WATER AND SEDIMENTS GEOCHEMISTRY AND ELEMENTAL FLUXES ON A LARGE DAM: CASE STUDY OF THE RIDRACOLI RESERVOIR

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INTRODUCTION

Lakes and reservoirs are studied all over the world and their biological, geological, engineering and geochemical aspects have been extensively investigated. Problems with reservoirs on their water quality assessment are potential public health impacts and are usually due to the spread and transmission of diseases (Jobin, 1999; Ampadu *et al.*, 2015), the release of contaminant from anthropogenic sources, such as industries or urban areas adjacent to the reservoir, eutrophication of the water body (Van Ginkel & Silberbauer, 2007; Munyati, 2015), thermal and density stratification and related chemical deterioration (Hawkins, 1985; Mao *et al.*, 2018; Ziaie *et al.*, 2019). In general, the study of Large Dam Reservoirs is of worldwide interest due to their central role as water resources and related environmental impacts. Reservoirs are essentially managed water bodies constructed by man, and, therefore, there is a particular need for the managers to understand their physics, chemistry, and biology (Jørgensen *et al.*, 2013). The construction of a barrier not only affect the water flow, trapping the water resource, but also interferes with the transport routes of sediments and on the entire catchment downstream and upstream. Sediments are forced to deposit in the newly formed basin and, without sustainable management, will reduce the volume of the reservoir and affect the quality of water (Ghaleno *et al.*, 2015). Sediment accumulation, dynamics of deposition and movement, and quality are often a source of concern in reservoirs management, and geochemical tools can be useful for assessing potential risks. Potentially harmful elements (PHEs) can accumulate in sediments exceeding the background concentrations up to several times, which may lead to potential hot spots of harmful substances (Milačič *et al.*, 2017). In this PhD project we studied the water, sediment, and water-sediment interaction in order to characterize the area of study, understand the relationship between elements and element mobility, and evaluate the environmental conditions of a Large Dam system.

AREA OF STUDY

The study area is located on the northern Apennines of the Emilia-Romagna Region, Italy (Fig. 1), and is part of Foreste Casentinesi, Monte Falterona, and Campigna National Park. The geology of the study area includes several units of the Successione Romagnola, dated from 20 to 11.6 million years ago (Neogene; Miocene; Burdigalian, Langhian, and Serravallian). In the study area terrains from the Marnoso Arenacea Formation (MAF) dominates, an alternation of sandstones and marls (Ricci Lucchi, 1978; Ricci Lucchi & Valmori, 1980). This Formation includes 14 members identified according to distinctive parameters such as lithology (arenite/pelite (A/P) ratio), the average thickness of the strata, the composition of arenites, and the stratigraphic position (Benini *et al.*, 2009a, b) (Table 1).

MATERIALS AND METHODS

Since 2015 several sampling campaigns have been carried out to collect samples of water from vertical profiles, from the water column, by Niskin bottle (Toller *et al.*, 2020), sediments from the bottom of the reservoir and its tributaries, using a Van Veen Grab, and sediments from streams and rivers of the nearby area (Toller *et al.*, 2021). In the area close to the dam, sediments and interstitial waters were sampled with two gravity cores, a first one in October 2015 and a second one in April 2016. Data were also collected through an Automatic Benthic

Chamber (CBA), used to assess the benthic flows of dissolved chemical species (Spagnoli *et al*., 2019) and useful to study the water column and the water-sediment interface by measuring environmental parameters and to collect water samples over time.
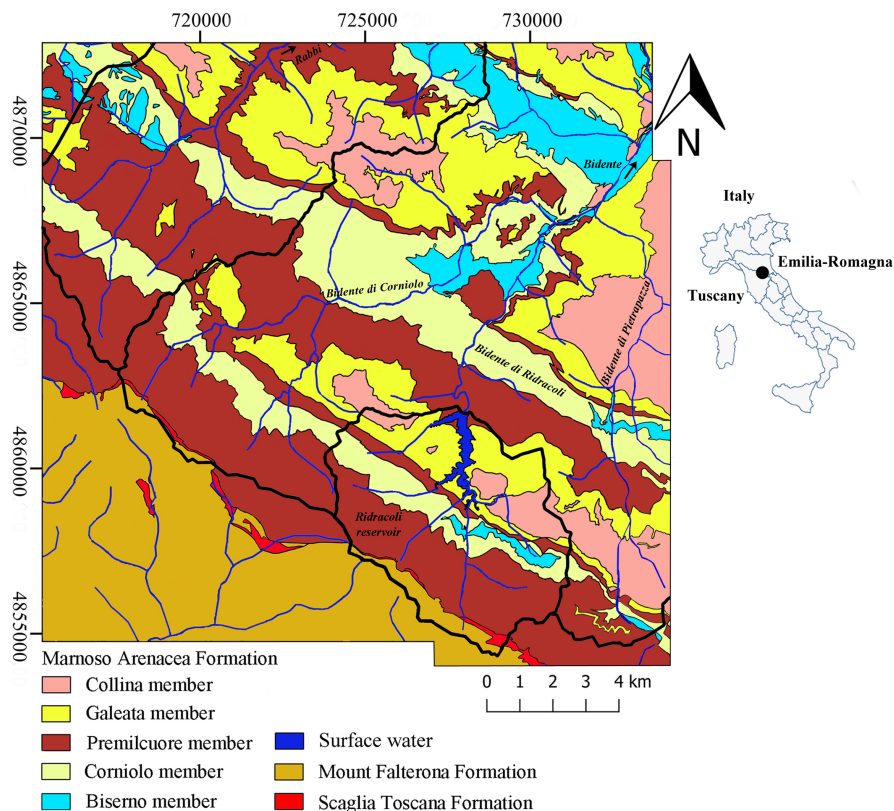

Fig. 1 - Area of study surface geology and Ridracoli reservoir, map coordinate system WGS84-UTM zone 32 N (modified data from Geoportale Regione Emilia-Romagna). From Toller *et al*. (2021).

Table 1 - Distribution (%) of members included in the Ridracoli reservoir catchement. Listed are also the age, sandstone/pelite ratio (A/P), and the formation. Refer to Fig. 1 and to the surface geology of the Emilia-Romagna region for more details (http://ambiente.regione.emilia-romagna.it/en/geologia/temi/geologia/geology?set_language=en).

Member	%	Age	A/P (Lithology)	Formation
Monte Falco	4.3	Upper Oligocene	Pelite almost absent	Falterona Mount (FAL)
Biserno	3.0	Langhian-Serravallian	0.2-0.33	Marnoso-Arenacea (MAF)
Camaldoli	3.2	Upper Oligocene-Miocene	2-10	Falterona Mount (FAL)
Collina	8.8	Langhian-Serravallian	0.2-0.33	Marnoso-Arenacea (MAF)
Corniolo	15.6	Langhian-Serravallian	0.33-0.5	Marnoso-Arenacea (MAF)
Galeata	18.7	Langhian-Serravallian	0.33-0.5	Marnoso-Arenacea (MAF)
Montalto	0.2	Miocene	0.33-2	Falterona Mount (FAL)
Premilcuore	41.9	Langhian-Serravallian	1-2	Marnoso-Arenacea (MAF)
Scaglia Toscana	1.3	Upper Eocene-Lower Oligocene	Argillites, marly argillites and silty marls	Scaglia Toscana (STO)
Fosso Fangacci	0.2	Upper Oligocene-Lower Miocene	< 1	Siltstones of Fosso Fangacci (SFF)

The physical (T, dissolved oxygen (DO), pH, EC, and Total Dissolved Solids - TDS) and chemical parameters, as well as the chemical data of reservoir water, anions and cations, were analysed using an Ion Chromatograph (Dionex ICS 3000) and the metal were analysed by ICP-MS (Agilent 7800) at the Romagna Acque laboratories at Capaccio.

The bulk chemical composition of the sediments (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5 as wt.% and As, Ba, Ce, Co, Cr, Cu, La, Nb, Ni, Pb, Rb, S, Sr, Th, V, Y, Zn, Zr as mg/kg) was evaluated by X-ray fluorescence spectrometry (XRF) at the XRF laboratory of BiGeA Department, Bologna (Panalytical Axios 4000).

The analysis to evaluate the concentrations of Carbon, Hydrogen, and Nitrogen in the sediments were carried out by CHNS-O Analyzer in Ravenna (Thermo Fischer FLASH 2000) and the particle size data come from a Micromeritics SediGraph 5100 of Ravenna Campus for Environmental Sciences.

The pseudo-total composition was evaluated for 43 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Th, Ti, Tl, U, V, Y, Zn, and Zr) applying a modified aqua regia digestion and an analysis by inductively coupled plasma mass spectrometry (ICP-MS) at the Bureau Veritas Minerals (BVM) of AcmeLabs laboratories in Vancouver (Canada).

The BCR sequential extraction procedure was also performed on selected samples following the three-step methodology proposed by European Community Bureau of Reference (Rauret *et al.*, 1999; Sahuquillo *et al.*, 1999). This methodology investigates the metal partitioning within the sample through the application of different reagents in order to identify their association with relevant sediment fractions: the exchangeable sites and carbonates, the Fe and Mn oxides and hydroxides, the organic matter and sulphides.

For leaching test, a UNI EN 12457-2 (2002) procedure was used, a compliance test for the leaching of granular waste and sludge, which in this case was adapted for the environmental assessment of bottom sediments.

A further extraction has been done for the analysis of polycyclic aromatic hydrocarbon (PAHs), organic compounds containing of hydrocarbon containing only carbon and hydrogen present in coal and tar deposits, which are extracted by Soxhlet with a mixture of acetone/cyclohexane (1:1) solvent and analysed by GC-MS (Agilent 6850) connected to a 5975 Agilent HP quadrupole mass spectrometer at the laboratories of Ravenna and Rimini Campus of the University of Bologna after silica gel clean-up (Fabbri *et al.*, 2013).

Data collection and processing were performed using Microsoft Excel software, GCDkit 5.0 in R 3.4.3 (Janoušek *et al.*, 2006), R studio, CoDaPack and Past4.0 (Hammer *et al.*, 2001) suites, whereas QGIS 3.12 Bucarest was used for map production and spatial analysis. Datasets have been elaborated to produce descriptive statistical analysis, and multivariate approaches (cluster analysis and principal component analysis) in order to obtain a better indication of geochemistry (Filzmoser *et al.*, 2005; Templ *et al.*, 2008; Reimann *et al.*, 2008).

RESULTS AND DISCUSSION SUMMARY

From the physical and chemical analyses of the water column over time, an alternation of water stratification and mixing processes in the water body of the reservoir emerged, settled by seasonal changes in temperature and density of the water (Fig. 2a). The upper reservoir water (epilimnion) becomes warmer than the bottom waters (hypolimnion) and the boundary between these layers (metalimnion) turns into a thermocline. The thermocline and the density difference act as a barrier limiting the mixing of the water column (Magee & Wu, 2017; Winton *et al*., 2019) and the diffusion of heat and DO between epilimnion and hypolimnion (Burns, 1995), not allowing the layers to be mixed. This stratification leads to the establishment, at the bottom, of an anoxic condition in late summer (October, Fig. 2b). This affects concentration and mobility of some elements such as Fe and Mn, which are found at high concentrations in the bottom in late summer (Fig. 2c), both are constantly monitored at the treatment and purification plant located downstream the dam, and of interest as of concern for water quality.

At the same time, on the solid fraction, the analyses of organic matter, total inorganic and grain size composition of surface sediments within the Ridracoli reservoir and surrounding areas, assessed the presence of a

clay minerals and carbonates, reflecting the geological background of the Marnoso Arenacea Formation (MAF), in addition to inter-elements relationship and grain size influence on sediment chemistry by PCA (Principal Component Analysis; Fig. 3, Table 2) (Toller *et al.*, 2021). Moreover, significant differences have been observed by cluster analysis between the reservoir and its surrounding areas, as well as within it (Fig. 4).
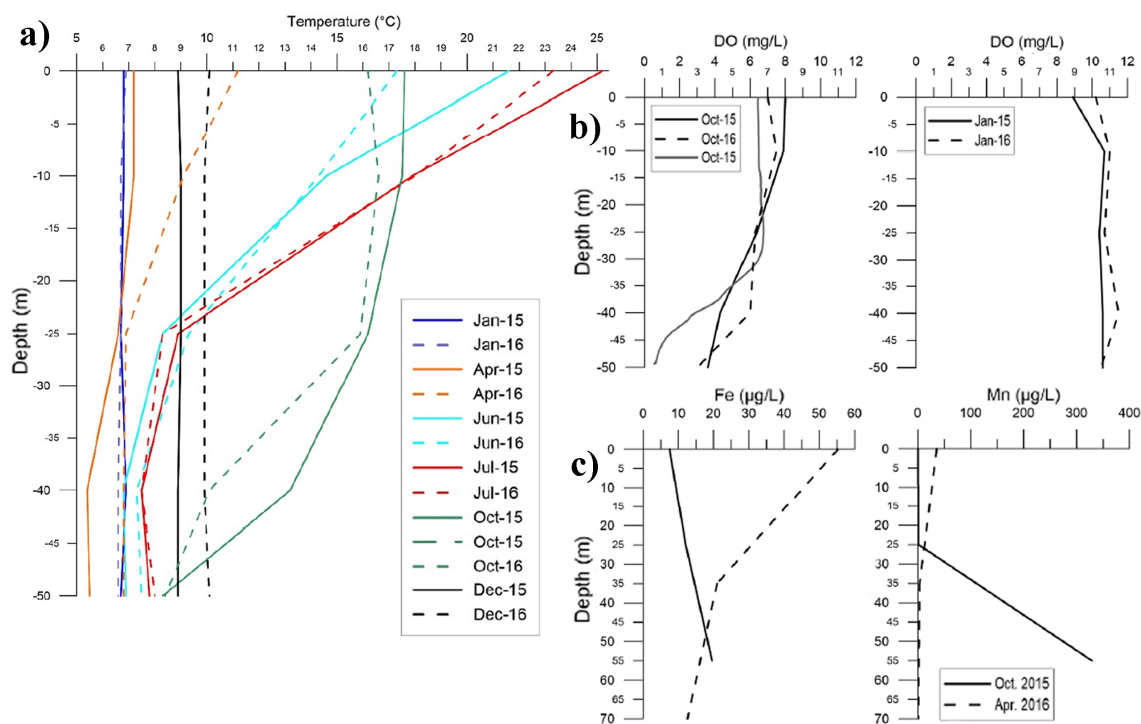

Fig. 2 - a) Reservoir temperatures along the water column; b) Dissolved oxygen (DO, mg/L) distribution along the water column in 2015 and 2016 for the two representative conditions of anoxic conditions in October and January as representative of the rest of the year. The grey line on the October graph indicates data collected continuously along the water column, down to the reservoir bottom, by the CTD probe; c) Fe and Mn concentrations along the water column in October 2015 and April 2016 *via* Niskin bottle sampling (Toller *et al.*, 2020).
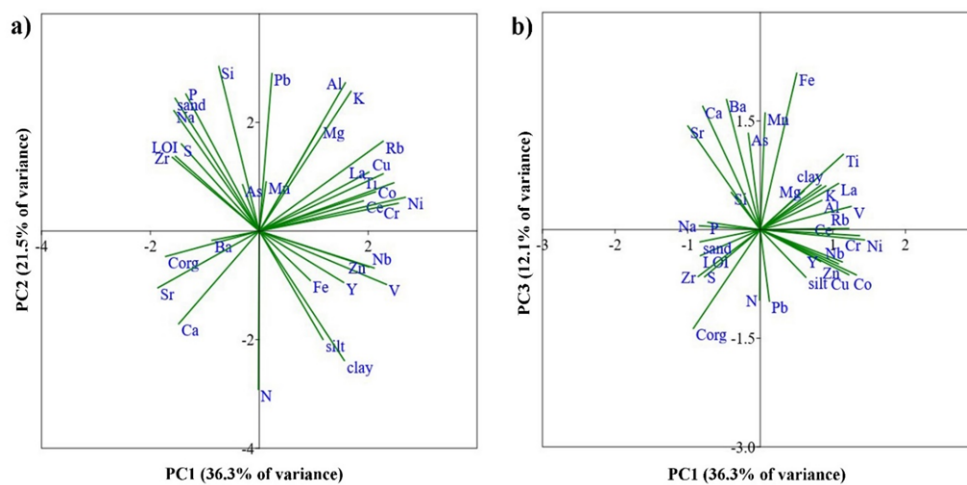

Fig. 3 - Loadings for PC1 *vs*. PC2 (a) and PC1 *vs*. PC3 (b). From Toller *et al*. (2021).

Table 2 - Interpretation of the first three Principal Components (PCs) extracted from the log-transformed data of the Ridracoli reservoir. Both variables with positive and negative loadings are interpreted (Toller *et al.*, 2021).

| Component	% of variance explained	Positive association	Interpretation	Negative association	Interpretation
PC1	36.3	Cr, V, Rb, Cu, Ti, La, K, Nb, Ni V, Zn Al, Co, clay	Fine-grained fraction	Ca, Na, Zr, Sand	Coarse-grained fraction, eventually carbonate rich
PC2	21.5	Si, Al, K, Al, Na, Mg, Pb, Sand	Siliciclastic sandy fraction	N, clay	Fine-grained organic rich
PC3	12.1	Sr, Ba, As, Ca, Mn, Fe	Authigenic phases (carbonates, iron and manganese oxyhydro-oxides)	Corg	Carbon-rich organic matter
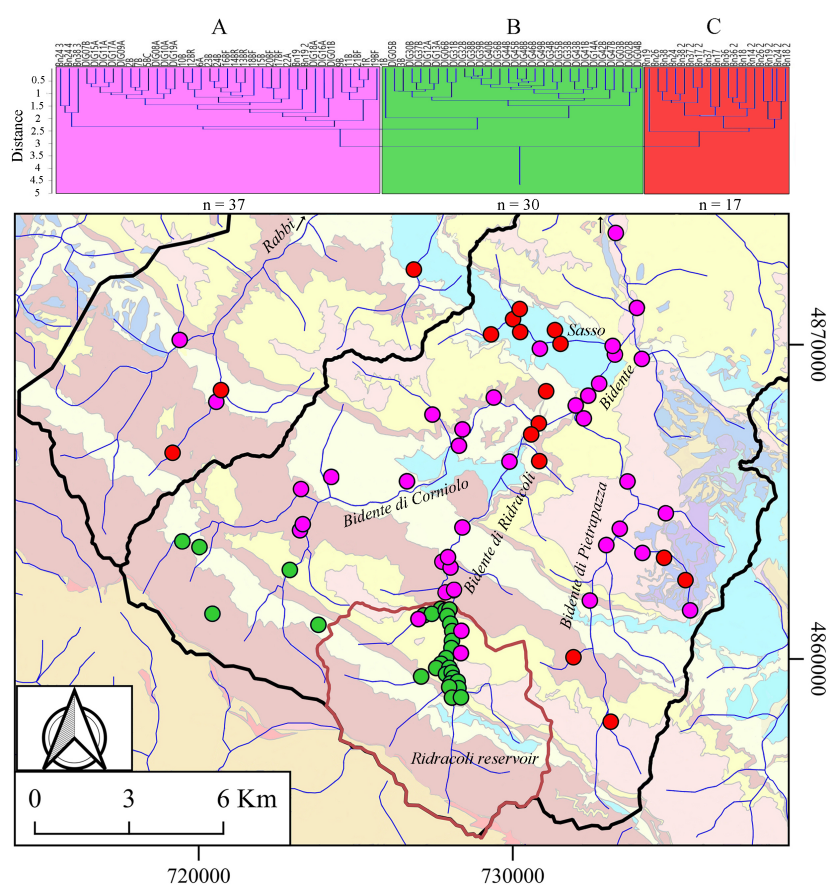
Fig. 4 - sample stations of the area of study grouped by colors (A, white; B, violet; C, blue; D, green) according to the results of cluster analysis. Background is the simplified geology of Fig. 1.

The effects of the dam on the area have been seen also comparing the geochemical composition of sediments along some branches of Bidente River, we evaluated the geochemical evolution and the variation downstream of the river rod interested by the dam and neighbouring ones, on the other hand, without dam.

We deeply characterized sediments from Ridracoli reservoir, deepening the knowledge of the solid fraction, investigating their pseudo total composition (Aqua Regia digestion, AR), their degree of elements extractability and enrichment factors valuating mobility and concentrations, and comparing obtained values with the limits by law and literature, therefore also evaluating them from an environmental point of view.

Once we had assessed the composition of water and sediment within the Ridracoli catchment, we were interested in understanding their interaction, paying particular attention to the bottom of the reservoir near the dam. Data from sediment cores, interstitial waters, and benthic chamber from this spot were analysed to determine early diagenesis processes and elements flows from and towards sediment and water column. In this way we observed that the organic matter degradation, early diagenesis, and mineral formation occur at water-sediment interface.

Finally, the leaching test and extraction procedures showed, within the reservoir, a well define partitioning of elements between the exchangeable, reducible, oxidable and residual fractions, which appeared peculiar to each sampling station, both as regards spatial distribution that in depth. From an environmental point of view, no data showed anomaly, no PHEs or any of the parameters considered of interest by the legislation was above the proposed limits for the environmental regulations of excavated soils and rocks or for the element mobility in the environment.

CONCLUSIONS

Data show that a thermal stratification seasonally affects water quality, determining the formation of an anoxic layer in late summer that induce the mobilization of heavy metals and, more in general, of PHEs. Overall, this environmental condition is determined by processes of absorption and release, nitrification and denitrification, organic matter degradation and based on the equilibrium between the soluble and insoluble fractions of the water-sediment system. These data suggest that in late summer the thermal stratification with the consequent release of Mn and Fe, and less of PHEs from the sediment creates an anoxic environment in the lower fraction of the water column, that results enriched in metals. On the opposite, in late winter the almost complete mixing of the water column, the lower consumption of oxygen and nitrate and lower release of metals at the water-sediment interface, create an oxic and metal-poor water body. From this context it is to state no water withdrawal problems emerge during the year, with the exception of the late summer.

Water analysis showed a Ca-Mg-HCO₃ composition, while sediments displayed a clayey-silt, sand-silt to silty sand composition in texture, with an Al_2O_3 clayey fraction inside the reservoir and a CaO and carbonate once with coarser size outside. All these aspects reflect the geological background of alternated sandstones and marls of the MAF (Marnoso Arenacea Formation) members. Statistical analyses revealed a strong association of the fine grain size with a large number of elements (As, Co, Cr, Cu, Ni, Pb, and Zn among the others). Sediment samples from the bottom of the reservoir, showing fine size adsorbing above elements, and for this reason they display higher concentrations of PHEs respect to samples with coarser grain size from tributaries. Although the role of organic matter is still undefined, these data suggest it affects As, V, MnO and Pb behaviour. Data collected propose the presence of the dam influences the PHEs enrichment inside the reservoir compared to the surrounding areas. The high degree of extraction observed for PHEs (Zn, As, Pb, Cu, Co, Ni) has been principally correlated to the Fe-Mn oxy-hydroxides.

The study of early diagenesis processes and of the fluxes at water- sediment interface from the bottom of the reservoir provided data about the accumulation and the burial of sediments in this site, which allows to organic matter decomposition and nitrification influencing concentrations of heavy metals such as Fe and Mn. Concomitantly, were observed a consistent organic matter degradation, dissolved oxygen consumption near the water-sediment interface, nitrate and sulphate reduction in the upper layers, and Fe-Mn oxides/hydroxides reduction both on surface and in depth. Positive flows of TIC, Mn, Fe, Al, B, Ba, Ca, Cl, K, Li, Mg, Na, Se, and Sr of towards the water column, linked to early diagenesis, were highlighted as more consistent in late summer then in late winter. Further, cores analyses suggested the importance of redox processes at the water-sediment interface, where they determine nutrient and elements mobilization (or retention), also allowing their entry in the water column. Sequential extraction allowed to identify elements mobility and in particular to assess the different partition in each sediment fraction, and thus confirming and giving more information on above positive flows origin. In particular Ca, Sr and Mn, derive from carbonates and the exchangeable fraction, Fe, Pb, As, Co and Zn from the once linked to oxides and hydroxides, while low extraction percentages were detected for the fraction

linked to sulphides and organic matter. Finally, higher amounts of Al, V, Cr, Cu were observed in the residual fraction. Data collected indicates that sediments composition and fractionation change along the reservoir due to the seasonal presence of the anoxic layer.

In conclusion, this study demonstrates that Ridracoli is a good quality reservoir for potable water usage, in agreement with the limits provided by Italian and International Legislation and guidelines, enrichment factors and literature, and can be helpful for the resource management and the planning of future interventions.

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