U.S. DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY

Pb ISOTOPES AND TOXIC METAL ABUNDANCES IN THE FLOODPLAIN AND STREAM SEDIMENTS FROM THE VOLTURNO RIVER BASIN (CAMPANIA, ITALY): NATURAL AND ANTHROPOGENIC CONTRIBUTIONS

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Open File Report N 99-366

Abstract

We present here a progress report of an environmental geochemical study of the Volturno river basin (Southern Italy). Forty new major-, minor- and trace-element chemical analyses and one-hundred Pb isotopic compositions of stream sediments and drill cores are used to establish geochemical backgrounds and baselines in this populated, industrialized, and agricultural area. Lead isotopic compositions distinctive of certain isotopic reservoirs such as gasoline used in Western Europe and abundances of various toxic elements potentially dangerous to human health (e.g. Zn, As, Pb, Cd, Cr, etc.) are correlated. The isotopic and trace element data can be used to suggest possible sources of contamination including: lead from gasoline ($^{207}Pb/^{206}Pb$=1.109-1.111), natural lead leached out of rocks and soils ($^{207}Pb/^{206}Pb$=1.198-1.200) and lead from treated or untreated urban wastes ($^{207}Pb/^{206}Pb$=1.147-1.162). The Pb isotopic composition of the stream sediments overlap the values of $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ of lead in gasoline, suggesting an important contribution from an anthropogenic source. The results also plot along a mixing line that overlaps the field of volcanic rocks outcropping in the area which is consistent with a contribution from volcanic and sedimentary rocks in the area.

1.1. Geology

The Volturno river basin (Fig. 1b) in the Southern Appenines is the largest of Southern Italy in terms of area (5455 km^2), length (175 km) and water flow (annual mean 98 m^3/s). The Southern Appenines represent a thrust fault chain built up in response to the closing of the Tethys Ocean in Mesozoic times. In the Campanian area in particular, deformation began in the Langhian, and continued during the Late Pliocene and Quaternary, when the Appenine chain partly overlapped the Bradanic Foredeep terrain. During the Late Pliocene, following the uplift of the chain, a large number of horst and graben structures were created. Closely related to these structures are several volcanoes and volcanic fields: Roccamonfina, Somma-Vesuvius, and the Phlegrean Fields (Bonardi et al., 1993).

The main geologic units found in the Volturno basin are (Fig. 1b):

-Mesozoic sedimentary rocks (M. Matese, M. Maggiore, Lagonegro, Taburno-Picentini, Molise and Sicilidi Formations);

-Neogenic sedimentary rocks of the Foredeep Basins (Ariano, Altavilla and Villamaina, Irpinian Basins);

- Quaternary clastic sedimentary rocks and pyroclastic rocks.

The Plio-Quaternary structures also strongly affect the shape and directions of the main river basins on the region, such as Volturno.

1.2. Land use.

About a half million people live in the Volturno River basin area (ISTAT, 1993); 68% of them reside in towns, 10% in villages (with more than 500 residents) and the rest (about 20%) in isolated houses. The study area falls within the provinces of Benevento, Caserta, and Avellino, and is characterized by industrial, agricultural, and large livestock operations. In the past, the economy of the area was based on agriculture. Soon after World War II, there has been a progressive economic diversification in area. Large factories have opened, attracting many other smaller businesses.

Sampling and analytical methods.

A critical step in establishing the impact of human-induced activities on the environment is the determination of background and baseline values of toxic metals. In this context, stream sediments can be used to sample the effects of pollution, as their geochemical signatures generally reflect upstream drainage geochemistry (Swennen R. and Van der Sluys J., 1998). In order to ensure that the samples used in our study of backgrounds and baselines of toxic metals are representative of the area, geographical, hydrogeological, and historical sample area description was carried out for each of the potential sample locations. In addition, artificial or man-made banks, channels, and levies were mapped so that they could be avoided. In this study, we have used 615 stream sediments samples collected from about 2200 km^2 (Fig.

1). The sampling density of the stream sediment was about 3.5 samples per km^2. The samples were dried ,sieved, and the >80 mesh fraction retained for chemical analysis. The samples were analyzed at the ACME Analytical Laboratories (Canada) by ICP-AES for Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sr, Th, Ti, U, V, W, Zn. Twenty-eight samples from nine drill cores in the flood plain where crushed using an agate mortar to avoid metal contamination, and were analysed by standard chemical techniques (XRF, ICP, INAA, ICP-MS) for minor and trace element compositions at ACT Laboratories Ltd, Ancaster, Canada.

The Pb isotopic compositions of the 26 stream sediments and 28 drill cores samples were measured using a Finnigan-MAT 262 mass spectrometer at the U.S. Geological Survey, Reston, VA. About 1 g of undisturbed drill core sample and 200 mg of stream sediment sample were prepared for their lead isotopic compositions using a step-leaching procedure. The samples were leached using 1.5N HBr-2N HCL (12:1), placed in an ultrasonic bath (<35 C) for 3 h (drill core) and on a warm hot plate (stream sediment). The samples were then centrifuged for 5 min at 5000 MPR obtaining a leachate (Leach 1=L1) and a residue fraction (R). The lead isotopes were separated using standard anion-exchange resins (Biorad ® AG1x8, 100-200 mesh in chloride form). All the reagents were obtained by distillation to reduce the Pb blanks to (much less than 1 ng during this study). The samples were loaded on single Re-degassed filaments with the classic method of the silica gel and phosphoric acid; the isotopic data were collected in a static running mode. NBS 981 standard values yield averages for ($^{206}Pb/^{204}Pb=16.920$, $^{207}Pb/^{204}Pb=15.648$, $^{208}Pb/^{204}Pb=36.630$); total analytical uncertainties are ~ 0.1 % (2 σ). The ratios were corrected for mass fractionation by about 0.1% per mass unit relative to standard NBS 981.

Results and discussions.

The distribution patterns of Pb concentrations and Pb isotopic compositions are similar in heavily industrialized areas used for electrolytic treatment, zinc plating, alloys industries, and paint factories, among others, and from densely populated areas probably due to the contributions of road traffic.

The range of compositions of various elements in the Volturno stream sediments is as follows: Pb: 4 - 570 ppm; Zn: 32 - 612 ppm.; Cu: 5 - 655 ppm; As: 1 - 12ppm.; Cr: 7 - 74 ppm; Sb: 1 - 5ppm (Table 1a); for the drill cores the ranges are: Pb: 3 - 39 ppm.; Zn: 34 - 537 ppm; Cu: 3 - 32 ppm; As: 8 - 39 ppm; Cr: 8 - 87 ppm; Sb: 0.6 - 2 ppm (Table 1b). The high Cu, As, and Sb concentrations in the sediments are probably related to the manufacturing plants in some industrial areas. The high Cd concentrations are probably related to industries producing metal coatings, precision instruments, and paints.

Stream sediments and drill cores were leached and analyzed for their Pb isotopic compositions (Table 2). Results point to an anthropogenic (leachate) component that is distinctly different from the natural (residue) component. In fig. 2 we report the $^{206}Pb/^{207}Pb$ values plotted as a function of stratigraphic position for the Volturno drill cores. The range of isotopic values for leachates (black symbols) and residues (red symbols) are nearly the same. However, for individual leachate-residue pairs the leachate is generally lower in $^{206}Pb/^{207}Pb$ than the residue. More importantly, note the general trend in the drill core samples as a function of depth. The $^{206}Pb/^{207}Pb$ isotopic compositions for each pair of (residues and leachate) increase from the surface (~2 m) as a function of the depth (~9.5 m) and then decrease near the bottom of the drill cores (~11.5m). In fig. 3, the $^{206}Pb/^{207}Pb$ isotopic compositions of flood plain drill core samples range from 1.20 to 1.21 (leachate) and 1.19 to 1.21 (residue); for the stream sediments, the compositions are between 1.13 - 1.24 (leachate) and 1.15 - 1.24 (residue). The known composition of lead alkyls added to gasoline in Europe (Dunlap C.E. et al., 1999; Monna et al., 1995; Facchetti 1989) during the 1970's has a ratio of $^{206}Pb/^{207}Pb$ of about 1.09-1.13; in contrast, volcanic rocks (Somma-Vesuvius, Phlegrean Fields and Roccamonfina) and limestones from the area have average $^{206}Pb/^{207}Pb$ values of about 1.20 to 1.22 (Vollmer, 1976; Vollmer and Hawkesworth; D'Antonio and Tilton, 1995; Ayuso et al., 1998) and thus are distinctly different from than the compostions thought to represent anthropogenic contaminants.

Our preliminary data indicate a direct correlation between the lead concentrations and the lead isotopic compositions of the anthropogenic fraction (leachates) from the stream sediments and drill core samples. ^{14}C dating of peat and intercalated sands and clays show that the entire stratigraphic sequence spans up to 7.2 k.y. B.P. These data, together with the trace element abundances and Pb isotopic compositions of the sediments allow us to identify background (uncontaminated sediment) levels. Our results are consistent with contributions from gasoline and from various local sources into the leachable component of the sediments.

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Figure Captions.

Tab. 1a

Major- and trace-elements analyses of the Volturno stream sediments.

Tab. 1b.

Major- and trace-elements analyses of the Volturno drill cores samples.

Tab. 3

Lead isotopic compositions of the Volturno stream sediments and drill cores samples.

Fig. 1a.

Simplified geological map of the Volturno watershed.

Fig 1b.

Map of the Volturno river watershed and sample locations (blue dots) of the stream sediments.

Fig. 2

$^{206}Pb/^{207}Pb$ vs. stratigraphic position for the Voltuno drill cores samples. In red are the residues (Res.) and in black the leachates (L1).

Fig. 3

$^{206}Pb/^{204}Pb$ vs. $^{206}Pb/^{207}Pb$ for the Volturno drill cores samples and stream sediments. Also reported are the field of gasoline and field for aerosol form urban/industrial areas (Monna et al., 1995), and the field of volcanic rocks in the area (Vollmer, 1976; Vollmer and Hawkesworth; D'Antonio and Tilton, 1995; Ayuso et al., 1998).

Table 1a

wt % or ppm	VT 9	VT 19	VT35	VT 57	VT 65	VT 95	VT 131	VT 136
Fe wt.%	3.6	2.19	3.68	3.22	1.75	5.04	2.53	3.61
Ca	5.85	9.45	2.25	7.01	7.2	1.55	6.01	5.76
P	0.105	0.044	0.073	0.271	0.047	0.074	0.232	0.088
Mg	0.39	0.41	0.63	0.4	0.43	0.37	0.47	0.44
Ti	0.18	0.11	0.22	0.13	0.06	0.3	0.1	0.17
Al	2.87	0.62	5.22	3.35	1.12	2.2	3.28	1.1
Na	0.15	0.04	0.1	0.1	0.05	0.06	0.1	0.05
K	0.39	0.17	0.51	0.66	0.25	0.27	0.65	0.26
Mo ppm	3	0.5	2	3	0.5	1	1	1
Cu	65	5	31	255	13	16	95	53
Pb	227	4	52	203	9	34	48	46
Zn	275	37	122	370	42	115	612	127
Ag	0.3	0.15	0.15	0.3	0.15	0.4	0.8	1.1
Ni	17	8	10	18	13	11	23	18
Co	7	6	8	7	7	11	8	10
Mn	463	567	901	412	550	1010	535	472
As	12	1	12	9	1	8	9	1
U	5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Au	1	1	1	1	1	1	1	1
Th	14	4	26	8	5	14	15	7
Sr	125	176	105	117	165	72	154	127
Cd	0.5	0.4	0.4	1.3	0.3	0.4	1.2	0.4
Sb	1	1	1	4	1	5	1	1
Bi	3	1	4	1	1	3	3	1
V	72	65	73	51	34	137	53	102
La	38	12	62	44	15	33	43	14
Cr	20	7	13	23	10	13	74	18
Ba	206	60	380	254	100	184	280	134
B	8	1.5	10	17	6	5	11	7
W	1	1	1	1	1	1	1	1

Table 1a

	VT 142	VT 190	VT 192	VT 218	VT 257	VT 326	VT 346	VT 378
Fe wt. %	2.14	1.96	3.16	4.2	1.2	2.35	2.17	1.95
Ca	9.87	9.95	3.69	4.8	5.44	5.07	10.91	14.23
P	0.084	0.069	0.135	0.059	0.033	0.083	0.068	0.079
Mg	0.48	0.55	0.52	0.48	0.34	0.92	0.6	5.88
Ti	0.07	0.03	0.15	0.22	0.03	0.03	0.02	0.12
Al	1.8	1.85	2.47	0.87	0.7	1.55	1.97	2.64
Na	0.07	0.05	0.14	0.06	0.02	0.04	0.05	0.10
K	0.38	0.32	0.65	0.23	0.14	0.38	0.38	0.51
Mo ppm	1	1	1	0.5	0.5	0.5	0.5	1
Cu	69	39	61	14	11	33	52	21
Pb	570	19	91	18	19	18	26	21
Zn	101	70	107	79	32	80	66	50
Ag	0.3	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Ni	20	21	20	16	14	43	28	11
Co	7	8	8	9	5	11	9	6
Mn	532	751	686	868	421	816	844	433
As	3	5	8	3	3	8	2	4
U	11	7	2.5	2.5	29	7	2.5	2.5
Au	1	1	1	1	1	1	1	1
Th	16	13	7	4	4	6	6	5
Sr	159	183	145	141	133	163	216	106
Cd	0.5	0.3	0.6	0.3	0.1	0.1	0.5	0.9
Sb	4	1	1	1	1	2	1	1
Bi	3	4	1	1	1	1	1	1
V	42	28	70	123	21	41	28	79
La	25	27	25	10	10	17	17	23
Cr	20	19	17	16	14	36	25	10
Ba	209	158	219	100	64	141	153	188
B	8	8	12	5	4	12	10	7
W	1	1	2	1	1	1	1	1

Table 1a

	VT 409	VT 414	VT 422	VT 435	VT 465	VT 469	VT 497	VT 567
Fe wt.%	8.68	5.59	4.07	3.04	4.43	3.47	1.75	1.42
Ca	2.83	3.58	5.43	6.42	3.11	5.93	4.53	6.29
P	0.186	0.19	0.159	0.166	0.095	0.119	0.073	0.035
Mg	0.97	1.02	1.19	1.83	0.35	1.01	0.44	0.47
Ti	0.47	0.29	0.21	0.17	0.22	0.17	0.05	0.01
Al	3.84	3.94	4.37	3.22	1.45	2.26	1.04	0.89
Na	0.42	0.48	0.58	0.30	0.13	0.19	0.04	0.02
K	1.52	1.69	1.71	1.36	0.42	0.76	0.3	0.16
Mo ppm	1	1	1	1	0.5	0.5	0.5	1
Cu	96	138	62	74	45	37	28	18
Pb	205	118	175	29	168	27	213	10
Zn	147	140	136	83	105	88	50	34
Ag	0.15	0.3	0.15	0.15	0.15	0.15	0.15	0.15
Ni	23	19	18	15	15	17	22	20
Co	21	15	13	11	11	10	8	8
Mn	1110	741	769	495	725	627	577	764
As	1	3	5	3	4	4	2	6
U	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Au	1	1	1	1	1	1	1	1
Th	13	13	14	9	6	8	5	4
Sr	237	252	278	228	131	195	101	132
Cd	1	1.1	1.1	0.7	0.9	1	0.3	0.1
Sb	1	1	1	1	1	1	1	1
Bi	3	1	1	1	2	1	1	1
V	323	198	135	105	147	116	45	19
La	35	33	35	26	17	20	13	9
Cr	19	14	15	10	13	15	22	12
Ba	440	431	474	342	151	247	128	78
B	14	19	19	9	4	8	6	15
W	1	1	1	1	1	1	1	1

Table 1b

SAMPLE	S2(1.5-2m)	S2(4.5-5m)	S2(8.5m)	S5(5-5.6m)	S5(8-8.5m)	S11(8.5-9m)	S11(10.5m)	S12(10-10.5m
SiO2 wt.%	45.19	30.72	54.61	41.56	63.56	43.37	44.76	52.23
Al2O3	16.58	7.25	18.29	16.21	8.94	12.28	13.29	10.09
Fe2O3 Tot.	5.69	1.91	3.85	5.60	2.37	4.69	4.86	3.05
MnO	0.06	0.11	0.09	0.09	0.08	0.08	0.13	0.10
MgO	2.44	1.28	0.96	2.34	1.49	1.53	1.77	1.45
CaO	4.90	3.71	2.38	10.17	8.78	14.33	11.86	14.57
Na2O	0.81	4.03	3.40	0.94	1.48	0.46	0.77	1.14
K2O	3.00	2.94	7.68	2.53	2.62	2.02	2.18	2.18
TiO2	0.68	0.21	0.50	0.60	0.27	0.48	0.57	0.36
P2O5	0.19	0.06	0.17	0.18	0.06	0.45	0.19	0.13
LOI	21.17	43.74	8.63	19.08	9.76	20.30	19.76	15.34
TOTAL	100.72	95.96	100.56	99.31	99.40	99.98	100.14	100.65
Ba ppm	313	442	1020	378	499	546	444	453
Sr	251	222	554	239	362	302	284	305
Y	24	17	29	22	14	20	22	18
Sc	14	2	5	12	7	9	10	7
Zr	156	196	309	167	104	175	173	143
Be	5	6	9	4	2	5	4	3
V	151	30	78	133	46	93	93	63
Au	4	>1	2	4	>1	2	2	3
As	15	14	21	11	14	12	12	8
Br	105	226	32.2	27.2	9.8	5.1	7.5	2.5
Co	16.4	4.4	7.6	16.4	7.3	15.9	15.3	11.9
Cr	115	9.8	7.9	109	55.4	71.3	86.6	57.3
Cs	13.4	15	18.7	12.2	5.7	11.6	9.5	6
Hf	4.3	5.1	7.2	4.6	2.8	4.5	4.6	4.2
Hg	>1	>1	>1	>1	>1	>1	>1	>1
Ir	>2	>2	>2	>2	>2	>2	>2	>2
Mo	3	>2	>2	>2	2	>2	3	>2
Rb	264	172	282	177	118	145	136	106
Sb	1	0.8	1.1	0.7	0.5	1	0.8	0.5
Sc	15.4	2.5	5	14.4	8	10	11.3	8.3
Se	>0.5	>0.5	>0.5	0.5	>0.5	1.2	>0.5	>0.5
Ta	1.6	1.9	2.6	1.4	0.7	1.7	1.6	0.9
Th	17.7	23.8	30.5	16.4	8.6	17	14.7	9.7
U	5.2	7.3	13.6	4.9	2.4	8.9	3.8	4.4
W	3	3	3	2	2	3	2	2
La	54.3	47.5	76.4	48.4	28.7	46.2	46.2	31.9
Ce	101	91	144	86	54	82	86	61
Nd	38	33	56	34	24	32	36	25
Sm	7.33	5.05	9.34	6.48	4.53	6.18	6.68	5.05
Eu	1.47	0.87	2.39	1.31	1.07	1.24	1.34	1.05
Tb	0.7	0.5	0.7	0.7	0.4	0.7	0.7	0.5
Yb	2.58	1.84	2.9	2.5	1.4	2.23	2.77	2.05
Lu	0.39	0.3	0.46	0.38	0.22	0.36	0.42	0.31
Cu	39	5	6	34	10	30	28	15
Pb	32	28	47	31	23	30	25	22
Zn	311	327	537	96	35	113	86	74
Ag	>0.4	>0.4	>0.4	>0.4	>0.4	>0.4	>0.4	>0.4
Ni	43	4	2	43	14	29	37	25
Cd	>0.5	>0.5	>0.5	>0.5	>0.5	>0.5	>0.5	>0.5
Bi	5	5	5	5	5	5	5	5

Table 1b

SAMPLE	S13 (2m)	S13 (4m)	S14 (4m)	S14 (7m)	S14 (9-9.4	S15(2m)	S15(4-4.5m)	S15 (9-9.5m)
SiO2 wt.%	52.01	41.95	47.80	36.46	51.22	48.83	23.76	41.10
Al2O3	13.34	15.61	19.31	11.98	10.83	21.52	7.45	13.90
Fe2O3 Tot.	4.55	5.56	6.04	4.86	10.95	6.03	3.64	5.34
MnO	0.14	0.09	0.21	0.17	0.19	0.15	0.15	0.23
MgO	1.82	2.34	1.50	2.06	2.16	1.17	0.91	2.32
CaO	9.25	7.26	5.15	19.90	4.72	1.75	3.47	13.10
Na2O	1.60	1.43	1 35	0.55	2.16	1.17	0.76	0.66
K2O	2.24	2.26	3.21	1.88	4.92	3.39	1.81	2.31
TiO2	0.58	0.65	0.69	0.51	1.04	0.68	0.25	0.58
P2O5	0.16	0.17	0.19	0.09	0.10	0.47	0.14	0.15
LOI	14.85	23.51	15.21	22.39	12.27	15.58	56.25	19.00
TOTAL	100.53	100.82	100.65	100.85	100.56	100.73	98.56	98.70
Ba ppm	496	353	618	174	523	589	350.5	229
Sr	296	244	350	1092	380	229	224	397
Y	27	24	37	19	21	41	11.5	22
Sc	10	13	10	10	12	10	3.5	11
Zr	224	155	354	130	267	407	120	150
Be	4	4	10	3	4	11	3.5	4
V	90	121	115	92	177	122	108	104
Au	7	3	2	>1	2	2	>1	>1
As	9	10	28	10	24	31	39	11
Br	35.6	51.6	24.2	52.9	8.4	8.6	48.1	11.4
Co	17.8	16.7	15.4	10.5	14.3	12.6	6.1	13.2
Cr	78.8	111	61.8	74.7	80	44.4	23.6	81
Cs	9.3	0.9	27.7	9.8	5.9	32.9	29.1	10.4
Hf	5.5	3.9	7.9	3	5	9.1	2.8	3.7
Hg	>1	>1	>1	>1	>1	>1	>1	>1
Ir	>2	>2	>2	>2	>2	>2	>2	>2
Mo	>2	3	>2	5	>2	>2	23	2
Rb	140	145	247	112	127	237	110	134
Sb	0.8	0.9	2	0.5	0.5	1.8	1.6	0.6
Sc	11.1	14.3	11.4	10	12.8	10.1	3.8	11.1
Se	>0.5	>0.5	>0.5	0.5	>0.5	>0.5	1.4	>0.5
Ta	1.4	1.5	2.4	0.9	0.9	2.5	1	1.2
Th	15.5	15.3	40.2	11.1	12.8	47.5	11.6	12.9
U	3.7	3.3	6.2	3.8	4	5.5	28.7	2.8
W	>1	3	5	2	1	4	5	2
La	50	49.6	107	35	47.2	111	28.9	39.4
Ce	91	87	185	65	87	218	54	74
Nd	39	35	69	27	39	75	21	30
Sm	7.24	6.86	12.4	4.91	8.08	12.6	3.26	5.51
Eu	1.48	1.3	2.25	0.95	1.75	2.37	0.78	1.14
Tb	0.7	0.6	1.1	0.5	0.9	1.1	0.3	0.6
Yb	2.78	2.55	3.96	1.85	2.1	3.67	1.14	2.17
Lu	0.43	0.4	0.6	0.29	0.32	0.58	0.17	0.33
Cu	32	37	31	19	3	30	11	22
Pb	36	25	68	22	22	84	18	24
Zn	81	105	105	69	167	103	34	83
Ag	>0.4	>0.4	>0.4	>0.4	>0.4	>0.4	>0.4	>0.4
Ni	39	50	27	31	16	23	12	35
Cd	>0.5	>0.5	>0.5	>0.5	>0.5	>0.5	>0.5	>0.5
Bi	5	5	5	5	5	5	5	5

Table 2

ID	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{208}Pb$
VT 9res.	38.3945	15.6095	18.4239	1.1803	0.4799
VT 9 L1	38.2180	15.6340	18.1610	1.1616	0.4752
VT 19res	38.5716	15.6228	18.6947	1.1966	0.4847
VT 19L1	38.5891	15.6120	18.6732	1.1961	0.4839
VT 35res	38.9694	15.6669	18.8957	1.2061	0.4849
VT 35L1	38.8778	15.6587	18.5036	1.1817	0.4759
VT 57res	38.5730	15.6285	18.7209	1.1979	0.4853
VT 57 L1	38.2590	15.5978	18.5890	1.1918	0.4859
VT 65res	38.6651	15.6372	18.6760	1.1943	0.4830
VT 65L1	38.4691	15.6127	18.5209	1.1863	0.4814
VT 95res	38.8555	15.6399	18.8534	1.2055	0.4852
VT 95L1	38.4359	15.6008	18.5019	1.1860	0.4814
VT 131res	38.5878	15.6136	18.6378	1.1937	0.4830
VT 131L1	39.3093	15.5890	18.4016	1.1804	0.4681
VT 136res	38.2933	15.5993	18.3496	1.1763	0.4792
VT 136L1	38.1383	15.5864	18.2043	1.1680	0.4773
VT 142res	38.2277	15.6159	18.1882	1.1647	0.4758
VT 142L1	38.0753	15.5759	18.1265	1.1638	0.4761
VT 190res	38.7127	15.6375	18.7111	1.1966	0.4833
VT 190L1	38.5753	15.6125	18.6274	1.1931	0.4829
VT 192res	38.4177	15.6209	18.4355	1.1802	0.4799
VT 192L1	38.1353	15.6019	18.1731	1.1648	0.4765
VT 218res	38.5895	15.6339	18.6804	1.1949	0.4841
VT 218L1	38.4303	15.6186	18.4942	1.1841	0.4812
VT 257res	37.7195	15.5706	17.8363	1.1455	0.4729
VT 257L1	37.3221	15.5306	17.5063	1.1272	0.4691
VT 326res	38.6001	15.6231	18.6602	1.1944	0.4834
VT 326L1	38.6104	15.6338	18.6310	1.1917	0.4825
VT 346res	38.6648	15.6259	18.7141	1.1976	0.4840
VT 346L1	38.6745	15.6308	18.6847	1.1954	0.4831
VT 378res	38.8433	15.6590	19.4163	1.2399	0.4999
VT 378L1	38.6581	15.6587	19.4402	1.2415	0.5029
VT 409res	38.3267	15.6258	18.2853	1.1702	0.4771
VT 409L1	38.2786	15.6285	18.2135	1.1654	0.4758
VT 414res	38.3466	15.6047	18.3589	1.1765	0.4788
VT 414L1	38.2895	15.6315	18.2287	1.1662	0.4761
VT 422res	38.3468	15.6497	18.3360	1.1716	0.4782
VT 422 L1	38.1796	15.6219	18.1589	1.1624	0.4756
VT 435res	38.7908	15.6402	18.8006	1.2021	0.4847
VT 435L1	38.5582	15.6344	18.6389	1.1922	0.4834
VT 465res	38.2875	15.6103	18.3346	1.1745	0.4789
VT 465L1	37.9575	15.5620	18.0976	1.1629	0.4768
VT 469res	38.6145	15.6189	18.7366	1.1996	0.4852
VT 469L1	38.5044	15.6148	18.5763	1.1897	0.4824
VT 497res	37.9837	15.5793	18.0809	1.1606	0.4760
VT 497L1	37.9792	15.5973	18.0118	1.1548	0.4743
VT 567res	38.6251	15.6464	18.5751	1.1872	0.4809
VT 567L1	38.7592	15.6152	18.7940	1.2036	0.4849
VT 593res	38.6411	15.6660	18.5957	1.1870	0.4812
VT 593L1	38.3858	15.6021	18.4689	1.1837	0.4811

Table 2

Depth in m	ID	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{208}Pb$
1.5-2res	S2	38.9163	15.6565	18.8571	1.2044	0.4846
1.5-2L1	S2	38.9373	15.6620	18.8670	1.2046	0.4845
3.5res	S2	38.8619	15.6449	18.8324	1.2037	0.4846
3.5L1	S2	38.9482	15.6748	18.8488	1.2025	0.4839
4.5-5res	S2	39.1286	15.6744	19.0229	1.2136	0.4862
4.5-5L1	S2	39.0452	15.6517	18.9999	1.2139	0.4866
6-6.5res	S2	38.9534	15.6374	18.9500	1.2118	0.4865
6-6.5L1	S2	38.9107	15.6352	18.9180	1.2100	0.4862
7.5res	S2	39.0541	15.6519	19.0056	1.2143	0.4866
7.5L1	S2	39.0301	15.6488	18.9852	1.2132	0.4864
8.5res	S2	39.1082	15.6638	19.0192	1.2142	0.4863
8.5L1	S2	39.0077	15.6366	18.9906	1.2145	0.4868
5.5-6res	S5	38.8716	15.6383	18.8735	1.2069	0.4855
5.5-6L1	S5	38.8390	15.6282	18.8755	1.2078	0.4860
7-7.5res	S5	39.0102	15.6578	18.9529	1.2105	0.4858
7.7-5L1	S5	38.9278	15.6381	18.9302	1.2105	0.4863
8-8.5res	S5	38.8784	15.6407	18.8750	1.2068	0.4855
8-8.5L1	S5	38.8761	15.6392	18.8801	1.2072	0.4856
8.5-9res	S11	38.9570	15.6528	18.9200	1.2087	0.4857
8.5-9L1	S11	38.9246	15.6368	18.9245	1.2103	0.4862
10.5res	S11	38.9031	15.6455	18.8943	1.2077	0.4857
10.5L1	S11	38.8440	15.6245	18.8853	1.2087	0.4862
10-10.5res	S12	38.8083	15.6430	18.8198	1.2031	0.4849
10-10.5L1	S12	38.8909	15.6410	18.8808	1.2071	0.4855
11res	S12	38.7817	15.6538	18.7463	1.1976	0.4834
11L1	S12	38.8304	15.6313	18.8855	1.2082	0.4864
2res	S13	38.8565	15.6432	18.8425	1.2045	0.4849
2L1	S13	38.7697	15.6200	18.8324	1.2057	0.4857
4res	S13	38.8632	15.6429	18.8436	1.2046	0.4849
4L1	S13	38.8444	15.6386	18.8385	1.2046	0.4850
4.5res	S13	38.8750	15.6467	18.8626	1.2055	0.4852
4.5L1	S13	38.9168	15.6583	18.8754	1.2055	0.4850
4res	S14	38.9165	15.6409	18.8688	1.2064	0.4849
4L1	S14	39.0089	15.6920	18.8254	1.1997	0.4826
5-5.5res	S14	39.0900	15.6758	18.9795	1.2108	0.4855
5-5.5L1	S14	38.9584	15.6404	18.9435	1.2112	0.4862
7res	S14	38.9890	15.6771	18.8926	1.2051	0.4846
7L1	S14	38.8343	15.6321	18.8558	1.2062	0.4855
9-9.4res	S14	39.0277	15.6453	19.0081	1.2149	0.4870
9-9.4L1	S14	38.9903	15.6474	18.9764	1.2128	0.4867
2res	S15	39.0758	15.6817	18.9296	1.2071	0.4844
2L1	S15	39.0379	15.6807	18.8951	1.2050	0.4840
3.5res	S15	38.9476	15.6489	18.9109	1.2084	0.4855
3.5L1	S15	38.9291	15.6453	18.9102	1.2087	0.4858
5.5res	S15	38.8868	15.6525	18.8588	1.2048	0.4850
5.5L1	S15	38.9961	15.6833	18.8867	1.2043	0.4843
9-9.5res	S15	38.9141	15.6536	18.8899	1.2067	0.4854
9-9.5L1	S15	38.8484	15.6335	18.8756	1.2074	0.4859

Fig. 1a GEOLOGICAL MAP

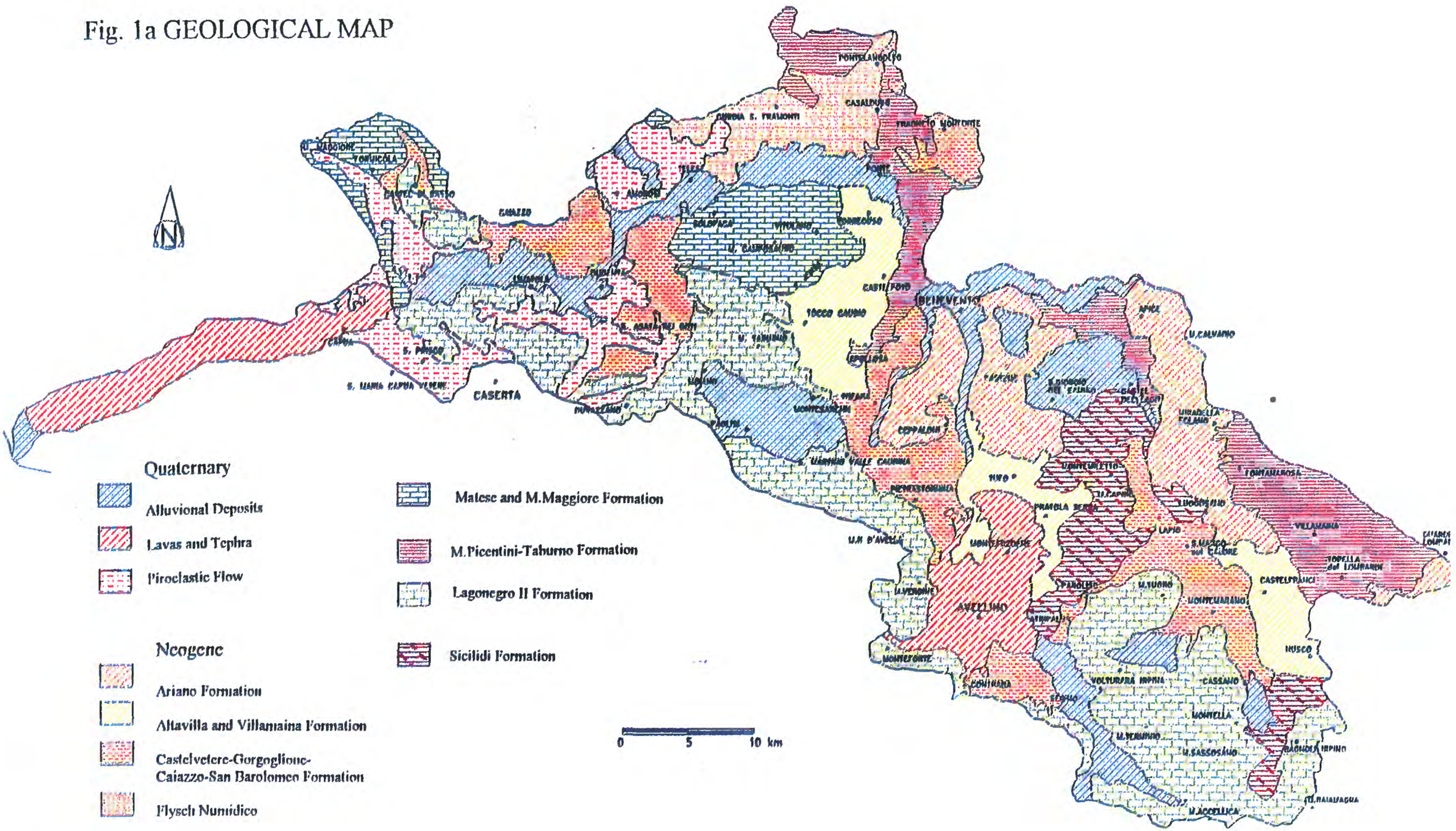


Fig. 1b SAMPLE LOCATION

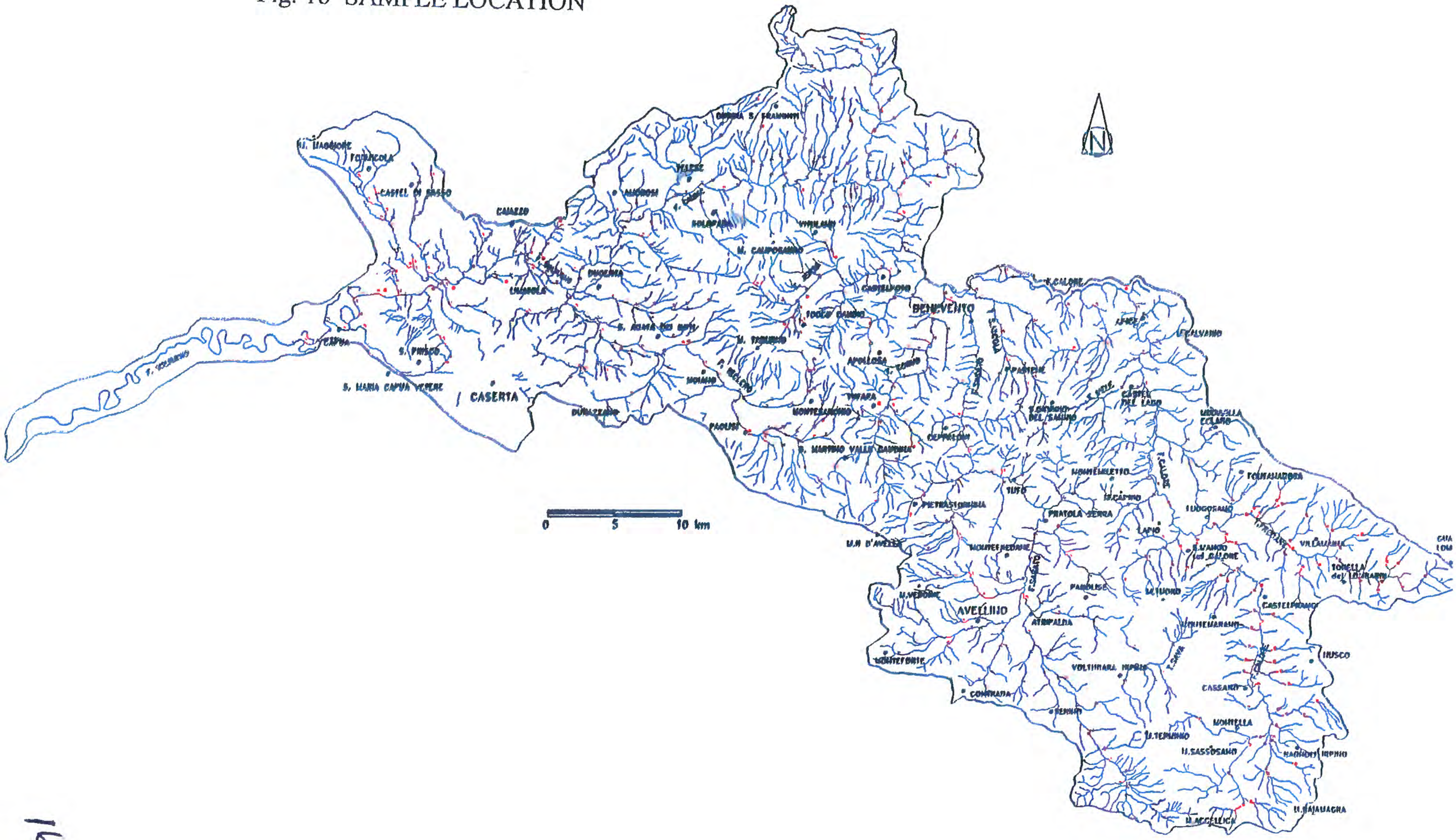
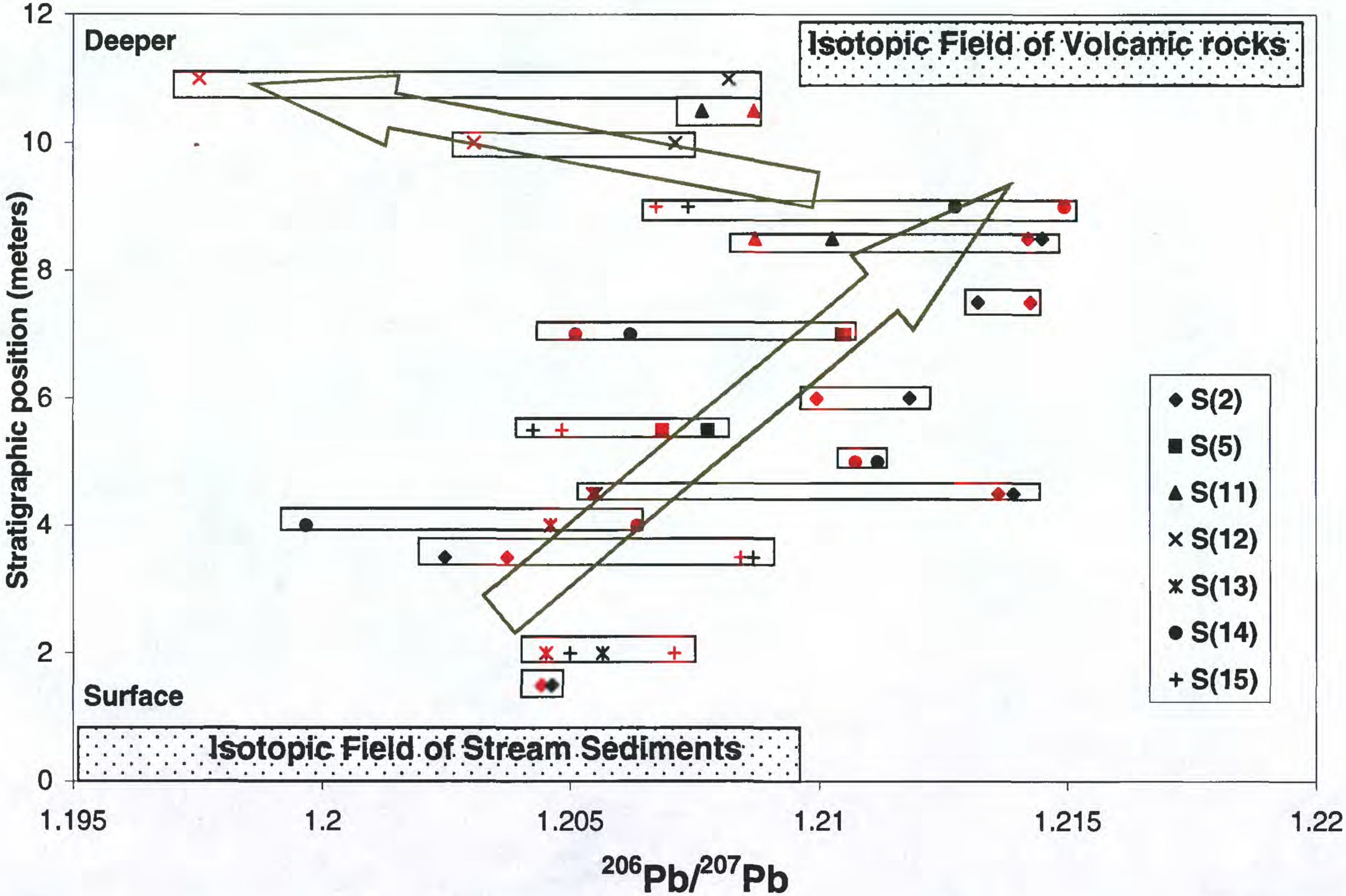
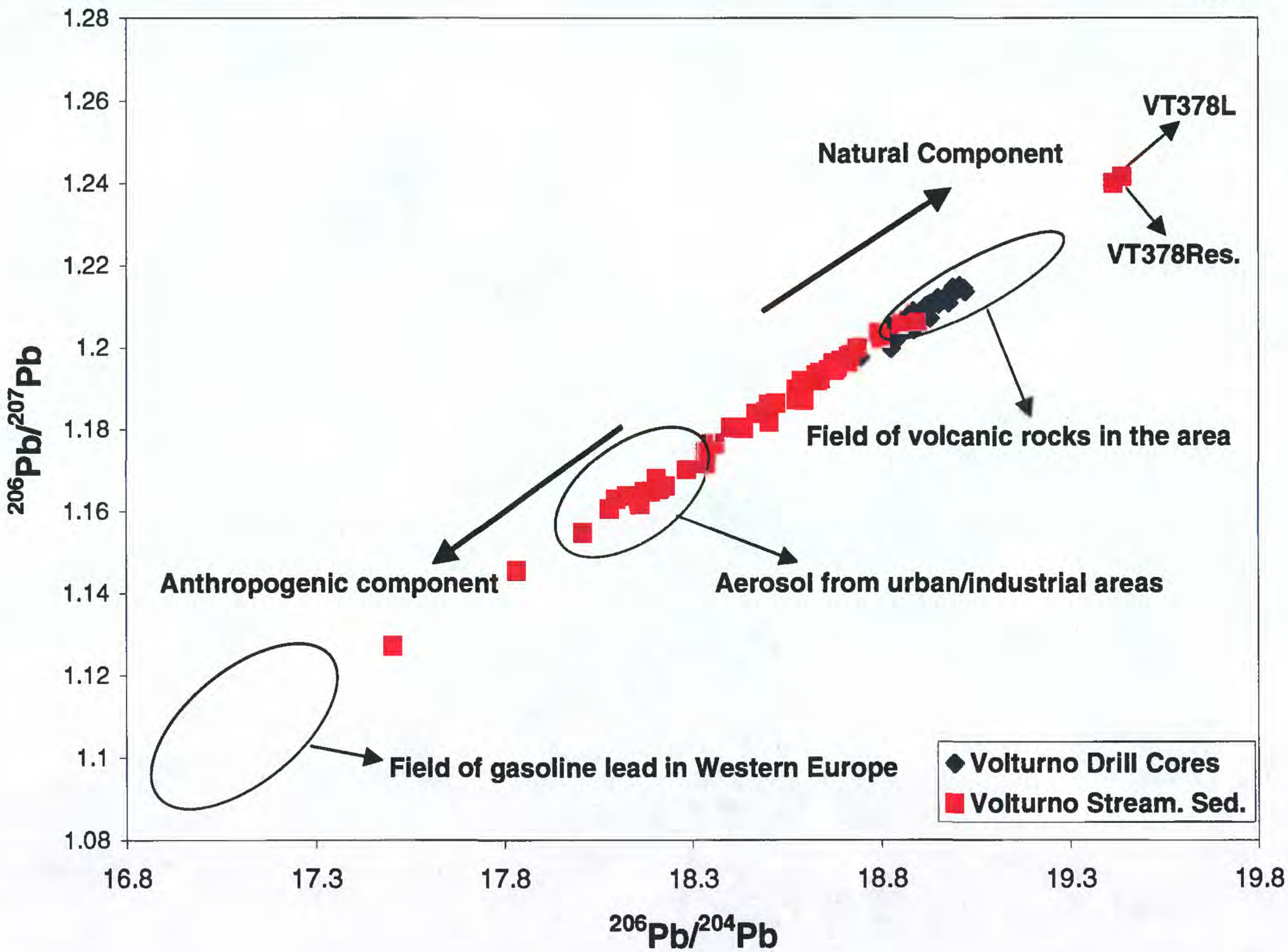


Fig. 2



Deeper
Surface
Isotopic Field of Volcanic rocks
Isotopic Field of Stream Sediments
Stratigraphic position (meters)
0
2
4
6
8
10
12
1.195
1.2
1.205
1.21
1.215
1.22
206Pb/207Pb
S(2)
S(5)
S(11)
S(12)
S(13)
S(14)
S(15)

Fig.3


1.28
1.26
1.24
1.22
1.2
1.18
1.16
1.14
1.12
1.1
1.08
16.8
17.3
17.8
18.3
18.8
19.3
19.8
206Pb/207Pb
206Pb/204Pb
VT378L
VT378Res.
Natural Component
Field of volcanic rocks in the area
Anthropogenic component
Aerosol from urban/industrial areas
Field of gasoline lead in Western Europe
Volturno Drill Cores
Volturno Stream. Sed.