sand and coarse silt fraction of

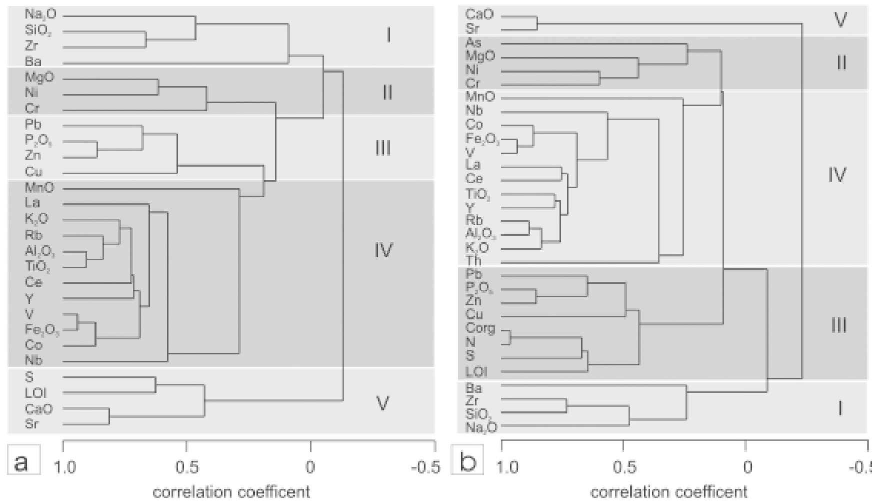

Fig. 3. Dendrograms of R-mode cluster analyses: a) cluster analysis carried out on the complete data base; b) cluster analysis on the data from the 1997 survey which also include Corg and N (group numbering as in Fig. 3a).

each sample. The presence of Ba in this group is explained by its affinity for plagioclases, but the low similarity degree suggests that barium is also carried by other phases (e.g., barite).

Group II - includes MgO, Ni and Cr, which reflect the "ultramafic" fraction of the sediments. They originate from the direct erosion of ophiolitic sequences and from the recycling of sedimentary rocks enriched in ultramafic debris, such as the Macigno Formation (Dinelli *et al.*, 1999a) which occurs as outcrops in the northern part of the catchment.

Group III - includes Pb, P_2O_5, Zn and Cu. These elements are geochemically quite different and in this sense, the group can be interpreted as "pollution related". In fact, all these elements are widely used in technological and agricultural activities (Cooper and Thornton, 1994). In addition, the presence of phosphorus might indicate a common source (phosphate fertilizers, Adriano, 1986) or an important control of organic compounds on metal dispersion.

Group IV - includes MnO, La, K_2O, Rb, Al_2O_3, TiO_2, Ce, Y, and a sub-group formed by Co, Fe_2O_3 and Nb. All these elements can be ascribed to the fine-grained siliciclastic fraction, dominated by clay minerals. A slight compositional difference in sheet silicates might control the decoupling between Al_2O_3 and Fe_2O_3. The cluster of Ti, La, Ce, Y and Nb suggests that a relatively fine grained fraction of the sediment is associated with various types of accessory minerals that concentrate these elements.

Group V - includes S, LOI, CaO and Sr. Ca, Sr and LOI are controlled by carbonate minerals, whereas S is related both to sulphate minerals and to organic matter present in the sediments, as discussed in the following sections.

Similar trends are obtained if only the 1997 samples are taken into account. In this case, Corg and N data are also included in the cluster analysis (Fig. 3b). Corg and N appear to correlate with LOI and S, as well as with Pb, P_2O_5, Zn and Cu. Once more, this peculiar geochemical association can be ascribed to a generic anthopogenic source, that likely includes several distinct contributions within the catchment, e.g.: various kinds of industrial activities, agricultural practices and sewage discharges, as discussed in greater details in the following sections.

Stream sediments: relationship with bedrock geology

Stream sediments generally reflect the mineralogical composition and the presence of outcrops in the drainage basin, upstream of the sampling sites (Rose *et al.*, 1979). In order to evaluate this contribution, the chemical data from the present study were compared to those from the major geological units in the basin. Data from the sandstones of the Macigno Formation (Dinelli *et al.*, 1999a) and from the sandstones and shales of the Cervarola Formation (Andreozzi *et al.*, 1997; Dinelli *et al.*, 1999a) were considered. These formations are predominant in the north-eastern part of the basin. Additional unpublished data (from the authors) on the marine Pliocene clays outcropping in the southwestern part of the basin are also included in the plots, as a reference for the southern tributaries.

For some elements, there is a marked grain-size effect in the reference data, especially in the SiO_2, CaO, K_2O vs. Al_2O_3 plots (Fig. 4). In these cases, the reference data on sandstones are clearly separated from the other ones due to the higher quartz and feldspars and lower carbonate contents with respect to the more fine-grained reference rocks. In the MgO vs. Al_2O_3 plot (Fig. 4), the

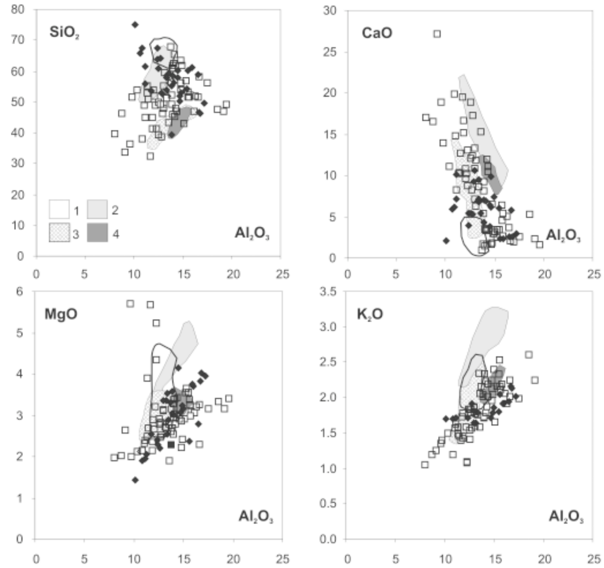

Fig. 4. Scatter-plots of SiO_2, CaO, MgO and K_2O vs. Al_2O_3 for all the samples collected in the Arno catchment. Diamonds refer to stations of the Arno river, squares are the stations in the tributaries. The fields represent data from the literature corresponding to major geological units in the Arno basin (Andreozzi et al., 1997; Dinelli et al., 1999a and unpublished data from the Authors): 1 - sandstones of the Macigno Fm.; 2 - sandstones of the Cervarola Fm.; 3 - shales of the Cervarola Fm.; 4 - Pliocene clays.

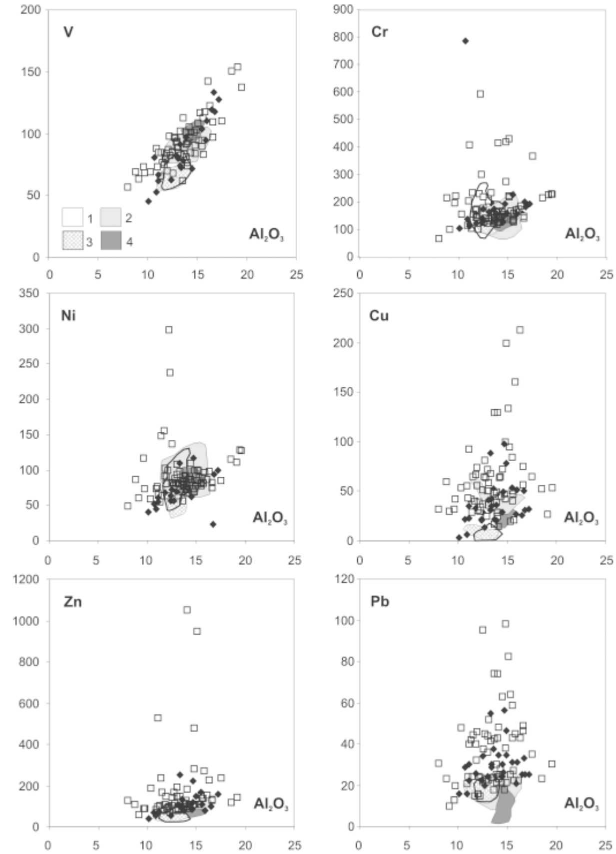

Fig. 5. Scatter-plots of V, Cr, Ni, Cu, Zn and Pb vs. Al_2O_3 for all the samples collected in the Arno catchment. Symbols as in Fig. 4.

magnesium enrichment in the sandstones of the Macigno and Cervarola Formations has been related to the abundance of the ultramafic fraction in these clastic rocks (Dinelli *et al.*, 1999a).

The data on the stream sediments display a wide dispersion, greater in the tributaries than in the Arno river, for Al_2O_3 and the other elements (Figs. 4 and 5). This reflects the larger geological variability of the tributaries when compared to the Arno river, which acts as an homogenizing container. In general, a good overlap between stream sediments data and major geological units was observed (Figs. 4 and 5); only a few low (<10.5 wt%) and high (>17.0 wt%) Al_2O_3 data fell outside the rock fields, which is consistent with the carbonate-rich and clay-rich composition of some sediments. MgO is enriched in some samples, due to the influence of ophiolitic rocks which are widespread in the central portion of the basin (Angelone *et al.*, 1993; Vaselli *et al.*, 1997) and to the relative abundance of ultramafic rocks in the upper portion of the clastic Macigno and Cervarola formations (Dinelli *et al.*, 1999a). With respect to the heavy metals (Fig. 5), the reference rock data can be viewed as background values, and all data show a high degree of clustering and overlapping. A general positive correlation exists between metals and Al_2O_3 in the stream sediments despite the presence of some anomalous sediments. The number of anomalous samples progressively increases according to the sequence Ni, Cr, Zn, Pb and Cu, which suggests increasing contributions of elements from anthropogenic source(s). Based on the background values (Me′) calculated by the regression of heavy metal data (Me) against Al_2O_3, after removing the outliers (Hilton *et al.*, 1985), the metal enrichment factor [EF = (Me – Me′)/Me] exceeds 1 in three stations for Ni (EF up to 3.4), in six stations for Cr (EF up to 6), in ten stations for Zn (EF up to 9.5), in seventeen stations for Pb (EF up to 3.6) and in twenty-five stations for Cu (EF up to 5.4). Almost all the metal anomalies occur in the tributaries, whereas low concentration values generally occur in the Arno river sediments.

Spatial distribution of elements

The geochemical maps were designed using all the stations available and the data from all sampling periods. In the case of multiple data from the same station, a mean value was calculated and plotted. Class subdivision was based on the percentile values (10, 25, 50, 75, 90), thus

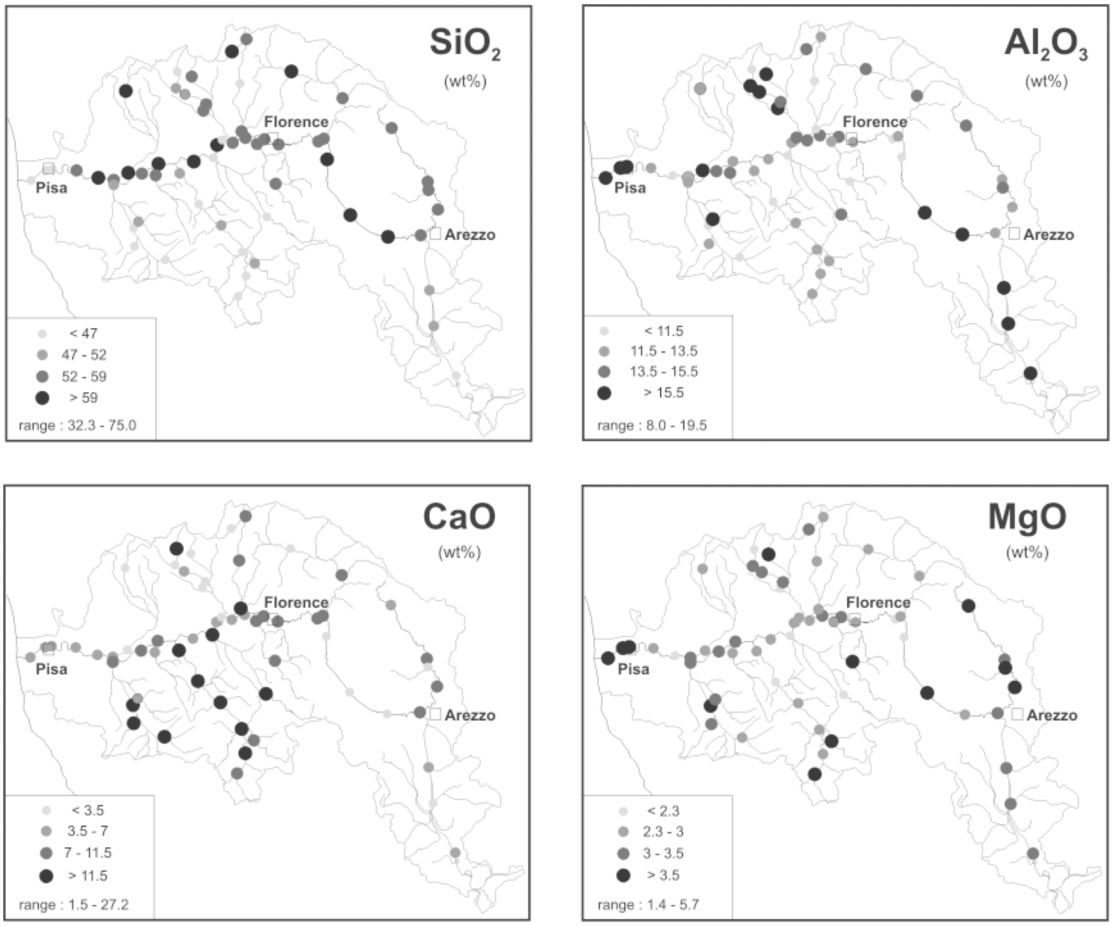

Fig. 6. Geochemical maps of SiO_2, Al_2O_3, CaO and MgO for the Arno catchment. When multiple data exist for one station, the mean value is calculated and plotted. Class intervals refer to 25, 50, 75, 90 percentile of the distribution.

emphasizing the occurrence of higher values.

Maps shown in Figs. 6 and 7 delineate some significant geochemical features related to the geological setting of the Arno river catchment. SiO_2 is generally high in the Arno river, with the exception of the station close to the mouth of the river, whereas it is markedly depleted in the southern tributaries. CaO follows the opposite distribution, high contents are concentrated in the southern tributaries where Pliocene-Pleistocene calcareous sands and marls outcrop. Al_2O_3 contents are generally intermediate in the main portion of the Arno river, but high contents are observed in the stations close to the mouth of the river and in the Chiana tributary, where clay-rich sediments occur in the drainage basin. This is also consistent with V distribution (Fig. 7). Interestingly, high MgO values are observed in the Era, Elsa and Pesa tributaries, which are also related to high Cr and Ni contents (Fig. 7). The occurrence in the sub-basins of scattered ophiolitic masses, particularly serpentinites, explains these anomalies. On the contrary, Ni and Cr do not correlate to MgO in the Ombrone and Bisenzio tributaries. In these rivers, the high Cr values are related to the presence of tanneries and textile factories nestled around Pistoia and Prato. The same sites are also anomalous for Cu, Zn and Pb, all these elements being related to anthropogenic source in the heavily urbanized surroundings of Florence. Florence itself also strongly influences the distribution of these metals in the Arno river, but their concentrations seem to decrease to normal values at about 20 km downstream from the town. High Pb values are also observed in the Elsa and Usciana rivers, as a result of the major villages and industrial settlements in the area.

The maps of P_2O_5, S, Corg and N (Fig. 8) display spatial features consistent with those of the heavy metals, as indicated by the dendrogram of Fig. 3b. Major anomalies occur in the Arno river downstream of Florence and in the Bisenzio and Ombrone tributaries, not only at the closing of the basin but also in the upper section of the rivers. These anomalies correspond to the high urban density and to the presence of many industrial settlements. Anoma-

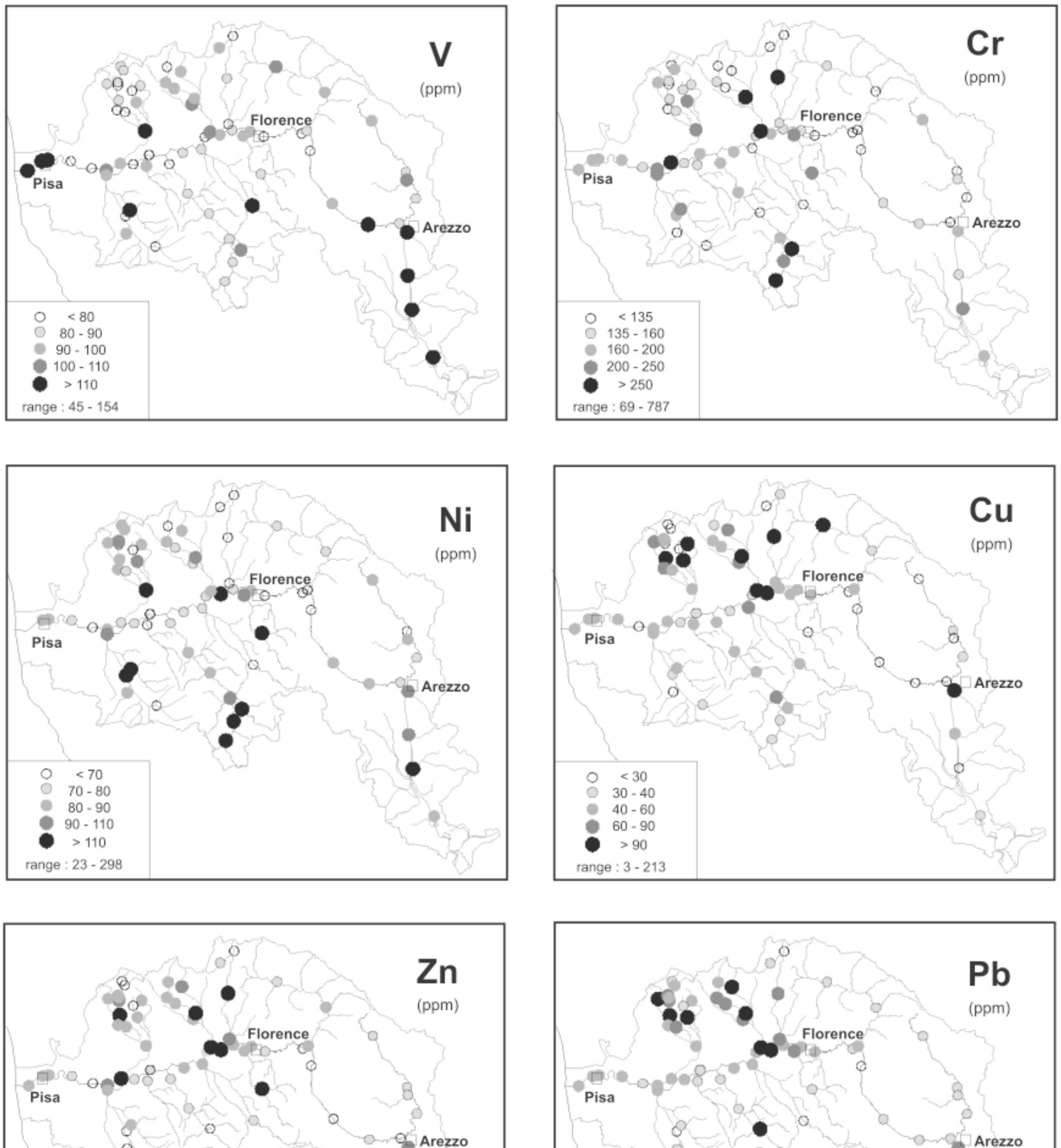

Fig. 7. Geochemical maps of V, Cr, Ni, Cu, Zn and Pb in the Arno river catchment. Data handling is the same as in Fig. 6; class subdivision refer to 10, 25, 50, 75, 90 percentile of the distribution.

lies of Corg and N also occur in the Chiana valley, south of Arezzo, where agriculture is widespread and flourishing. N enrichments might also be related to the wash up of excess fertilizers into the river.

Relatively high sulphur contents characterize the southern tributaries which drain the recent marine deposits and scattered outcrops of marine evaporites, both Messinian and Triassic (Dinelli *et al*., 1999b).

With respect to phosphorus, several anomalous areas are recognized, partially consistent with those outlined

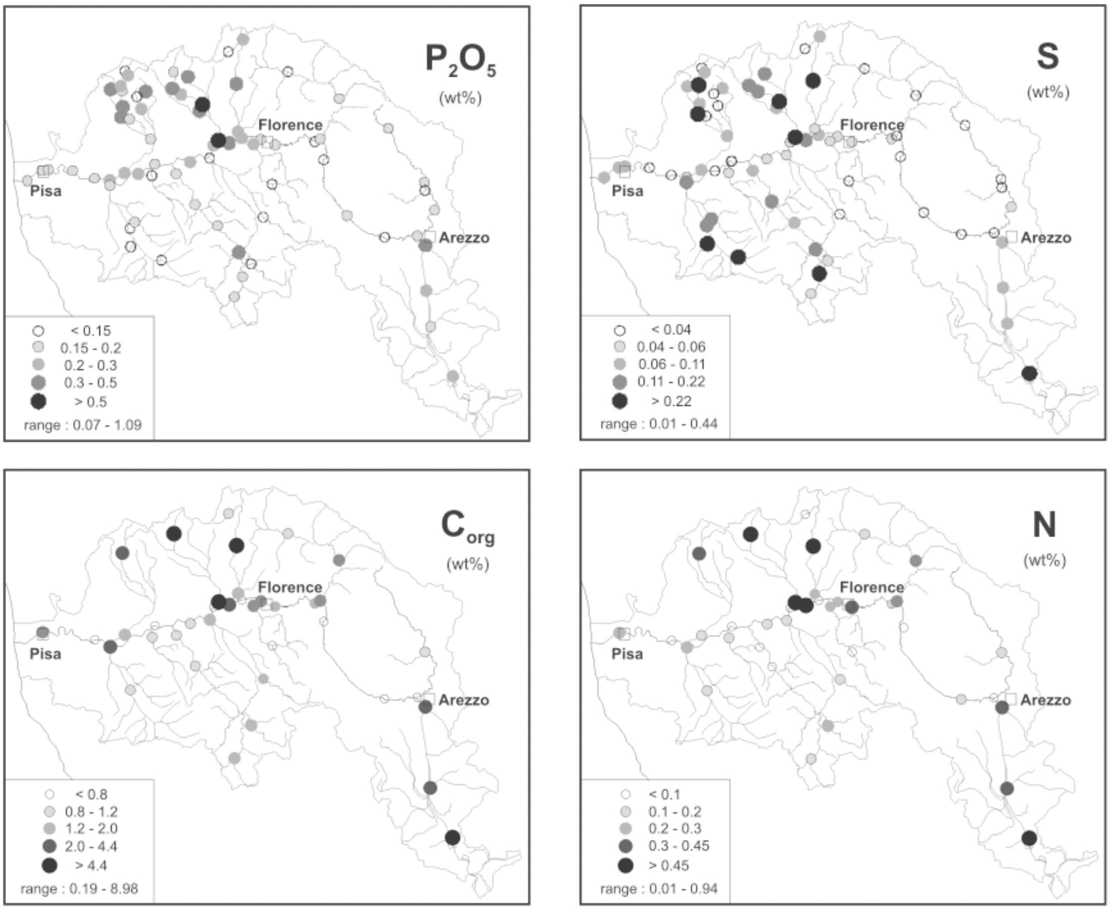

Fig. 8. Geochemical maps of P_2O_5, S, Corg and N in the Arno river catchment. Only the 1997 samples are represented; class intervals are the same as in Fig. 7.

for Corg, N and some heavy metals. In the area north of Florence, between Pistoia and Prato, many plant and flower nurseries are operating and fertilizers might be the major source of phosphorous to the river. High P_2O_5 contents are also observed in the Chiana sediments (0.26 to 0.52 wt%) where important sources of phosphorous might be from domestic effluents and fertilizers used in the intensive and widespread farming activity in the catchment.

Organic carbon and nitrogen

The Corg and N data from the 1997 survey of the Arno sediments show variations between 0.19 and 2.53 wt% and 0.01 and 0.45 wt%, respectively, whereas in the tributaries wider concentration ranges are observed: 0.65–8.98 wt% for Corg and 0.06–0.94 wt% for N. There is an excellent relationship (r = 0.91) between C and N (Fig. 9), with an intercept close to zero (0.03), suggesting that the N content of the sediments is mainly controlled by organic sources. Most measured C/N ratios are in the range 3.2–12.4 (C/N average 8.7), considerably lower than those expected for pristine terrestrial organic matter (14 to 30; Muller, 1977), but there are some exceptions, i.e., the ratios of 13.3 and 19.0 for the Arno sediments at Rignano (A17) and Rosano (A16) localities before Florence. However, the low N content of the sediments at the Rosano station (0.01 wt%—near the detection limit) likely affected the unusually high C/N ratio value of that site. On the whole, the low C/N values of the Arno catchment are consistent with those of various river sediments (world rivers: C/N ~ 9, Meybeck, 1982; Bengal basin: 2–11.4, Datta *et al.*, 1999; Po river: 6.6–11.9, Vignati *et al.*, 2003) and indicate a predominantly mixed origin of organic matter throughout the basin. They reflect both the soil contribution to the river sediments (Meybeck, 1982), the enhanced degradation of the organic matter (Datta *et al.*, 1999), which favours the breakdown of C-C bonds rather than C-N bonds, and the presence of urban sewage inputs, with typical low C/N ratios (Magesan *et al.*, 2000; Vignati *et al.*, 2003). Urban sewage is probably important for the samples A15 and A12, collected in the Arno river east of Florence and downstream from the Bisenzio river confluence, respectively. On the other hand, the ag-

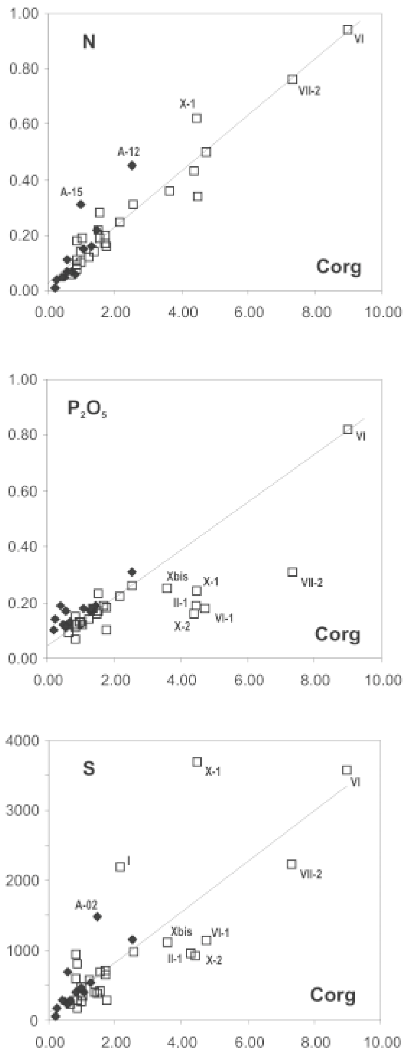

Fig. 9. Scatter-plots of N, S and P_2O_5 vs. Corg for the samples collected in the Arno river catchment. In each plot the correlation line represents the main trend (see text). Symbols as in Fig. 4.

ricultural contribution is significant for the sample X-1 from Chiana valley and for some other samples distributed above the regression line (Fig. 9). However, according to the intersection value of the regression line close to zero, the influence on the C/N ratio by nitrogen from inorganic sources (e.g., fertilizers) appears generally small, in spite of the widespread use of nitrous fertilizers (>50.000 ton/year) which represent 52% to total nitrogen load to the Arno river water (Mazzoni, 2001).

The relationships between organic carbon, phosphorous and sulphur are slightly more complex. The Corg-P_2O_5 co-variation (Fig. 9) is very good (r = 0.96), if we exclude six samples from Usciana (II-1), Ombrone (VI-1), Bisenzio (VII-2) and Chiana (Xbis, X-1, X-2) tributaries enriched in Corg (3.58–7.32). The intercept (0.06) is consistent with P_2O_5 values of the catchment rocks (0.08–0.17 wt%). This suggests an anthropogenic phosphorus contribution with a potential organic origin from urban and animal waste effluents. The samples that were excluded are scattered away from the main trend and are plotted in the area of lower P_2O_5/Corg ratios.

The S-Corg regression line (Fig. 9) for the Arno river and its tributaries is good (r = 0.79), indicating that sulphur in the sediments is mainly related to organic matter. However, appreciable inorganic sulphur is also present, as supported by the intersection value higher than zero (166 ppm). In the Arno river, large positive deviations in the sulphur content may be attributed to the presence of considerable amounts of inorganic sulphate and/or biogenic sulphide compounds in the sediments, such as in the Pisa Ovest (A02) where there is seawater ingression (as a sulphate source), and in the Nave di Badia (A13), likely from iron sulphide occurrence (Cortecci *et al.*, 2002). In the tributaries, large positive deviations for the samples from the Chiana (X-1) and Era (I) rivers are probably due to sulphate particles from fertilizers and natural sources, respectively. The negatively deviating samples also display low P_2O_5/Corg ratios.

Effect of organic matter on heavy metal distribution

The relationships between selected heavy metals for the 1997 sampling survey (Cu, Zn, Pb) and Corg are shown in Fig. 10, along with those for Al_2O_3. Irrespective of the subdivision between tributaries and major rivers, it appears that copper is well correlated (r = 0.81) to the organic matter present in the sediment and that fine grained aluminosilicate minerals are only secondary in controlling Cu distribution. Some sites deviate from the general trend (and were not included in the regression calculation): those particularly rich in Cu are located in Sieve (IX-1) and Chiana (X) tributaries far from any major industrial areas, where agricultural activities are particularly widespread and copper anomalies might originate from chemicals used in various farming practices. Those richer in Corg are instead located in the Ombrone (VI, VI-1) and Bisenzio (VII-2) rivers, already mentioned for their dense and diversified industrial activities. Such samples along with some from Chiana (X-1, X-2) and Usciana (II-1) plot on a line nearly parallel to the main trend line, suggesting that in these samples the excess of organic matter is not an important Cu carrier.

With respect to the Zn behaviour, it appears to be similar to one observed for copper, both show a good correlation at low Zn and Corg values and for low metal content in the samples with intermediate Corg content (Xbis, X-1, X-2, II-1, VI-1). The samples rich in Corg (VI, VII-2) are also enriched in Zn, whereas the strong anomalies found for Cu (IX-1, X) at low Corg disappear. No signifi-

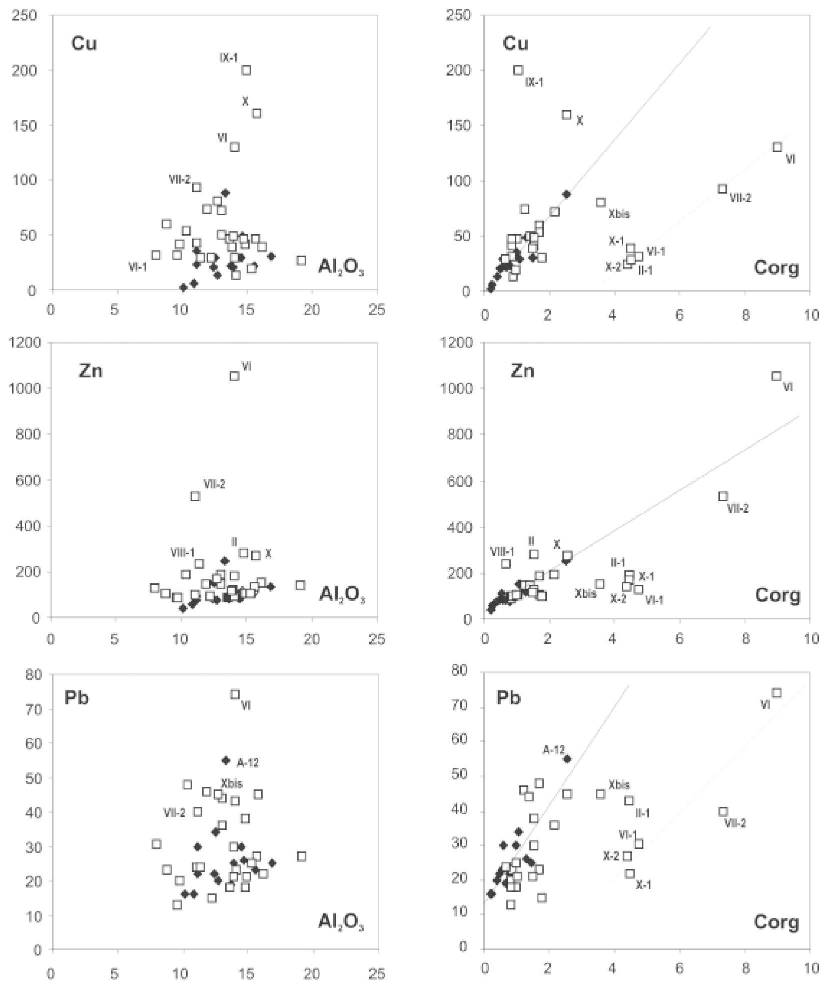

Fig. 10. Scatter-plots of selected heavy metals (Cu, Zn and Pb) vs. Corg compared to those vs. Al_2O_3. In each plot, the full line represents the main trend, the dotted line refers to samples with excess of organic matter (see text). Symbols as in Fig. 4.

cant correlation (r = 0.08) exists between Zn and Al_2O_3, suggesting a scarce control of clay on Zn distribution. This is also true for Pb, since the samples in the Pb-Al_2O_3 plot (Fig. 10) are widely scattered. On the other hand, the Pb-Corg correlation is rather good (r = 0.67), if we exclude the samples with intermediate and high Corg content. The control of organic matter on Pb distribution is significant at low Corg values. For the samples with Corg values higher than 3.5%, the excess of organic matter does not appear to be an important Pb carrier, as observed for copper and in part for zinc, although the highest Pb content occurs in the Corg richest sample (VI).

Conclusions

The detailed chemical analysis of the stream sediments of the Arno river and its catchment indicates that sediment features reflect the mineralogical and chemical composition of the rocks in the drainage basin, but anthropogenic pollution is an important contributor of some heavy metals (Cu, Zn, Pb) and organic matter. Multiple sampling performed at some stations showed very slight seasonal variations, which are caused by different hydrologic conditions.

The chemical data display a wide dispersion, greater in the tributaries than in the Arno river, which acts as a homogenizing container, but in general a good overlap exists between the stream sediments and the major geological units. SiO_2 is high in the Arno main course and in the northern tributaries, where sandstones of various formations are present, but it is depleted in the southern ones. In this portion of the basin, limestone-clay rocks are widespread, resulting in a CaO enrichment, whereas high S values reflect the occurrence of recent marine deposits and marine evaporites. Al_2O_3 content is high close to the mouth of the river and in the Chiana valley where clay-rich sediments occur. The high MgO values of the central and southern portion of the basin are related to the presence of ophiolitic masses; those of the upper portion refer to the ultramafic fraction of Macigno and Cervarola formations.

In general the distribution of Ni and Cr is consistent with the occurrence of MgO, and their high content is related to the inorganic fraction of the sediments. However, in highly industrialized areas, such as Usciana, Ombrone and Bisenzio basins, high Cr values (250–790 ppm, enrichment factor EF up to 6) are associated to anomalies of Cu (90–213 ppm, EF up to 5.4), Zn (230–1054 ppm, EF up to 9.5) and Pb (50–98 ppm, EF up to 3.6). Copper (and sulphur) anomalies also occur in tributaries (Chiana) far from the major industrial areas, where agricultural practice is widespread. Among all the heavy metals originating from anthropogenic sources, copper dispersion is very diffused throughout the area studied here. The Corg and N data suggest a small content of inorganic nitrogen in the sediments, and the low C/N values emphasize the role of urban and animal waste effluents. The distribution of Corg, N and P_2O_5 is consistent with that of heavy metals, but the relationships between Corg and N, S, P_2O_5 and heavy metals indicate a mixed origin for the organic matter (industrial, agricultural, urban) and point to the role of inorganic sources, both natural and anthropogenic, in providing metals to the Arno river catchment.

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