Minero-chemistry of lake sediments and environmental assessment: the case of the Pietra del Pertusillo reservoir (Southern Italy)

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INTRODUCTION AND AIM OF THE WORK

The Pietra del Pertusillo freshwater reservoir is a major artificial lake of environmental, biological and ecological importance located in the Basilicata region, southern Italy. The minero-chemistry of lake and fluvio-lacustrine sediments of the reservoir have been evaluated to assess the environmental quality. The composition of fluvial sediments were also studied to understand the factors affecting the behavior of elements in the fresh-water reservoir, with particular attention paid to heavy metals. There is no Italian specific regulatory values concerning the element threshold concentration for lake and river sediments. For this reason, soil threshold values are used as a standard for sediments of internal waters and the evaluation of the environmental quality depicted by sediments of the reservoir has been performed using enrichment factors obtained with respect to the average composition of a restored local upper continental crust. We suggest this method as an innovative standard in similar conditions worldwide. In our catchment the trace elements that may be of some environmental concern are Cr, Cu, Zn, As, and Pb although, at this stage, the distribution of these elements appears to be mostly driven by geogenic processes. However, particular attention has to be paid to As, constantly enriched in the lacustrine samples and especially in the fine-grained fraction.

Geological setting and sampling strategy

The High Agri Valley is a Quaternary basin located in the axial zone of the Southern Apennines mountain belt (Fig,1), an east-verging fold-and-thrust belt developed as an accretionary wedge from the late Oligocene to the early Pleistocene. The tectonic units, are represented by the Liguride and Sicilide complexes, derived from the Liguria-Piedmont Ocean; the Apennine Platform carbonates and the several units mainly composed of deep-sea sediments of the Lagonegro basin. These units, representing the substratum of the HAV, were tectonically emplaced over Plio-Pleistocene foredeep basins located on top of the Apulian Carbonate Platform. Bedrock consists of Tertiary siliciclastic sediments, namely Albidona and Gorgoglione Flysch Formations. The first formation (Albidona Flysch) is composed by an alternating gray-yellowish sandstone, marl and silty clays with whitish carbonate intercalations outcropping in the eastern portion of the HAV basin. The Gorgoglione Flysch formed in a piggy-back trough during the Apenninic orogenic compressional stage.

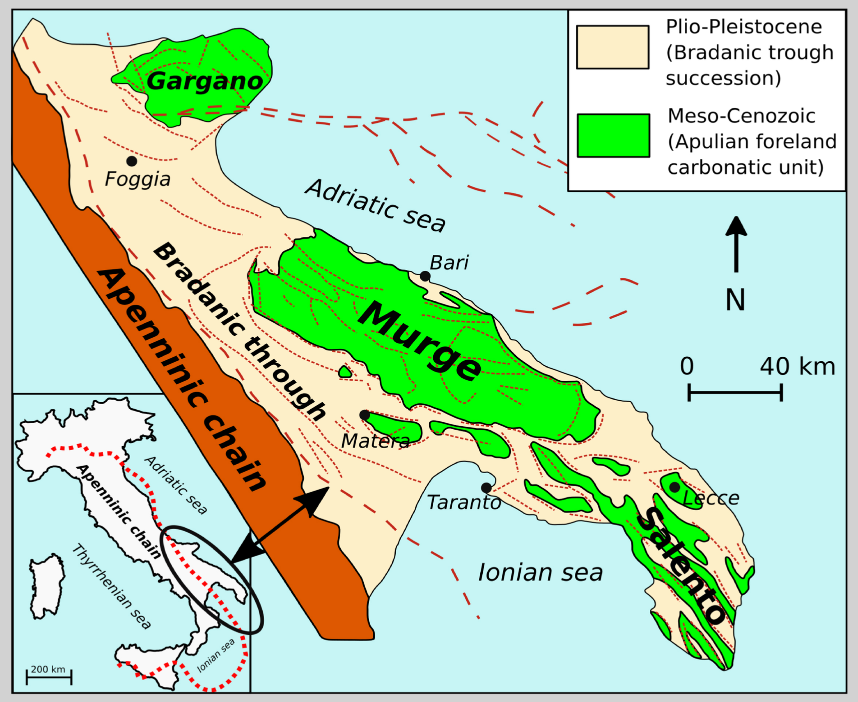

Fig.1 Geology of the three main paleogeographic domains of Southern Apennines (modified from Prosser, 1996)

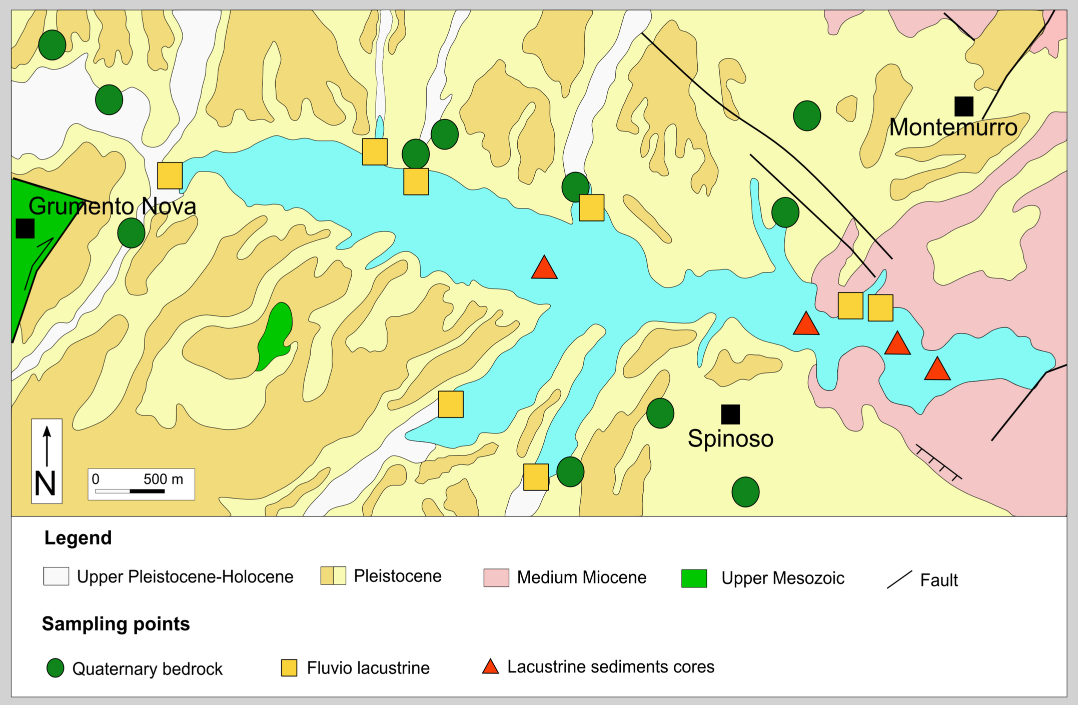

Fig.2 Samples position of quaternary bedrock deposits, fluvio-lacustrine sediments and lake sediments cores (modified from Lentini et al., 1991)

The sampling work (Fig.2) had several purposes in order to assess: a) the average chemical composition of the upper continental crust close to the Pietra del Pertusillo reservoir; b) the minero-chemical composition of the detrital supply close to the entry points of the reservoir; c) the distribution and the concentrations of trace elements in the bulk and fine fraction (< 4µ) of deep lacustrine sediments.

Several specimens were collected as follows: 27 Meso-Cenozoic parent rock samples, with a predominate siliciclastic pelitic fraction; 15 silty-clayey samples from the Quaternary fluvio-lacustrine deposits, outcropping in the drainage basin and, during the low-standing periods, along the shores of the reservoir; 14 fluvio-lacustrine sediments samples collected at the confluences of the active tributaries of the reservoir; 15 samples from lake-bottom sediments, from 4 sediment cores (F, R, T and V).

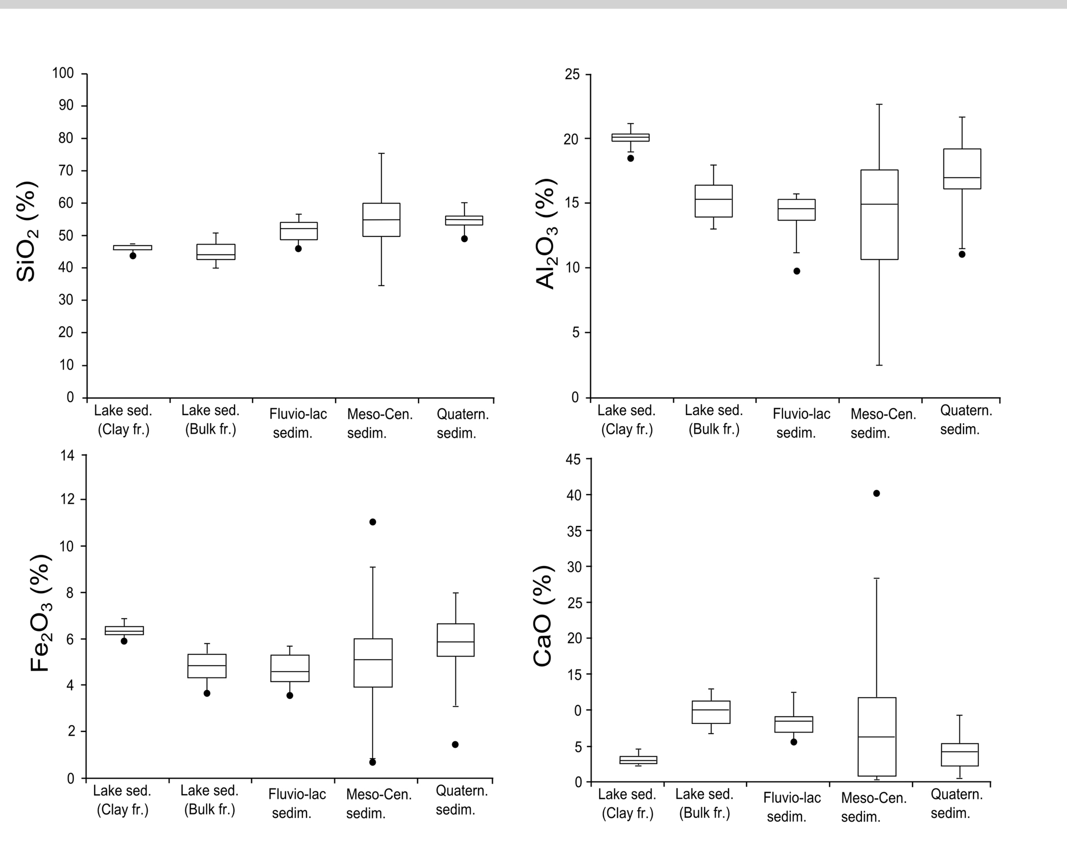

Fig.3 Box-and-whisker plots for major elements in the analyzed samples. Horizontal bar in the box refers to the median value; the ends of the whiskers are the maximum and minimum values of variables; the top and bottom of the boxes are the values of first and third quartiles; dark circles represent the outliers values of the dataset

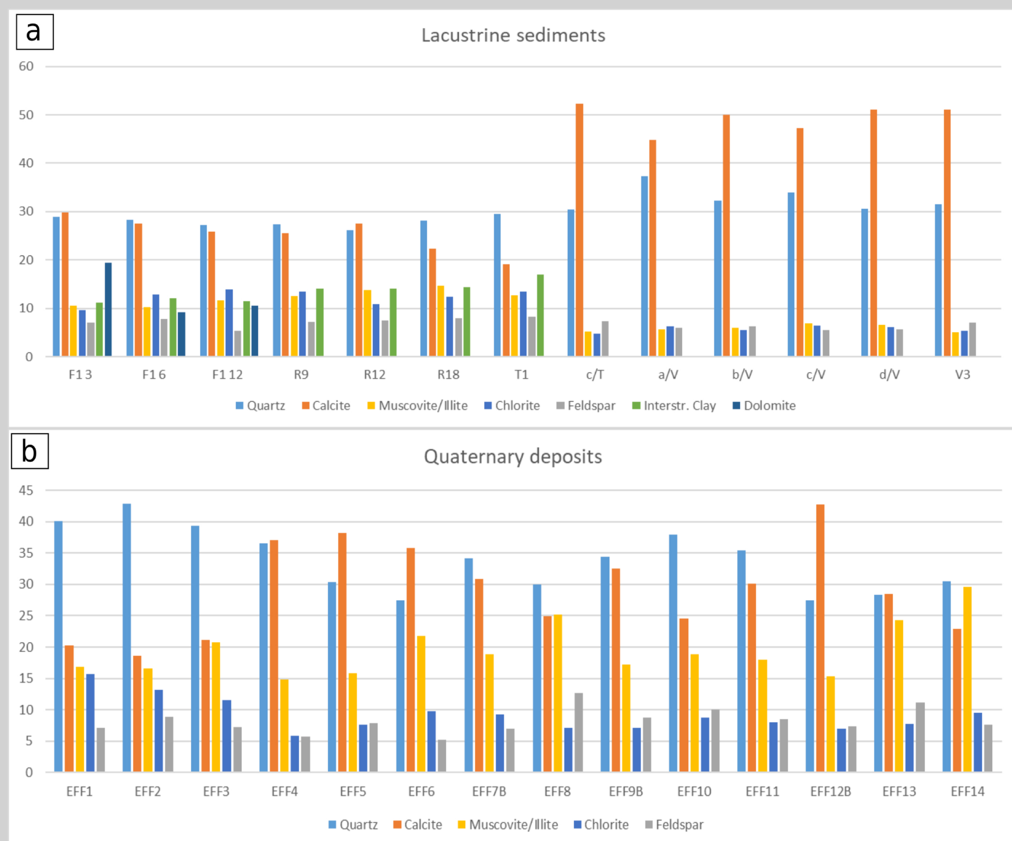

Fig.4 (a) Mineralogy composition of lake sediments; (b) Mineralogy composition of fluvio-lacustrine samples

Geochemistry, Mineralogy and Enrichment factors

In the analyzed sediments, the main major oxides are SiO_2, which is the dominant oxide, followed by Al_2O_3,Fe_2O_3 and CaO (Fig.3). Mineralogy of lake and fluvio-lacustrine samples mainly consists of quartz with less presence of feldspars, calcite and clay minerals, such as chlorite, illite, interstratified clay minerals (Fig.4). Enrichment factors, calculated respect to global UCC and local bedrock composition, indicate that the trace elements that may be of some environmental concern are Cr, Cu, Zn, As, and Pb (Tab.1). Cr is enriched in the fine fraction of lake sediments and, more in general, Cr is more enriched in clay-rich minerals such as chlorite. Cu is particularly abundant in rocks containing mafic minerals (Gorgoglione, Galestri, and Albidona Fms) and in some present-day sediments, suggesting Cu is associated with the secondary phases deriving by the weathering of mafic silicates. Zn is enriched with respect to the local upper continental crust in very few (EF>2), suggesting that naturally occurring local conditions may affect the Zn distribution in the analyzed catchment. As is constantly concentrated in the fine fraction of the lacustrine samples (EF > 2 with respect to the local bedrock) thus reflecting the great adsorption capability of As in clay fine fraction. Similarly, Pb is enriched in most of the lacustrine sediments and specifically in the fine fraction.

	V		Cr		Co		Ni	
	$(EF)_{bedrock}$	$(EF)_{UCC}$	$(EF)_{bedrock}$	$(EF)_{UCC}$	$(EF)_{bedrock}$	$(EF)_{UCC}$	$(EF)_{bedrock}$	$(EF)_{UCC}$
Lacustrine (bulk.fr.)	1.32	1.20	1.44	1.38	1.05	1.08	1.31	1.33
Lacustrine (clay)	0.95	0.86	0.98	0.93	0.62	0.63	0.76	0.77
Fluvio-lacustrine sed.	0.98	0.70	0.79	0.54	0.04	0.48	1.36	0.80
Meso-Cenoz sed.	1.06	0.76	1.10	0.74	1.14	0.67	1.11	0.65
Quat. dep.	1.02	0.73	1.00	0.68	1.03	0.60	1.01	0.59
	Cu		**Zn**		**Pb**		**As**	
	$(EF)_{bedrock}$	$(EF)_{UCC}$	$(EF)_{bedrock}$	$(EF)_{UCC}$	$(EF)_{bedrock}$	$(EF)_{UCC}$	$(EF)_{bedrock}$	$(EF)_{UCC}$
Lacustrine (bulk.fr.)	1.35	1.36	1.45	0.16	2.18	1.49	1.43	0.90
Lacustrine (clay)	1.35	1.36	1.35	1.29	1.62	1.10	3.80	2.39
Fluvio-lacustrine sed.	0.94	0.94	1.49	1.39	1.29	0.96	1.18	3.13
Meso-Cenoz sed.	0.87	0.87	0.97	0.91	0.89	0.66	1.08	2.86
Quat. dep.	1.03	1.02	0.08	0.22	1.58	1.17	1.36	3.62

Tab.1 Trace elements enrichment factors median values relatively to global UCC and local bedrock for the analyzed samples. $EF_{UCC} = (X/Ti)_{sample}/(X/Ti)_{UCC}$; $EF_{loc.bed.} = (X/Ti)_{sample}/(X/Ti)_{loc.bed.}$

	V	Pb	Cr	Co	Ni	Cu	Zn	As
units	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Lacustrine (bulk frac.)	114	24	100	13	40	40	110	7
Lacustrine (clay frac.)	154	42	120	16	50	50	150	8.50
Fluvio-lacustrine sedim.	104	23	62.8	12	48	30	141	6.85
Meso-Cenoz sedim.	108	14	80	14	40	30	100	5
Quat. dep.	127	31	90	18	40	40	120	10

Tab.2 Selected trace elements median values in the collected samples.

	SiO_2	Al2O3	Fe_2O_3	CaO	V	Pb	Cu	Zn	As	Co	Ni	Cr
	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
UCC (McLennan et al., 2006)	65.89	15.20	4.50	4.20	107	17	25	71	2	17	44	83
Local bedrock	54.24	14.65	5.56	6.74	108.17	17.69	35.03	93.38	5.60	14.34	36.14	78.95

Tab.3 Major oxides, selected trace elements and REEs median values in the collected samples.

	V	Pb	Cu	Zn	As	Co	Ni	Cr
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Italian D.M. 367/03	ND	30	ND	ND	12	ND	30	50
Canadian ISQGs 2001	ND	35	35.7	123	5.9	ND	ND	37.3

Tab.4 Thresholds limit concentration for both Italian D.M. 367/03 and Canadian ISQGs 2001 regulations.

Lake sediments standard quality and the regulatory gap

The study of heavy metals contamination in aquatic environment has attracted increasing attention because of its abundance, persistence and environmental toxicity. There is a regulatory gap about dangerous substances in sediments of internal waters. Italian regulations, sets environmental quality standards for the substances in surface waters (fluvial, lacustrine, transitional and coastal) but not in its sediments. Commonly, the threshold values for dangerous elements in soils are used. A comparison between samples analysis with some legislative references concerning the quality of the internal waters sediments have been performed (Fig.5). The following laws have been taken into consideration: Italian D.M. 367/2003 "Regulation concerning the setting of quality standards in the aquatic environment for dangerous substances" and Canadian Interim freshwater sediment quality guidelines (ISQGs, 2001). A difference for chemical elements limits was observed and the two considered regulations do not consider the same chemical elements. The Canadian ISQGs do not include V, Co and Ni while the Italian D.M.367/03 does not consider V, Cu, Zn and Co (Tab.4). Therefore, mismatches between the two regulations have been observed as well. Considering the regulatory gap affecting the analyzed sediments we will discuss the data of the Pietra del Pertusillo catchment mostly considering the distribution of elements with respect to the local upper continental crust. This may represent an innovative approach under similar conditions worldwide. It would be useful to define a common and homogeneous regulatory reference for all countries, taking into account the same pollutants in the different environments.

Fig.5 Chemical composition of selected trace elements (Pb and As) in relation with thresholds values of the considered regulations (Canadian ISQGs and Italian D.M. 367/03). Note that, in lacustrine sediments, blue lines represent clay fraction while green line represent bulk fraction

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