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

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Table of contents

General Abstract

The study of Large Dam Reservoirs is of worldwide interest for their central role as water resources and related environmental impacts. In this context, the interesting in the exploration of water and sediments composition, as well as their interaction, has increased in last decades.

In this PhD project we investigated the Ridracoli artificial basin, that is the main water reservoir of the Emilia-Romagna region (Northeast Italy), located in the upper part of Bidente River on Apennines, and represents the principal drinking water supply of the area. This work is aimed to characterize waters and sediments to better understand their composition, interactions and processes that occur into the reservoir, to assess if and how all these aspects can have environmental implications.

From physical and chemical analyses of water column, emerged an alternation of water stratification and mixing processes in the water body of the reservoir, attributable to seasonal changes in water temperature, density and levels which lead to the establishment, at the bottom, of an anoxic condition in late summer. This affects concentration and mobility of some heavy metals as Fe and Mn, 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, the analyses of organic matter, total inorganic and grain size composition of surface sediments within Ridracoli reservoir and surrounding areas, assessed the presence of a clay minerals and carbonates, reflecting the geological background of Marnoso Arenacea Formation (MAF), in addition to inter-elements relationship and grain size influence on sediment chemistry by PCA (Principal Component Analysis). Moreover, relevant differences have been observed by cluster analysis between the reservoir and its surrounding areas, as well as inside the same. By comparing few branches of Bidente River we evaluated the geochemical evolution and the effects of the damming on the area. After, we deeply characterized sediments from Ridracoli reservoir, investigating their pseudo total composition (Aqua Regia digestion, AR), degree of elements extractability and enrichment factors, and comparing obtained values with the limits by law and literature. Once assessed water and sediment composition in Ridracoli basin, we moved to understand their interaction, paying particular attention on the bottom of the reservoir near the dam. Sediment cores, interstitial waters, and benthic chamber data from this spot were analysed to determine early diagenesis processes and elements flows from sediment and water column. In this way we observed organic matter degradation, early diagenesis, and mineral formation occur at water-sediment interface. Finally, leaching test and extraction procedures highlighted, within the reservoir, a well define partitioning of elements between the exchangeable, reducible, oxidable and residual fractions, that appeared peculiar for each sampling station, both regarding spatial and in-depth distribution.

Collectively our results are useful for the comprehension of processes that occur in water and sediments of Ridracoli reservoir, giving important knowledges about the site that could be relevant for the management of the resource and the planning of future interventions.

Chapter 1 – General introduction and aims of the study

1.1 Water availability

Water is a fundamental resource for human activities, and its use, consumption and availability are among the main problems for every local or national administration.

The World water request is currently estimated at 46 × 10^3 km^3 per year, and projections for 2050 forecast an increase of about 6 × 10^3 km^3. Water use is increasing and will increase due to population growth, economic development and changing in consumption models (UN Water, 2018).

Italy has a total surface of 302.070 km^2 and an annual rainfall mean of 934.5 mm/year (Braca and Ducci, 2018; Braca and Mariani, 2019), but territorial diversification can largely vary the local situation from abundance to water shortage. As predominantly mountainous nation, most of the Italian watercourses have a torrential regime ruled by rainfalls and with an irregular intake, which exposes large areas to the risk of extreme events or dryness for some period of time. It is not the total amount of rainfall counted on an annual scale, but its distribution in time, in particular in shorter time intervals, which affects paths and management of the water resource. In Italy, the average annual volume of precipitations is about 300 × 10^9 m^3, of which renewable water resources are estimated about 170 – 190 × 10^9 m^3 per year. The national total water withdrawal accounts approximately 45 × 10^9 m^3, destined for agriculture (60%), energy and industrial sector (25%), and civil uses (15%). Consumed waters is provided for the 75% by lakes, reservoirs and rivers, and for the remaining 25% by groundwater (ISPRA, 2020).

The water demand is increasing in Italy as in the rest of the World, and to better improve the exploitation of the resource and, at the same time reducing waste, it is possible to act on plenty of interventions such as containment of consumptions, use of more efficient irrigation techniques, reuse of waste waters, improvement of the distribution network by decreasing network losses, and recovery or new construction of artificial reservoir which can better manage the resource. In this context, reservoirs play an important role allowing accumulation and storage of water.

1.2 Lakes and reservoirs

Lakes are natural water bodies, where flow from one or several streams, creeks, or rivers is impounded by any natural obstacle. Instead, a reservoir is an artificial lake created by a human made dam blocking a river with the aim to generate hydro-electric power, control floods, accumulate water for freshwater supply and for household or irrigation. Despite these advantages, building a reservoir implies several negative aspects, such as the deprivation of land and hinder fish swimming upstream for spawning.

The physico-chemical and biological events which take place and differ between lakes and reservoirs are related to their shape and size, as well as to the geographical, geological and morphological characteristics of the drainage basin.

The formation of a lake mainly occurs through the filling of a natural depression or the impoundment behind a natural dam. Several events can determine the formation of a depression, such as the geological deformation caused by tectonic to volcanic activity, elutriation, ice or water erosion, or slow melting of permafrost. Most of the existing lakes have been formed by glacial activity during the last ice Age. (Hutchinson, 1957; Wetzel, 2001). From a geological point of view, lakes, as reservoirs, have a short lifetime, with few exceptions such as Lake Baikal and Lake Tanganyika, which are million years old (Piccolroaz and Toffolon, 2018; Wilson et al., 2004). However, if compared to natural lakes, reservoirs are extremely short lived, designed for a lifetime of 50 years, because of deterioration of construction materials or by reduction of capacity caused by deposition of sediments. In particular, this latter process can lead to a complete filling in a few years in a very strong erosion catchment area. Nevertheless, reservoirs with an estimated lifetime of several centuries also exist (Nilsson, 2009).

In the early stages of a water body's life, the first phase is represented by the impoundment, the plankton benefits from the release of nutrients due to the degradation of submerged terrestrial vegetation. Subsequently, oligotrophication or eutrophication occur if the incoming water is poor in nutrients or is fertilized by animals or agricultural sources respectively. Finally, there is a sediment silt deposition in which the conditions for biogenic burial are suitable (Dean and Gorham, 1998; Mendonça et al., 2017).

The drainage basin characteristics, which clearly define lakes and reservoirs, include geological features, type and development of soils, chemical composition, geomorphological aspects, as slopes, and cover vegetation (Wetzel, 2001). Soil and vegetation affect not only the runoff, but also the composition and the amount of organic matter and sediments that enter the tributaries and reach the reservoir. The area of the drainage basin, related to that of the water body, is generally greater than 10:1 in the case of lakes, and it is less for reservoirs (Uhlmann, 2011). The drainage basin of a reservoir is also usually large enough to fill the artificial lake within a period of 1 year or less. The influence of the structure and uses of drainage basin on the quality of waters is therefore quite significant. Reservoirs behaviours are also ruled much more to atmospheric precipitation and runoff than lakes, which are largely supplied by groundwater (Hayes et al., 2017). A further differentiation is that lakes are often located near the centre of their catchment area, while reservoirs are located at the margin, predetermined by the morphology of the territory.

Reservoirs, as artificial lakes in which water is physically stored, increasing the availability of water over time for various purposes, are usually built where groundwater resources are not sufficient to satisfy the demand for drinking or irrigation water needs, or where the discharge of a river and the morphology of the site favour the construction of a dam. Reservoirs, indeed, increase the hydraulic load, providing the energy for electricity production for a total of 80% of the World's total renewable electricity supply, accounting the 20% of the global electricity production (Zarfl et al., 2015), and passively provide a floods control, if properly managed and designed with a sufficient holding capacity.

The retention time for reservoirs depends on their main usage and generally is shorter than that of a natural lake. Most of all reservoirs nowadays are multifunctional, mainly used for hydropower electricity production or flood control, with short residence times of few days up to some weeks, instead, those used for drinking purposes largely exhibit calculated retention times of about 1 year. The flowing in natural lakes, however, is lower, with retention times of years, frequently even of several decades. Reservoirs respond faster and are more sensitive to changes in the tributary water quality and inputs caused by alterations of the catchment usage and droughts, that have immediate impacts on reservoirs volumes or quality of the withdrawal waters.

Most of natural lakes exhibit a U-shape basin, with the deepest area localizes approximately in the centre, unlike reservoirs that display a V-shape basin with the deepest area normally proximal to the dam. Contrary to natural lakes, which present a dominant vertical framework, reservoirs are characterized by longitudinally different morphological frameworks: strongly riverine flow area, shallow and narrow regions below the tributaries' mouths; a transitional area of moderate depth; and a lesser drained lacustrine and deep area near the dam. This hydro-morphological structure and the flows system of reservoirs cause longitudinal differences in all physical, chemical, and biological characteristics of the water quality and sediment distribution (Figure 1.1; UNEP, 2000).

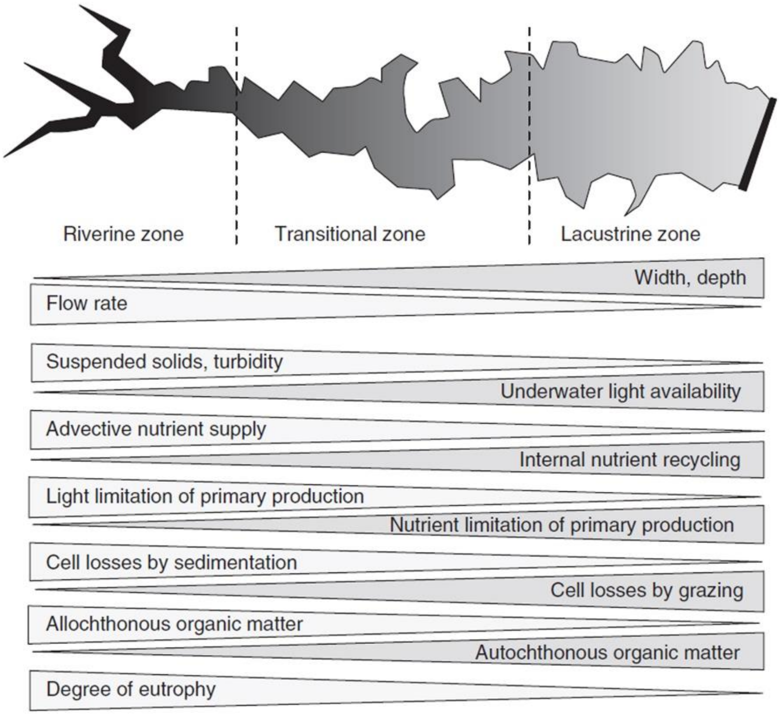


Figure 1.1, Diagram of the longitudinal zonation of the hydro-morphology and water quality in large reservoirs (Kimmel and Groeger, 1984).

In lakes sediments are mainly from an autochthonous organic provenance, internally produced within the site, instead in reservoirs the fraction of imported allochthonous mineral material from external areas is higher and sediments represent a fundamental component of their environment. Siltation is a serious problem but the import of suspended particles and nutrients in reservoirs can be reduced by pre-impoundments, located upstream of the water body (Paul, 2003; Paul and Putz, 2008) or by several other measures (Tigrek and Aras, 2012).

1.3 Reservoirs in Italy

Large Dams in Italy are fundamental strategic resources for the activities and economy of the Country in the energy, industrial, agricultural use and drinking water, creating an essential network of diversified and basic services for the population. The decree of 21st October 1994 n. 584 attributes to the competence of the State the barriers, containment dams or bulkheads, that exceed height of 15 m or that have a total volume greater than 1×10^6 m^3. Dams can be classified as Large or Small Dams. Small Dams, controlled by the local administrations, are strategic and fundamental for the local supply of water. They are estimated 8300 in Italy and nearly 50000 in the World, storing more than 15% of the global runoff (Nilsson, 2009). Conversely, Large Dams are supervised by the Dam Management of The Ministry of Infrastructure and Transport, and 534 of them are nowadays operational in

Italy, of which 60% are older than 50 years (ITCOLD). Thanks to innovative management procedures and proactive maintenance, those dams will maintain reliability and safety, but further infrastructure projects will be needed in future. The construction of reservoirs was strongly linked to the past industry and agriculture development of Italy to relative needs of improvement availability of water resources, and nowadays no more dams are under construction. From 25 to 400 new dams were built from 1920 to 1965 (8.3 new dam per year), a noticeable decrease until 4.3 new dam per year after the Vajont disaster in 1963. Since 2000, there is a maximum of about 550 reservoirs and a slow decrease in total number of new dams in the last 20 years (Figure 1.2).

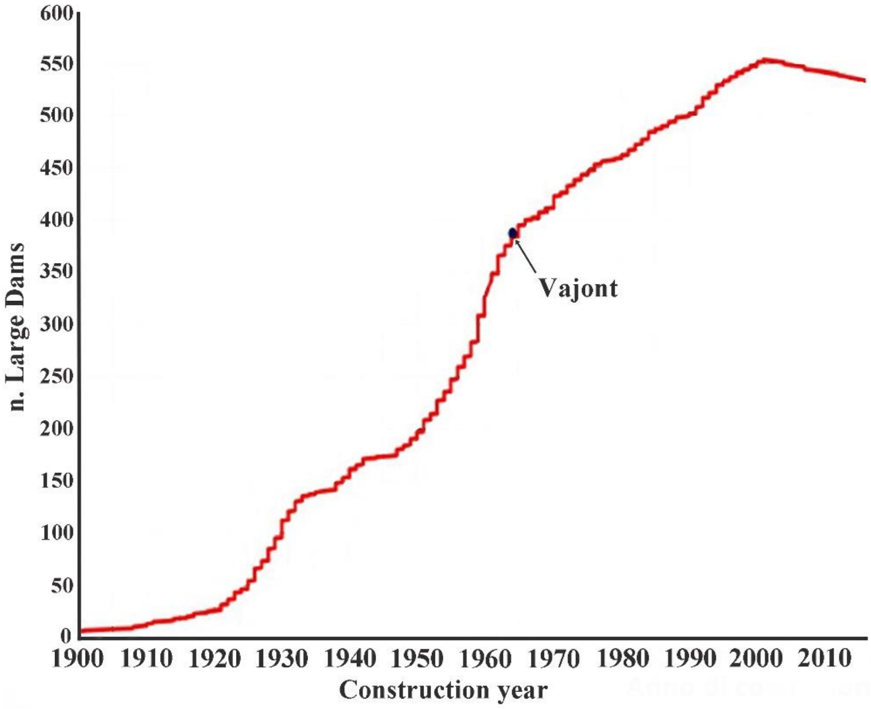
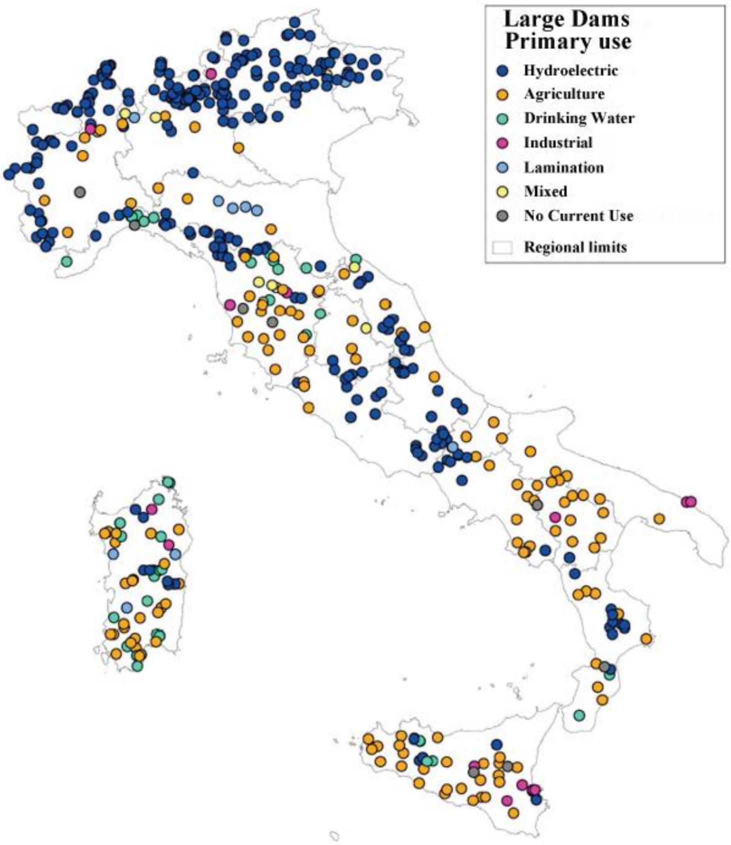


Figure 1.2, Graph reports the number of Large Dams in time in Italy (modified by ITCOLD database).

Most of dams in Italy have hydroelectrical purposes, followed by irrigation, potable and industrial in descending order (ISPRA, 2020). In 2020 the active dams with regular activity are 367, among which 37 have a limited reservoir, 93 have an experimental reservoir, 24 are out of order and 11 under construction. Large Dams’ distribution through the Italian territory and their primary use are shown in Figure 1.3.



Region	Number of Large Dam
Abruzzo	14
Basilicata	14
Calabria	22
Campania	17
Emilia-Romagna	24
Friuli Venezia Giulia	12
Lazio	20
Lombardia	13
Liguria	77
Lombardia	16
Marche	7
MolisePiemonte	59
Puglia	9
Sardegna	59
Sicilia	46
Toscana	50
Trentino- Alto Adige	37
Umbria	10
Valle D'Aosta	8
Veneto	18

Figure 1.3, Number of Italian's Large Dams per region (ISPRA, 2020) (right) and their distribution (left) according to the primary use of the reservoir (modified by ISPRA, 2020).

About the amount of water taken into account by Large Dam reservoir, Figure1.4 shows their distribution and impact by volumes. The total volume in Italy ascribable to Large Dams is 13.5 × 10^9 m^3.

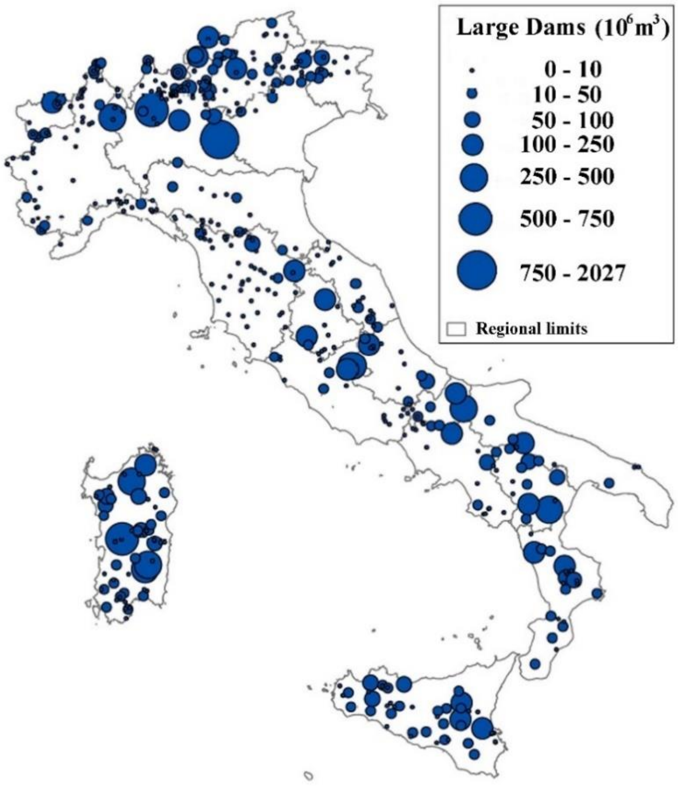


Figure 1.4, map of the Large Dams with proportional dot based on the maximum stored water volume determined by D. Lgs. 584/94 (modified by ISPRA, 2020).

1.4 Reservoir issues

The artificial reservoirs are anthropogenic constructions that, thanks to a barrier built by man, change the natural course of the waters. The river and the catchment area are then modified by some events that in a short time transform the system and trap the sediments inside the reservoir due to a physical barrier. The primary purpose of reservoirs is the storage of water, but it also implies the trapping of sediment as side effect. In time, deposition and accumulation of the solid fraction affect the conformation of the basin and dam modifies both the stability structures upstream and downstream of the barrier. A common effect is the trapping and accumulation of sediment, that increases over time in the bottom, and simultaneously is not transported downstream to the sea (Brandt, 2000; Choi et al., 2005). Throughout the time, accumulations will reduce constantly both the collection capacity of the tank and the natural supply of sediments along the river downstream and in coastal areas. The construction of a dam can affect the state of coastal areas, which are particularly sensitive to the decrease in the contribution of sediments from rivers, and the morphology of rivers up- and downstream.

Sediment accumulation affects the volume of the reservoir year by year and can eventually influence the chemical quality of the water resource (Krasa et al., 2005). Therefore, it is necessary to study every site collecting cartographic, bathymetric, textural and chemical data of the area in order to be analysed and elaborated for characterizations and environmental assessments for a better management.

The sediment that can be found in an artificial basin largely derives from the contribution of altered rock and surface soil in the areas upstream of the lake and in its tributaries. The type of material transported depends on the lithological characteristics of the catchment area. Crucial for the supply of sediments are the state and the configuration of the hydrological basin's boundaries, the water supplies, the hydraulic system, the seasonal hydrological variability and the use of the soil. All these aspects, combined with the background lithology, influence the amount and geochemistry of sediment transported into the lake (Linnik and Zubenko, 2000). Further influences on sediment transport and erosion are linked to soil management, as the vegetation cover, since deforestation and/or forest fires can significantly increase the transport of solids (Marques et al., 2007; Zuazo and Pleguezuelo, 2008), as well as periods of drought and floods which massively affect erosion rates. Furthermore, the tendency of the last years of rainfalls to concentrate intensely in short periods with extreme events increases the quantities of eroded material and the transport of sediments in a non-constant way. Moreover, more rain than snow increases the transport of sediment and the retreat of glaciers exposes a higher amount of unconsolidated material to erosion. Together all these aspects entail problems for the management of reservoirs and may alter the quality of the resource due to the variability of the sediment supply and turbidity.

Accumulated sediments therefore influence both quantitatively and qualitatively the water resource and their collection are a physical and inevitable consequence of the accumulation of the water resource. The reservoir capacity is an expensive and non-renewable resource, since a natural process of sediment elimination cannot occur, and everything must be managed in the best possible way to ensure its durability. The absence of management and maintenance of the reservoir could lead to the infilling by sediments, with the deletion of the advantages of the construction of the dam. The most drastic interventions to perform on a reservoir are the emptying and removal of sediments, the latter being expensive and with a high environmental impact causing in a short time the modification of catchment system, stopping the reservoir activities and producing a considerable amount of waste sediment that need to be treated, stored, or reused. For these reasons, recently the concept of "sustainability reservoir" has been introduced (Morris, 2015), according to which a reservoir has to be in an ideal condition, able to perform its function without the limit given by siltation. Smart management and targeted interventions may help to control inputs and outputs of sediments releasing it downstream or limiting the erosion upstream. The accumulation of sediment cannot be stopped as it is determined by plenty of factors but can be controlled in quantity and quality.

In the past, dams' sediment management plan designed a lifetime of about 50 to 100 years, which did not exceed the lifetime of the dam. The old dams hence did not envisage a long-term sediment management plan, but nowadays the need to prolong their activity and the concept of sustainability entail to learn more about these issues, together with dam monitoring and reinforcements.

Lakes and reservoirs affect the downstream river in different ways, except for lakes of arid or semiarid zones, where tributaries and downstream river regimes are unaltered, although damped. The seasonal discharge variation of the downstream river of a reservoir is totally different from that of the tributaries. The missing or changed temporal sequence of floods, droughts, and regimes in general completely alter the processes of riverbed formation, erosion, deposition, and ecological environments. Thus, seasonal ups and downs of the surface level are normal in reservoirs and dilute over time the normal flow of downstream water, keeping it above the minimum runoff guarantee. A reduced water level has generally potentially negative impacts on reservoirs' water quality (Elçi, 2008), as well as on hydrographic parameters, affecting the trophic state deteriorate, average and maximum depth, retention time, impact of extreme nutrient, suspended matter, and microbial loads resulting from floods. All these aspects are more evident during dry season.

1.5 Sediments in a reservoir

As already mentioned, the structure of the river and of the catchment area is modified and deformed in a short time, trapping the sediment previously transported to the sea inside the reservoir, due to the physical barrier built for water storage. The main issue linked to the accumulation of sediments in the reservoir is its effect on the maximum volumes of accumulable water resource and the fact that sediments can affect the water quality from a chemical point of view. Sediment trapped by a dam not only causes its accumulation in the reservoir, but at the same time creates a decrease in the downstream supply. Sediments accumulate along the entire bottom of the tank in different ways (Figure 1.5), the coarse sediment settles first in the upstream part, forming a delta where it enters the reservoir, while the fine once is transported further downstream (Randle and Bountry, 2017), depending on the morphology of the area and on the transport energy of the flow. It should be noted that sediments are not all deposited in the deepest point of the lake, but also near the outlet of the tributary, with a distribution related to the granulometry as well as to the morphology, following Stokes' physical law which establishes the equilibrium conditions of suspended solids as a function of the speed of the current and the diameter of particles (Randle and Bountry, 2017). The spatial sediment grain size in a reservoir is directly derived from the transport energy and mechanics. The processes described above, however, represent an ideal schematization that might not be reflected in nature.

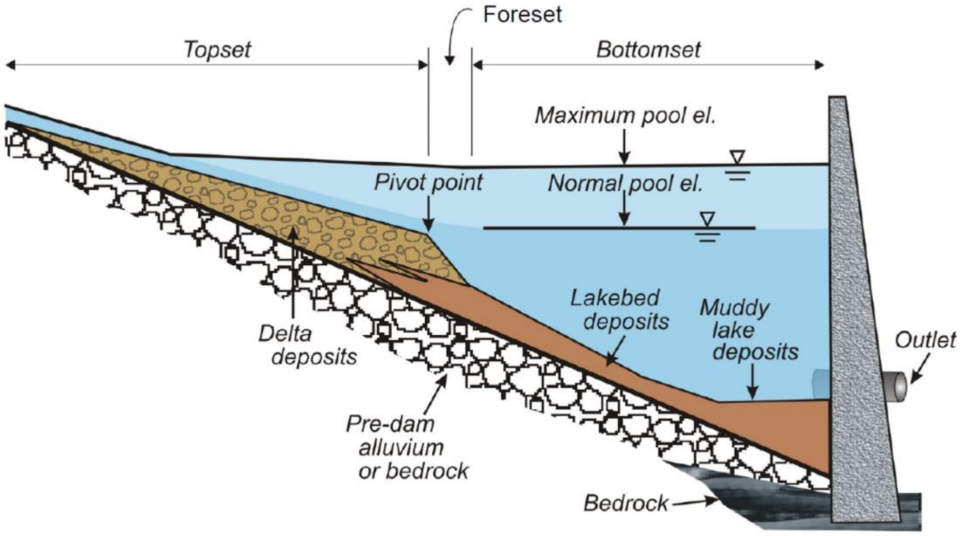


Figure 1.5, Schematic representation of a reservoir configuration and its sediment distribution (modified by Randle and Bountry, 2017).

The real sedimentation that takes place in an artificial lake can be measured and monitored combining topographic and bathymetric studies. Remote sensing techniques, such as aerial LiDAR for topography and GPS and multi-beam for depth using a boat, can be useful for evaluating the reservoir area and the bottom morphology, thus assessing changes in reservoir capacity. The volumes of deposited sediment can then be obtained by comparing the volumes of the different measurement campaigns, analysing with deep drilling and coring to reach recognizable layers by dating or by using acoustic waves to estimate the thickness of the deposit. Other techniques include monitoring of inputs and suspended sediments, by turbidity analysis or calculating inputs and outputs of the basin (Akrasi, 2005; De Ventre et al., 2009).

The sediment within a reservoir can be of various nature and types and can come not only from the geological background of the catchment area but can collect external inputs, due to wind transport or various anthropic activities. In addition to a predominant mineral component of the sediment, that reflects the lithologies emerging in the drainage basin and the products of their chemical alteration, there is also an organic component which represents a relevant input in natural environments. Its importance is linked to the fact that its presence consumes oxygen and that the degradation processes can occur even in the absence of oxygen by involving other oxidizing agents (for example oxides and hydroxides of Mn and Fe) which can alter the chemical state of water and sediments. Physical parameters, such as pH or redox, as the tendency to move from an immobile to a mobile phase depend on the conditions and state of equilibrium in which sediment and water are found and on the different affinities of released elements. Several types of chemical characterization analyses can be performed to evaluate concentrations of metals and other elements of concern. The sediment is in direct contact with water and naturally interacts by mutual exchange of elements (Linnik and Zubenko, 2000).

Italian law defines dredging mud as the material present on the bottom of a water body; subdivisible into dredging muds, not considered in Part IV of D. Lgs. n.152/2006 and excluded from the waste legislation, and into the not excludable muds (D. Lgs. n.152, 2006). In any case it is necessary to carry out characterization studies on sediments that need to be handled, on the chemical-physical characteristics and on the possible state of current and past local contamination, which will lead to plan a possible final usage of the considered matrix. If sediments are classified as non-waste, they can be used directly in interventions on banks or riverbeds, either in other suitable activities or industry. On contrary, waste sediments are properly treated and recovered. The sediment must have certain criteria for assessing harmfulness, by entering the limits proposed by D. Lgs 152/06 All. 5 Tab. 1 Column A, Column B, and acceptability limits beyond which the hazard checks will be necessary (D. Lgs. n.152, 2006).

1.6 Climate change impact on reservoirs chemistry and biology

Climate change can be considered as a significant statistical variation in both average temperatures and climate, which will influence in periods of time ranging from few tens to million years. This could result in an alteration of climatic conditions average, with extreme weather events occurring more frequently.

Lake surfaces warming and further events linked to climate changes, consist in rising temperature in early spring, in particular into the hypolimnion, increased period during which waters have temperatures higher than 10 °C, evaporation, water balance, heat balance and stratification, vertical water mixing, and change in the chemistry of the water body, affecting the ecological environment (Schneider and Hook, 2010). Increased average temperatures changes the rainfall regime multiplying in time the occurrence of extreme events (Meehl et al., 2000). The inputs of reservoirs, with the multiplication of extreme events and the melting of snow and glaciers, lead to the alteration of the regimes of streams and rivers with consequently modification of solutes and contaminants transport, showing an increase in solid, nutrients and contaminants intake to lakes and reservoirs. Alterations in the microclimate, local rainfalls and regimes modify aquatic habitats. In arid and semi-arid environments small streams can disappear while large rivers can become occasional, with side effects on water balances of reservoirs and on their chemistry, such as salinity. From an ecological point of view, by affecting availability of nutrients and warm temperatures, climate change can impact on the lengthening of the growth of some species, causing the disappearance of the populations suitable for cold climates and modifying biocenoses and biodiversity, deterioration of the trophy and increasing turbidity, with implications on the aquatic plant growth (Lee et al., 2015). The introduction of warmer water and nutrient enriched waters into rivers downstream of the dams could lead to biological communities changes, with the consequent need to revise the rules for minimum guaranteed flows.

Damming and reservoirs are important resources, producing energy from hydroelectric and mitigating the expected effects of climate change with destructive events. In the case of increased flows tares and solid transport, their function of containment and regulation of the floods could be strategic, and in the case of aridity or sub-aridity conditions, artificial reservoirs become essential as water reserve for multiple use. Is therefore necessary a further effort to evaluate new managerial and innovative plans, based on the different thermal and flow conditions.

In the context of global warming, reservoirs are expected to become even more important on a global scale for water management during dry periods and in an anticipated dramatic depletion of groundwater resources.

1.7 Geochemistry in reservoirs

Geochemistry provides information about waters and sediments characterization, useful for the study of lithological or anthropogenic inputs, of elements mobility, and to better understand and manage the environment of a reservoir as well as its drainage basin. From a chemical point of view, the study of water and sediment is an important issue as these two matrices are in direct contact with each other, interacting and releasing or absorbing elements which can accumulate in the solid fraction or dilute in the liquid ones, but that at certain concentrations are harmful for the environment or for human consumption (Palma et al., 2014; Akin and Kirmizigul, 2017). Geochemically, two main issues interest reservoirs: the quality of stored resource, that needs specific parameters to be consumed as drinking water, and the maintenance and monitoring of drainage basin and reservoir which must be free from pollution sources in order to better preserve the resource and the habitat of the flora and the fauna. Hence, together with water’s concentrations of metals, major and trace elements, it is fundamental, among the others, to obtain sediments’ total and pseudo composition, leaching test, and sequential extraction for an environmental characterization and assessment of the matrix of interest. In this context further aspects have to be considered, ad physical parameters like pH or redox state, and the tendency of an element to move through an immobile to a mobile phase, which depend on the conditions and the state of equilibrium in which sediment and water are and on the different affinity of the harmful mobile fraction (Al-Taani et al., 2015; Frémion et al., 2017).

The solid phase, in particular, represents the potentially toxic fraction for an environment as lakes and reservoirs, accumulating and releasing elements from the bottom (Linnik and Zubenko, 2000; Zhu et al., 2013; Yang et al., 2016). The sediment can be supplied by the geological background of the area, but also collected from external inputs like wind transport or anthropogenic activities such as agricultural or industrial once.

All the discussed assessments are also interested by chemical processes and influenced by the environmental conditions which are dynamic and affect the composition of water and sediments in time, influencing the behaviour of elements in the system.

1.8 Ridracoli reservoir

Ridracoli reservoir is located entirely within the province of Forlì-Cesena, in the territory of Bagno di Romagna, S.Sofia, and Premilcuore municipalities, about 10 km from the nearest municipality of S.Sofia. Here, about 50 km south of Forlì, in the upper part of the Bidente river, a hydroelectric and a purification plants was built. Since 1993 the study area is part of the Foreste Casentinesi- Campigna and Monte Falterona National Park, between Emilia-Romagna and Tuscany. The socio-economic development of Romagna, conditioned by the availability of water resources since 1960s, determined the institution of the Acquedotto della Romagna with the main purpose to provide drinking water to the 3 provinces of Forlì-Cesena, Ravenna, and Rimini, including 48 municipalities. The concomitant need to reduce the depletion of groundwater, due to the withdrawal from wells that also causes the subsidence in Romagna plan, led to evaluate other types of water supply.

The reservoir store waters from Bidente di Ridracoli catchment and adjacent catchment areas, shows an irregular branched shape, and extends into the valleys of the streams and tributaries, with a surface of about of 1 km^2 and a drainage basin of about 37 km^2.

The choice of building a dam and creating an artificial lake for drinking water in this site, was dictated by some favourable characteristics of the area, like its elevated and strategic position respect to the aqueduct, that exploits the gravitational thrust, its morphology, its waterproof lithostratigraphic characteristic, its distance from industries, cities, and cultivated fields, or any kind of human activity, its water chemical composition and ideal temperature for drinking use, and its limited solid supply.

The Ridracoli dam was built between 1978 and 1982, as an arc-gravity dam, which reacts to the force of the stored water thanks to the arc shape that discharges the water weight on the nearby mountains and on its base. The dam is 103.5 m hight and large from 10 m to 36 m from the top to the base, 432 m long and has a mass of 6 $\times 10^5$ m^3 of concrete. The water that reaches the Capaccio purification center is taken by an intake on the right shoulder. It has two enters at different altitude for a better management of the resource, a first one at 490 m.a.s.l. and a second one at 540 m.a.s.l., and a qualitatively better water can be caught depending on temperature and turbidity. The two entrances converge towards a well at 130 m depth and then proceed to the electric generator system and the potabilization center. On the western side of the reservoir, was build a gutter gallery to carry water from an indirect nearby catchment in order store it in the Ridracoli Lake.

The Ridracoli reservoir is managed by Romagna Acque Società delle Fondi S.p.a. and is the fundamental water resource of Romagna Aqueduct. As already mentioned, the primary use of the reservoir is of drinking water supply, and the regulation of Bidente river flow, a tributary of Ronco and Fiumi Uniti. Moreover, it functions as a hydroelectric producer in the nearby Isola plan, as sanctioned by the agreement between Enel and Consorzio Acque on 17/06/1977. Overall, the dam produces every year an amount of 38-40 $\times 10^6$ Kwh of electricity and provides to the community about 55 $\times 10^6$ m^3 of potable water.

The topography of the area was studied before the construction of the dam, during a survey in 1965 and subsequently digitized, while bathymetry campaigns were carried out in 2004, 2011, and 2014. Collected data allowed to evaluate the dynamics of sediments within the reservoir, giving a semi-quantitative assessment of volumes that were deposited and eroded on the valleys after dam construction. A 3D Discrete Element Modelling (DEM) was then produced with the aim to provide a realistic representation of the area, more informatic compared to the previous two-dimensional patterns (Figure 1.6).

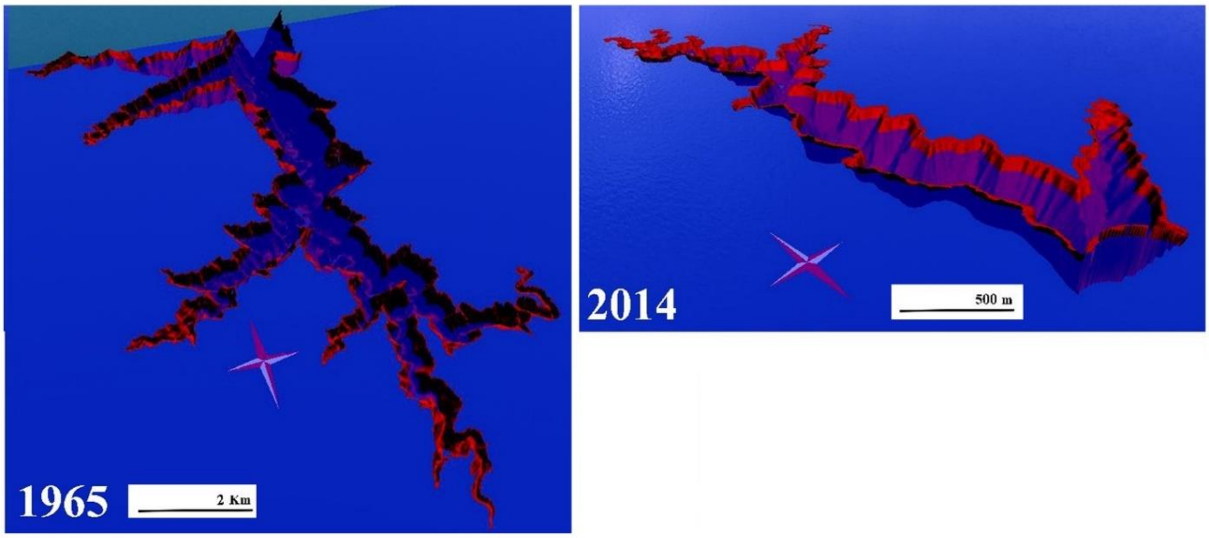


Figure 1.6, 3D Discrete Element Modelling (DEM) of the area of Ridracoli reservoir from topography of 1965 (left) and bathymetry of 2014 (right).

The siltation volume of a reservoir consists in the total volume of solid material deposited upstream the dam, inside the basin, during a specific period. The comparison of Ridracoli reservoir morphologies between 1965 and 2014 estimated the presence of about 4.8 × 10^6 m^3 of deposited sediment, distributed over a surface of 0.703 km^2 where the maximum water surface is of 1.035 km^2, and an eroded volume of about 2.9 × 10^6 m^3. These data show a strong component of sediment from the same area of the catchment covered by the reservoir, which has therefore undergone a modification due to the construction of the dam and the formation of the reservoir. The calculated contribution of the external sediment to the reservoir surface is about 1.9 × 10^6 m^3, which therefore occupies the volume destined for the water resource without being recovered inside the reservoir. These data, however, do not seem to be entirely reliable since the topography of 1965 does not include the works done in 1975, aimed at the construction of the dam and the safety of the area. In fact, two excavation phases were carried out in 1975: a first one concerning the safety of the slopes and their anchoring (layers at 218°/27°) and a second one for the stabilization of the base of the dam. The estimated total volume of removed sediment is 463 × 10^3 m^3, of which 315 × 10^3 m^3 from the stepped slope and 148 × 10^3 m^3 from deep excavation for foundations (Figure 1.7).

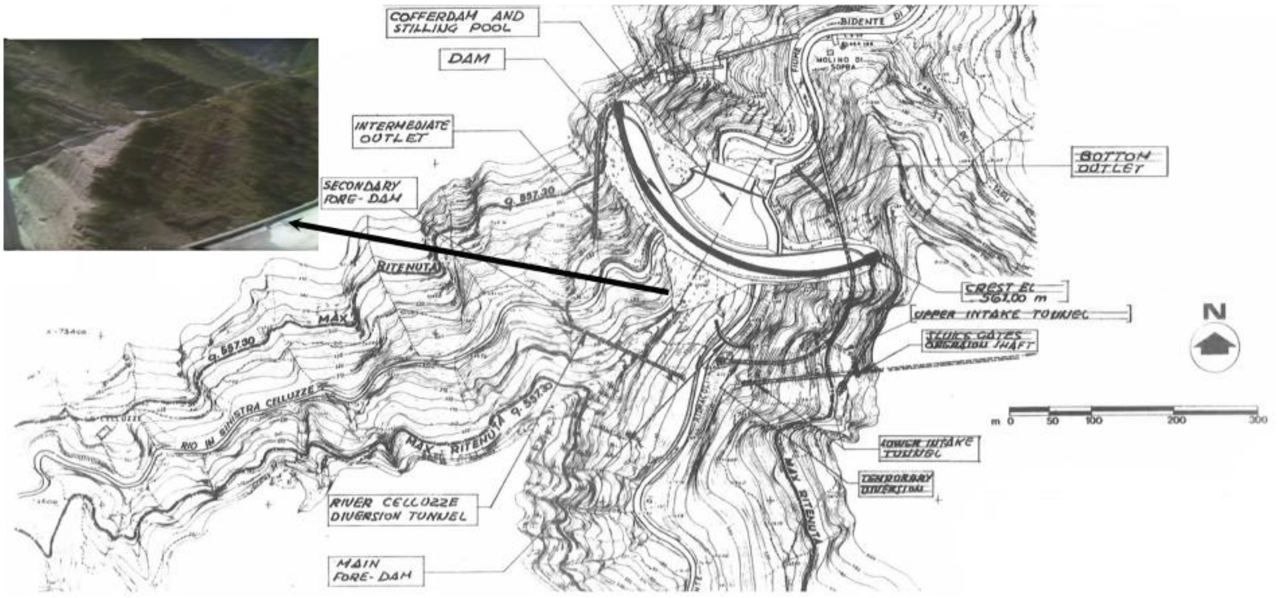


Figure 1.7, Ridracoli dam construcion project (right) and photograph of the excavated area (left) (Alpina, 1977)

Figure 1.8 shows the areas affected by erosion and those by deposition of sediment: the southern part of the reservoir, where its diameter is narrowest, displays sediment deposition in the centre (in red), and sediment erosion on the slopes (in blue). The northern part, instead, shows an unbalanced configuration towards the west, attributable to the confluence of the two branches of the reservoir and to the bedding of MAF layers, a dip slope to the east and thus opposing a lower resistance to erosion

(Grandori et al., 1990). The modification of Ridracoli's morphology in time, show an increase in slope of slopes and a filling of the valley floor.

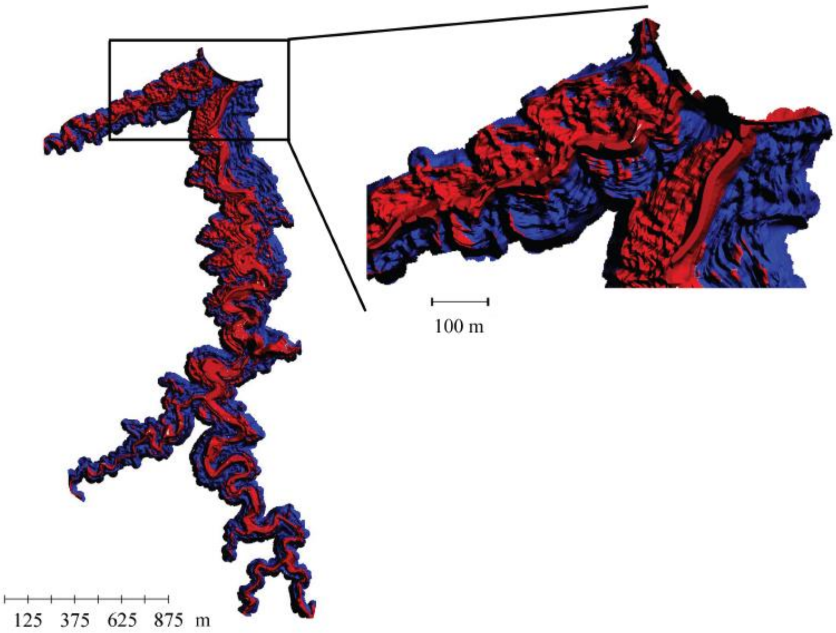


Figure 1.8, Maps of Ridracoli reservoir showing the deposited (in red) and eroded (in blue) sediment.

During the 31 years of Reservoir activity, since 1983 to 2014, the basin has field up with sediment for the 5.9% of the total volume of the reservoir, calculated on the maximum volume of 33.06×10^6 m^3 at 559.6 m a.s.l.. The percentage of annual landfill rate of Ridracoli is 0.19%, compared to the 0.6-0.8% of other sites worldwide (ITCOLD), showing that drainage basin doesn't bring consistent source of input sediments. Despite the extreme local variability that can affect the comparison with other reservoir sites, in Ridracoli the low values depend on the local geological and morphological conditions upstream the dam, from the proximity of springs and the surrounding vegetation, which filter the conveyed water helping the stability of slopes and limiting the erosion.

1.10 Aims of the doctorate

The purpose of the doctorate is to investigate waters and sediments interactions in a mountain area where a Large Dam is operating. Several aspects have been considered for each matrix, such as waters and sediments from streams and reservoirs, characterized and studied to better understand the geochemistry of the area and therefore useful to evaluate their interaction. The construction of a Large Dam reservoir implies the collection of a massive water body in a short time, affecting sediment and water chemistry, that represents the main object studied during this PhD.

In this context the role of reservoir, stream and cores sediment constitutes a valid base for the implementation of environmental management measures. The composition of sediments, in fact, plays an important role in the comprehension of the complex dynamics that occur within catchment basins and on water chemistry. In this type of environment, the study of sediment quality becomes relevant since the interaction between sediment and water, as well as the geochemical processes that interest this interaction, could affect water quality. Concentrations of major and trace elements from total and pseudo total concentrations of sediment allow to know distribution and stability of heavy metals and environmental contamination within the area of study and provide clues for the management of the reservoir. Sediments quality can be influenced by fluvial processes, climate, bedrock geology, soil composition, and anthropogenic products. Sediments represent a critical environmental compartment because they can incorporate contaminants and eventually release them under environmental changes, as pH and Eh variations (Baudo et al., 1990). In particular, the accumulation of sediment inside a reservoir is of concern for the water quality and should interest any reservoir management. The section of fine particle size of the sediment represents the geochemically more active component since it can adsorb large quantities of contaminants (Sodergen, 1997). Sediments also play a fundamental role in deposition, accumulation and transport of contaminants in an aquatic environment, that moving with the sediment may interact with various components of the biosphere (Karickhoff et al, 1979; Santiago et al., 1994). It is therefore of particular importance to determine the characteristics and concentrations of certain elements. In particular, within the study area, some potentially harmful elements may result from natural erosion of rocks containing elements or generate from accumulation.

To determine the characteristics of every single matrix of the system is fundamental to better understand the processes that take place, as well as the behaviour and mobility of elements. Concentrations of elements on a spatial scale, along the different river rods or within the reservoir catchment, and on a time scale, comparing the seasonal variation inside the reservoir, have been object of the study.

Overall, this PhD project aims to extract from an extensive geochemical database of different type of matrixes of Ridracoli reservoir and surroundings areas on northern Apennines the widest spectrum of information: the seasonal changes in water and sediment chemistry from the Ridracoli reservoir, inter-element and grain size relationship in sediments and geographical and geological differences, river branches chemistry and their evolution, potentially harmful elements behaviour, element mobility and environmental assessments on the reservoir area, early diagenesis studies at the bottom of Ridracoli reservoir, and finally fluxes at the water- sediment interface inside the reservoir. The geochemical system of the reservoir, tributaries and rivers will be interpreted to reconstruct and understand the environmental system of the area, the effects that the construction of the Large Dam had on the site and to predict the environmental risk on fresh water.

Chapter 2 - Assessment of seasonal changes in water chemistry of the Ridracoli water reservoir (Italy): Implications for water management.

Abstract

The Ridracoli artificial basin is the main water reservoir of the Emilia-Romagna region (Northeast Italy). The reservoir was made by construction of a dam on the Bidente River in 1982. It is used as the main drinking water supply of the region and for hydropower production. The physical and chemical parameters (temperature, pH, electrical conductivity, and dissolved oxygen) of shallow water are continuously monitored whereas vertical depth profiles of water chemical data (major anions and cations, as well as heavy metals) are available on a bimonthly base. The dataset used in this research is related to the years 2015 and 2016. Data show that the reservoir is affected by an alternation of water stratification and mixing processes due to seasonal change in water temperature, density, and the reservoir water level. In late summer and winter months, the water column is stratified with anoxic conditions at the bottom. During the spring, on the other hand, when storage is at its maximum, water recirculation and mixing occur. The reservoir is characterized by a dynamic system in which precipitation, dissolution, and adsorption processes at the bottom affect water quality along the reservoir depth column. The temperature stratification and anoxic conditions at the reservoir bottom influence the concentration and mobility of some heavy metals (e.g. Fe and Mn) and, consequently, the quality of water that reaches the treatment and purification plant. This study is relevant for water resource management of the reservoir. Assessing the seasonal changes in water quality along the reservoir water column depth is fundamental to plan water treatment operations and optimize their costs. The reservoir assessment allows one to identify countermeasures to avoid or overcome the high concentrations of heavy metals and the stratification problem (e.g., artificial mixing of the water column, new water intakes at different depths operating at different times of the year, blowers, etc.).

Keywords: geochemistry; artificial water reservoir; water quality; seasonal stratification; water resource management

2.1 Introduction

Artificial reservoirs are man-made infrastructures, generally constituted by a dam across a river, aiming at storing freshwater for consumptive (e.g., drinking or process water) and non-consumptive (e.g., fisheries and recreational) human use, as well as to provide hydroelectric power. Dam construction modifies the flow regime of natural water courses and the whole drainage basin in a relatively short period of time (Magilligan and Niskow, 2005; Marcinkowski and Grygoruk, 2017; Mailhot et al.,

2018) and can alter biodiversity both upstream and downstream (Jansson, 2006; Merritt et al, 2009; Schmutz and Moog, 2018).

Lakes and reservoirs are studied around the world and their engineering, biological, geological, and geochemical aspects have been extensively investigated. The major issues of particular relevance to reservoirs and the assessment of their water quality are potential public health impacts due to the spread and transmittal of diseases (Jobin, 1999; Ampadu et al., 2015) or the release of contaminant from industries and urban settlements adjacent to the reservoir; eutrophication (Van Ginkel and Silberbauer, 2007; Munyati, 2015); thermal and density stratification; and the associated chemical deterioration (Hawkins, 1985; Mao et al., 2018; Ziae et al., 2019). In reservoirs subject to thermal stratification, the suppression of vertical transport processes at the thermocline normally allows an oxygen gradient to occur, which can cause anoxic conditions to develop in the hypolimnion, favouring internal nutrient loading at the sediment–water interface. This may cause the release of phosphorus (Lake et al., 2007), but also ammonium, iron, and manganese from the sediments back into the water column (Munger et al., 2016; Chen et al., 2018) and create problems for water users requiring a constant water quality.

Silting of reservoirs due to sediment transport and trapping in the river system, bank and shore erosion and eventually bank and slope sliding cause a decrease in storage capacity and reservoir lifetime, as well as water availability (Morris and Fan, 1998; Arnason and Fletcher, 2003; De Araújo and Güntner, 2006; Randle and Bounty, 2017), and eventually affect water quality due to turbidity and sediment-associated pollutants (Thompson et al., 2007; UNESCO, 2011).

Reservoirs are, essentially, managed water bodies and, therefore, there is a particular need for the managers to understand their physics, chemistry, and biology (Jørgensen et al., 2013). In order to manage large water reservoirs in a sustainable manner and to minimize the occurrence of conditions that interfere with the beneficial uses of their waters, regular collection and analysis of data are required. The aim of this work is to assess the seasonal changes in water quality that may occur in the Ridracoli artificial basin, the main water reservoir of the Emilia-Romagna region, in northeastern Italy. An extended database consisting of continuous monitoring of physical and chemical parameters of shallow water, along with vertical depth profiles, is used to assess seasonal stratification and mixing processes along the water column (Calmano et al., 1993; Jørgensen et al., 2013). Changes of the monitored parameters can affect the water quality of the reservoir and do not guarantee an uninterrupted operation of the water management system. The importance of this study relies on the implications that seasonal changes in water quality can have for water and reservoir management, especially in terms of treatment and purification processes required for drinking water production, cost optimization, and other countermeasures to overcome the negative effects related to water stratification issue and dissolved heavy metal concentrations.

2.2 Study Area

Ridracoli water reservoir is located in the Casentinesi Forests-Campiglia National Park, between Romagna and Tuscany, on the Northern Apennines of Italy (Figure 2.1). It is at 480 m a.s.l., has a surface area of 1035 km^2, a capacity of 33×10^6 m^3 with a maximum depth of 82 m, and the total surface area of the drainage basin is 87,510 km^2. The climate is subcontinental and submountain, temperatures range from a minimum of around −6 to a maximum of 30 °C, while the yearly mean precipitation is 1400 mm/year.

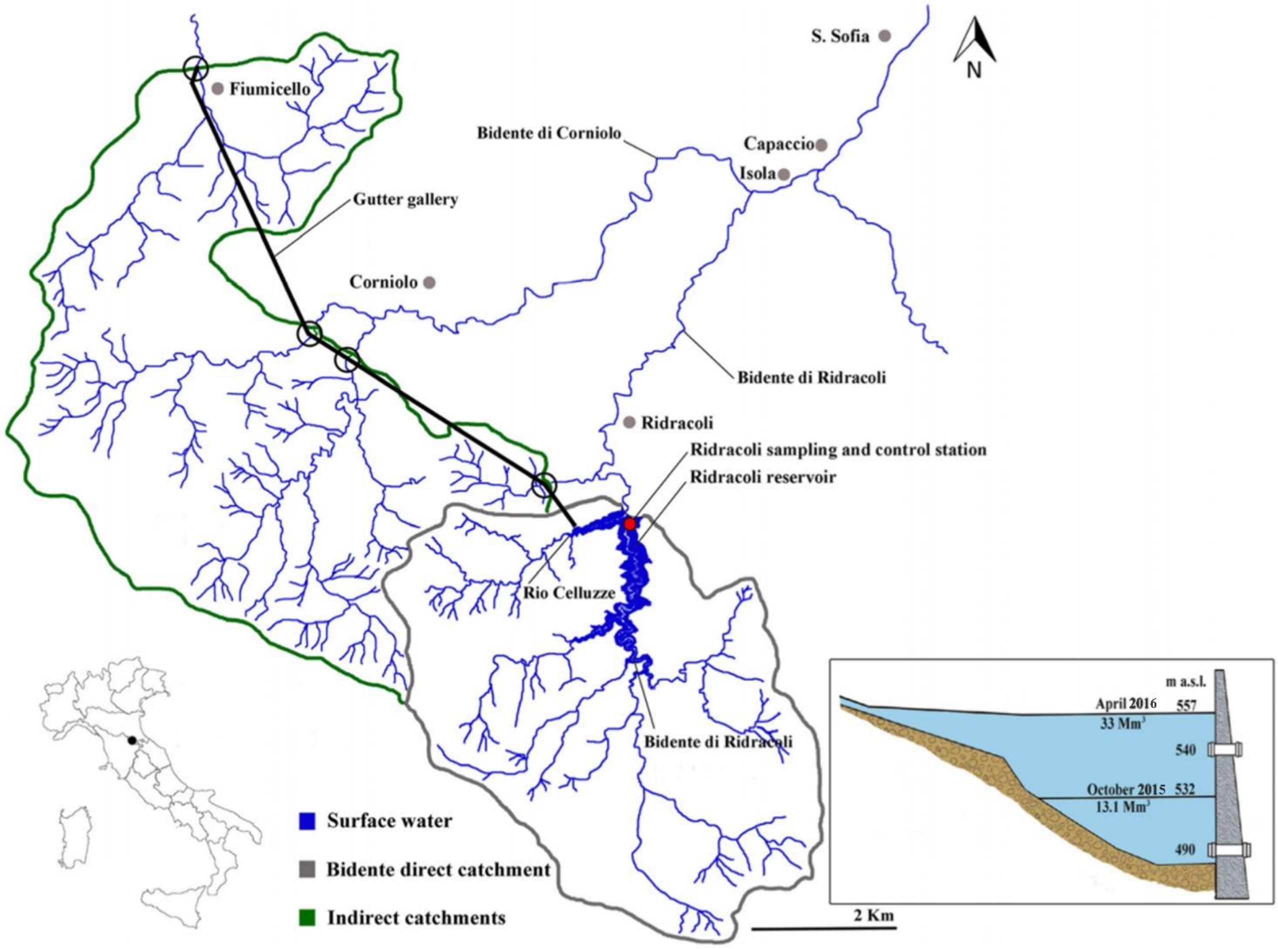


Figure 2.1, The Ridracoli water reservoir showing the main hydrography, direct and indirect reservoir catchments. Shown are also the gutter gallery (black line), Isola and Capaccio, where the water treatment plant and water analysis laboratory are located, respectively. In the small rectangular a sketch of the reservoir showing the two water intakes at 490 and 540 m a.s.l. and the maximum and minimum water level.

The construction of the dam began in 1975 and was completed in 1982 on the confluence between Bidente river and Rio Celluzze creek in the province of Forlì-Cesena. Ridracoli reservoir is directly fed by the Bidente catchment (about 36.9 km^2) and indirectly by another nearby catchment of about 51.1 km^2 through a gutter gallery, for a total surface of about 88 km^2 (Figure 2.1). The dam is a simple concrete arch gravity dam, 103.5 m high, with a crest 432 m long and a mass of 6 × 105 m^3 of concrete (Buffi et al., 2017; Buffi et al., 2018).

The landscape of the drainage area presents narrow and recessed valleys with rocky and densely wooded slopes. This site has been chosen for a number of positive characteristics: a central location with respect to the supplied area, guaranteeing an easy water distribution; good quality of the resource because of the altitude of the catchment and the absence of sources of pollution; and suitable morphology and geological features.

This site is also a nature reserve being part of the National Park, which favours the absence of human settlements ensuring the absence of anthropic pollution sources. The forest cover ensures also a mitigation of the impact of rainfall on the ground, reducing solid particle transport, limiting both water turbidity and reservoir siltation (Uhlmann et al., 2011). Monitoring of the hydrobiological regime of the basin indicates oligotrophic and ultraoligotrophic waters, with small chlorophyll concentrations, poor development of phytoplankton, and none revealed toxic events (Arpae, 2015; Arpae, 2018).

2.2.1 Geological Setting

The geology of the area presents units from the Successione Romagnola (Figure 2.2), dated from 20 to 11.6 millions of years ago (Neogene; Miocene; Burdigalian, Langhian and Serravallian) and includes an alternation of sandstones and marl called Marnoso-arenacea formation (MAF). This formation is a thick turbiditic unit deposited in the Tuscan-Umbrian portion of the Inner Periadriatic basin formed during the Miocene (Ricci Lucchi, 1978; Gandolfi et al., 1983). This basin was elongated in a NW–SE direction and represented a foredeep located in front of the growing Apennine orogenic wedge. In the area of the Romagna Apennines the MAF forms a belt 90 km long and 40 km wide and reaches a thickness up to 3.5 km (Ricci Lucchi, 1978; Gandolfi et al., 1983; Ricci Lucchi and Valmori, 1980). This deposit includes 14 members that differ according to lithology criteria as arenite/pelite ratio (A/P), average thickness of arenaceous levels, composition of arenites, and stratigraphic position (Martelli et al., 1994). In the Ridracoli reservoir catchment, the main MAF outcrops include the Members of Premilcuore and Galeata (Figure 2.2 and Table 2.1). The first one is the most arenaceous member of the late Burdigalian-Serravallian MAF; the respective body has a lenticular geometry and closes towards the south, causing the direct contact between the Corniolo Member and the Galeata Member. It is characterized by thick to medium layers, sometimes massive, with rare hemipelagic clays; the sandstone/pelite ratio (A/P) varies from 1/2 to greater than 2. It can reach a thickness of 150 m and its age belongs to the Langhian (15.97 ± 0.05 Ma and 13.65 ± 0.05 Ma, Middle Miocene) (Cornamusini et al., 2002). The Galeata Member consists again in an alternation of pelite and sandstone, sometimes calcarenites and hemipelagic, with an A/P of about 1/2–1/3. The sandstones are organized from thin to thick and sometimes very thick. The member thickness is about 400 m and the age is attributed to the upper Langhian–lower Serravallian interval (around 13.82 Ma, Middle Miocene) (Benini et al., 2009).

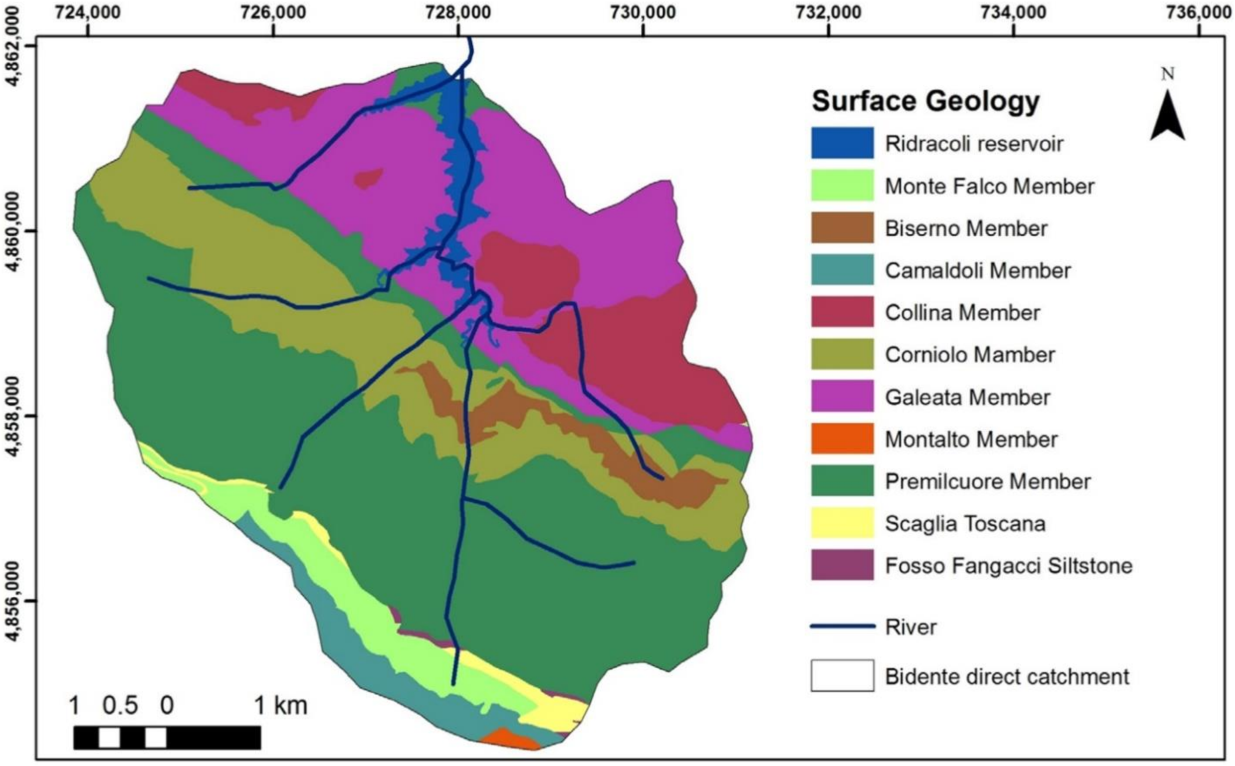


Figure 2.2, Surface geology of the Ridracoli reservoir catchment. (Map coordinate system: WGS84–UTM zone 32 N).

Table 2.1, Distribution (%) of members included in the Ridracoli reservoir catchement. Listed are also the age, sandstone/pelite ratio (A/P), and the formation. Refer to Figure 2 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)

2.2.2 Water Reservoir Management

The reservoir is managed by Romagna Acque Società delle Fonti S.p.A. and the primary use of the reservoir is to supply drinking water to 48 municipalities in the provinces of Ravenna, Forlì-Cesena, and Rimini, providing alone 50% of the entire water needs. The Romagna coast need a storage of water that could replace groundwater wells and unregulated surface streams, as well as to store water for about 1 million of people that usually move to the coastal area during the summer period. The secondary function of the dam is the production of hydroelectricity for the surrounding area and Romagna Acque’s own facilities.

The water routed to the Capaccio water treatment and purifying plant (Figure 2.1) is taken by two intakes on the west side of the reservoir, at 490 and 540 m a.s.l., in order to control water uptake based on temperature and turbidity (Figure 2.1). The two intakes converge and continue to the treatment plants, 11 km downflow (Isola, Figure 2.1). The unloading system consists of different solutions: surface spillways for water overflow when 559.60 m a.s.l. is reached; middle spillway at 505.80 m a.s.l. connected downstream by a channel; a bottom discharge conduit at 478 m a.s.l. that guarantees the minimum vital outflow of Bidente river, and another bottom discharge at 468 m a.s.l. that lets the water flow directly to the riverbed.

The water from the reservoir reaches the treatment plant and then it undergoes oxidation with ClO_2 or $KMnO_4$ to remove organic substances, turbidity, and reduce iron and manganese concentrations. After the clariflocculation treatment and filtration, the water is disinfected with ClO_2 or NaClO, while the sludge, which has been separated during the clariflocculation and filtration phases, is sent to a waste collection tank.

All distributed water is thoroughly checked to ensure compliance with the current Italian national legislation (D.M. 14 June 2017). The water produced and distributed by the Capaccio treatment plant has excellent characteristics and could be classified as oligomineral (fixed residue is 50–500 mg/L) and mineral (fixed residue is 500–1500 mg/L, D.Lgs. No. 105 of 25 January 1992; (D. Lgs, 1992)).

2.3 Methods

The dataset used in this research was related to the years 2015 and 2016. Data of rainfall and reservoir levels were collected from the control station of Ridracoli (565 m a.s.l., Figure 2.1), which records continuous daily rain, air temperature, air humidity, wind, and atmospheric pressure.

Physical and chemical parameters (temperature-T, pH, electrical conductivity-EC, redox potential-Eh, and Total Organic Carbon-T.O.C.), as well as chemical data (Fe, Mn, Al, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, $CaCO_3$, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) of reservoir water at the intake of the water treatment plant, are provided by the Capaccio laboratory in Santa Sofia, 10 km downstream Ridracoli dam. A Mettler Toledo (mod. T90) with a Rondo autosampler (METTLER TOLEDO, Schwerzenbach, Switzerland) was used for pH, EC, T, and alkalinity with a digital thermometer HD (Delta OHM Srl, Padua, Italy). Anions and cations were analysed with an ion chromatograph (mod. Dionex ICS 3000; Thermo Fisher Scientific, Waltham, Massachusetts, MA, USA) following the methodology UNI EN ISO 10304-1 (UNI ED ISO 10304-1, 2007) and UNI EN ISO 10304-4 (UNI ED ISO 10304-4, 1997). Samples were acidified (5% of HNO_3) prior the metal analysis and then concentrations were measured with an ICP-MS (mod. Agilent 7800, Santa Clara, CA, USA) following the methodology UNI EN ISO 17294-2 (UNI EN ISO 17294-2, 2016).

Reservoir samples collected in the Ridracoli water basin were taken from the sampling station close to the dam structure where a floating device was anchored (Figure 2.1). Monitoring was carried out with a bimonthly frequency by the Regional Agency for Prevention, Environmental and Energy of Emilia-Romagna-Arpae (D. Lgl. 152/06 part III; (D. Lgs, 2006)). Water samples were collected along the water column at the surface and 10, 25, 40, and 50 m deep from the surface. It has to be highlighted that the maximum depth of the monitoring sampling campaign by Arpae is always 50 m below the surface, even if the reservoir has a greater depth. The dataset includes physical and chemical parameters: T, dissolved oxygen (DO), pH, EC, and Total Dissolved Solids - TDS, and the following elements: HCO_3^-, SO_4^{2-}, Cl^-, NO_2^-, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, $CaCO_3$, Fe, Mn, As, Zn, and Cu, along with other heavy metals that are not discussed in the present study because of always being below the detection limits (B < 50; Cd < 0.04; CrTOT < 1; Hg < 0.01; Ni < 1; and Pb < 1; µg/L).

With the aim of gathering more chemical and physical information on major and trace elements distribution along the water column two more sampling campaigns were carried out in October 2015 and April 2016 by the University of Bologna (Italy) and CNR-ISMAR (Institute of Marine Science, Italy). The selected timing was planned to compare the two extreme situations of reservoir volume: maximum volume in April, after winter precipitation and minimum volume in October after the summer withdraw and usage. Water samples were collected at the top, middle, and bottom of the water column (0, 25, and 50 m in 2015 and 1, 35, and 70 m in 2016), at the same sampling station used by Arpae campaigns (Figure 2.1). In order to record continuous chemical–physical parameters along the column, the vertical profiles were carried out by a Niskin bottle (Osil Scientific International Ltd., Havant, Hampshire, UK) and a CTD probe (mod. Hydrolab MS5 (OTT Hydromet GmbH, Kempten, Germany).

2.4 Results

2.4.1 Reservoir Volume and Water Level

Precipitation, reservoir water level, reservoir volume, and water withdrawals for the year 2015 and 2016 are reported in Figure 2.3.

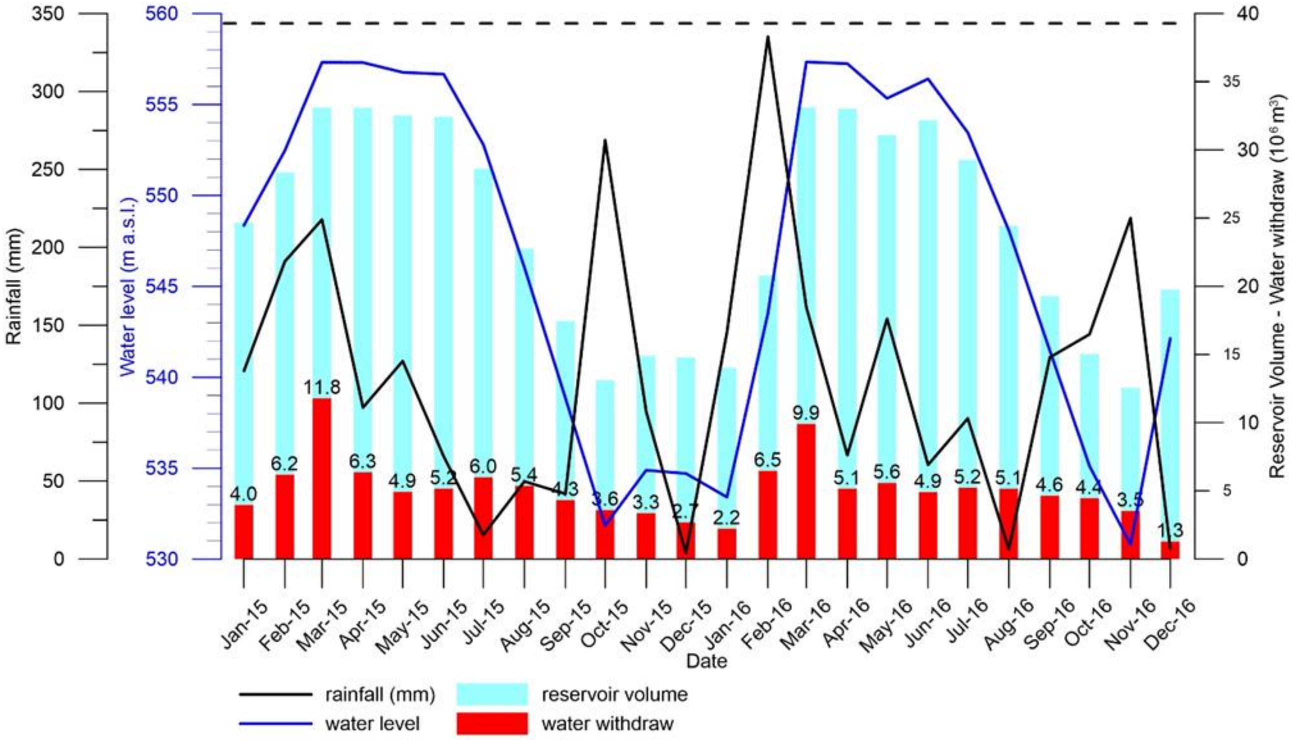


Figure 2.3, Rainfall (mm) and water level (m a.s.l.) on the left y-axes; reservoir volume and water withdraw (10^6 m^3) on the right y-axes in 2015 and 2016. The dash line indicates the surface spillway elevation at 559.60 m a.s.l.

Precipitations in 2015 and 2016 have a similar pattern with two peaks during the year, in February/March (217.8 mm, 2015; 335.2 mm, 2016) and in October/November (268.8 mm, 2015; 218.8 mm, 2016). The minima in precipitation were recorded during summer months (June–August) and in December, with monthly values less than 7 mm. In comparison, the period of April–September had an average rainfall of 75.4 mm/month and the two periods of January–March and October–November with 189.8 mm. The amount of total precipitation was about 1293.6 mm in 2015 and 1519.2 mm in 2016, in accordance with the annual average rainfall on Apennines in the Emilia-Romagna region (Pavan et al., 2008). The characteristic of precipitation over the region is known to strongly depend on the season, with a more intense seasonal cycle over the mountain area, where the precipitations peak is generally in October (Pavan et al., 2008).

The average water volume stored in the reservoir in 2015 and 2016 was 24.2 × 10^6 m^3, with a maximum value of 33.1 × 10^6 m^3 in March and April and a minimum of 12.5–15 × 10^6 m^3 in October–

November. This seasonal dynamic (visible for a longer time series at http://www.romagnacque.it/lacqua_in_diretta/diga_di_ridracoli/andamento_idrologico_annuo) fits the purpose of the reservoir since it was built to store water for the water demand of the dry season.

The reservoir volume changed seasonally depending on the balance between inputs from direct and indirect catchments (gutter pipe in Figure 2.1) and withdraw. The minimum volume coincides with the period right after summer, which is characterized by an average withdraw of 5.2×10^6 m^3 from April to September. The main water withdraw occurred in this period in order to accommodate water demands for summer tourism and agricultural use (irrigation season goes from May to October (Tomei et al., 2010)) with an amount of water of 32×10^6 m^3 in 2015 and 30×10^6 m^3 in 2016, and averages of 5.3 and 5×10^6 m^3/month, respectively. Lower water withdrawals occurred from autumn to winter (October–January), with average values of 3.4 and 2.9×10^6 m^3/month. Sometime in March, due to snow melting and intense spring rainfall, water reaches the maximum storage capacity and overflowed from the dam (see peaks in Figure 2.3).

2.4.2 Physical Parameters

Air, surface water, and intake water temperatures are shown in Figure 2.4. As expected, air and surface water temperatures at the reservoir show similar patterns, with maximum values in June and July and minimum values in January and February. Air temperature has a minimum value of 2.3 °C and maximum of 23.4 °C, averaged over two years. Surface water temperatures show slightly higher values than air, never below 6.8 °C, which reflects the heat storage capacity of lakes and water reservoirs (Wetzel et al., 2000; Rodriguez et al., 2004). During withdrawal and transport downstream to the Capaccio facility, the intake water temperatures decreased as shown by the differences in temperatures between the black and green lines of Figure 2.4, the temperatures measured at the treatment plant were on average of 9.1 °C with a standard deviation of 2.3 °C, whereas the surface water in the reservoir displayed an average 14.4 °C and a standard deviation of 6.7 °C.

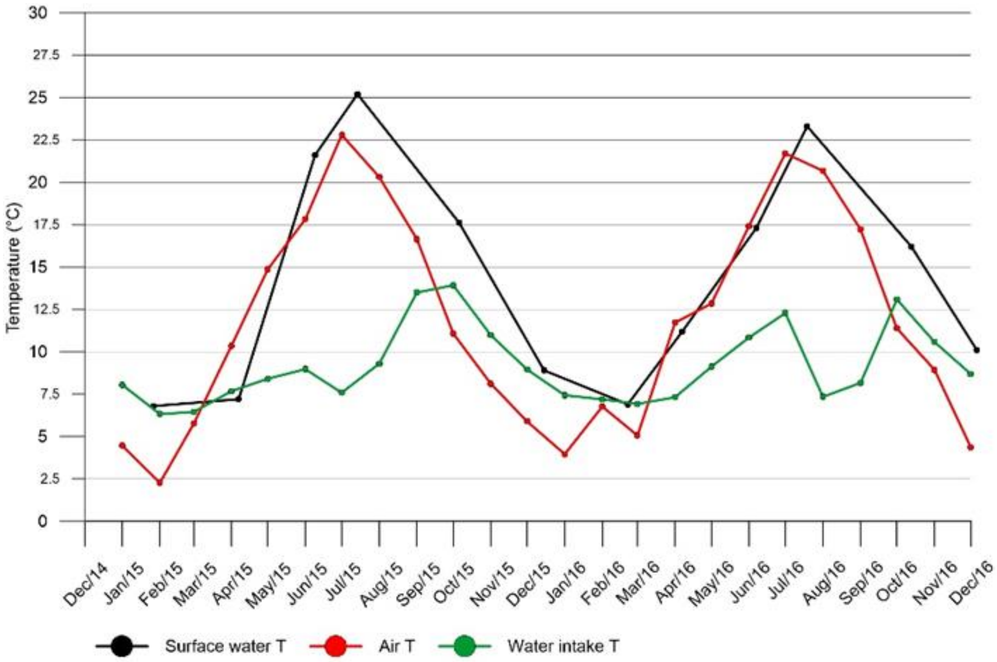


Figure 2.4, Temperature of surface water in the reservoir (black line), air at 2 m (red line), and water intake at the water treatment plant (green line) in 2015 and 2016.

The maximum difference in temperature between surface and bottom water was observed in July (17.7 °C in 2015 and 15.8 °C in 2016). Figure 2.5 shows a deep thermocline occurring in summer (June and July). The stratification started in April with a 5–8 °C temperature gradient between surface and deep cold water (around 8 °C). Solar heating of the water surface creates density gradients within lakes and water reservoirs preventing efficient mixing of the water column with consequent stratification of the water bodies (Winton et al., 2019). Changes in physical and environmental conditions may manifest in a seasonal stratification of the reservoir with cooler water layers at the bottom during summer months. In summer the surface water is warmed up by solar heating and reaches 24 °C whereas bottom water remains to about 8–9 °C. In the literature, these layers are classified as epilimnion, which is the first upper layer, metalimnion (with sharp thermocline), and hypolimnion at the bottom (Uhlmann, 2011; Lewis et al., 2019).

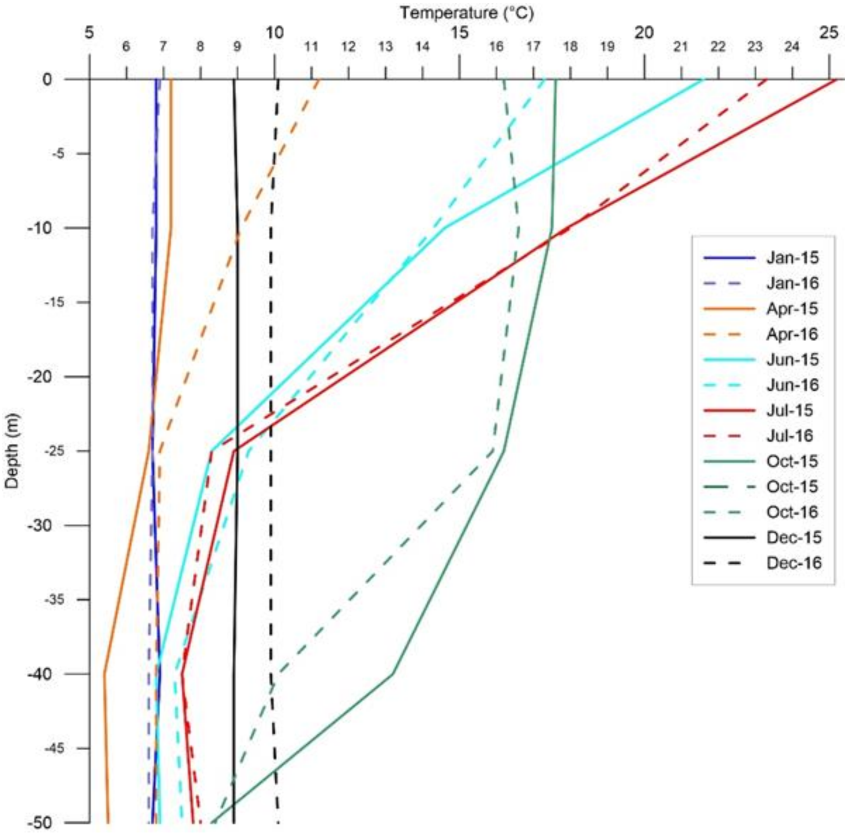


Figure 2.5, Reservoir temperatures along the water column.

In October, as the air temperature decreased, the surface water temperatures cooled down, reducing progressively the differences between layers along the water column. After October, until the warm months, the temperature throughout the vertical water column was almost constant, with no stratification in epilimnion, metalimnion, and hypolimnion.

In Figure 2.6 the concentration of dissolved oxygen (DO in mg/L) for the first 50 m of the water column was reported. During December, January, and April DO shows the higher values ranging constantly around 9–10 mg/L for the entire water column. The DO values started to decrease below 9 mg/L in June, July, and October and a clear minimum in DO saturation appeared in October, when DO concentration decreased until 0.6 mg/L from −30 m downward (grey line in Figure 2.6). This decreasing in DO confirmed the reservoir stratification, indicating the trophic quality of the water body.

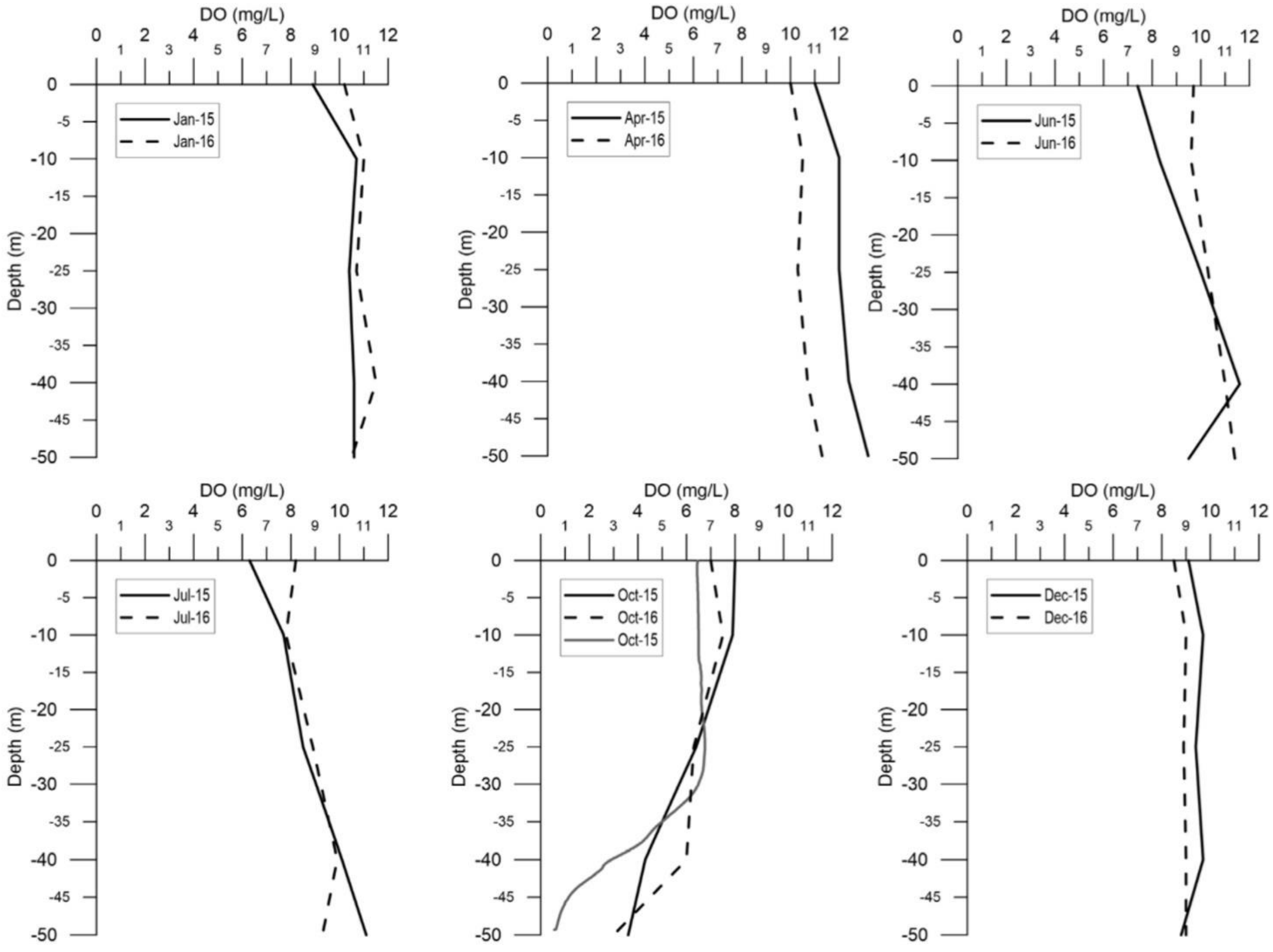


Figure 2.6, Dissolved oxygen (DO, mg/L) distribution along the water column in 2015 and 2016 for each monitoring campaign (6 per year). The grey line on the October graph indicates data collected continuously along the water column, down to the reservoir bottom, by the CTD probe.

2.4.3 Chemical Parameters

The summary statistics of the water samples considered in the present work is reported in Table 2.2, subdivided according to the water sample type. All the samples were Ca-Mg-HCO_3 (bicarbonate-calcium-magnesium water) according to Langelier-Ludwig (Langelier and Ludwig, 1942) (Figure 2.S1 in the Supplementary Material). With median EC varying between 300 at 20 °C (Surface Water, Table 2.2) and 315.5 µS/cm (Bottom Water, Table 2.2), water could be classified as oligomineral (D. Lgs., 1992) (Table 2.2). The surface and bottom water were quite similar as concerns the major hydrogeochemical features. Some differences appeared in the median values and maxima for NO_2^-, NH_4^+, and Mn higher in bottom waters and NO_3^-, Fe, and Zn higher in surface water. The samples at the Capaccio water treatment plant were quite comparable with the average reservoir, however indicating some differences in the median values of Mn, Fe, and Al, which were higher in the Capaccio water.

Table 2.2, Descriptive statistics (minimum, median, maximum, and median absolute deviation—MAD) of all water samples collected in the Ridracoli reservoir and Capaccio water treatment plant. The first group refers to all water samples collected in the reservoir, while second and third groups refers to the same water samples but divided into surface and deep samples, respectively. (To be noted: DO, EC, and Zn values of Capaccio water samples are missing because not measured; MAD values are missing ('n.a.' in table) for samples with the majority of concentrations below detection limits).

Parameters		**Average Reservoir**				**Surface Water (0 m)**				**Bottom Water (>−50)**				**Capaccio Water Treatment Plant**			
	Unit	**Min**	**Median**	**Max**	**MAD**	**Min**	**Median**	**Max**	**MAD**	**Min**	**Median**	**Max**	**MAD**	**Min**	**Median**	**Max**	**MAD**
Hardness ($CaCO_3$)	**mg/L**	156.0	174.5	197.0	9.0	156.0	170.0	184.0	7.0	165.0	181.0	197.0	9.3	151.8	160.0	13.9	6.1
T	**°C**	5.4	8.7	25.2	4.7	6.8	13.7	25.2	6.7	5.5	7.7	10.1	1.2	6.3	8.6	13.9	2.3
DO	**mg/L**	3.0	9.7	13.2	2.1	6.3	8.7	11.0	1.4	3.0	10.0	13.2	3.1	#	#	#	#
pH		7.4	8.3	8.6	0.3	7.5	8.4	8.6	0.4	7.4	8.2	8.4	0.3	7.6	8.0	8.2	0.2
EC	**µS/cm**	274.0	307.0	361.0	20.4	274.0	300.0	343.0	22.3	293.0	315.5	341.0	17.6	#	#	#	#
TDS	**mg/L**	380.7	417.9	463.9	19.3	381.4	408.1	441.9	15.7	403.0	433.3	463.9	19.2	372.5	392.0	427.4	13.1
HCO_3^-		178.9	212.9	240.3	12.0	180.6	207.0	224.5	10.5	201.3	219.6	240.3	10.6	185.1	195.2	215.0	7.4
SO_4^{2-}		20.0	23.0	25.0	1.4	21.0	23.6	25.0	1.5	20.0	22.9	25.0	1.4	19.6	22.6	25.3	1.3
Cl^-		4.0	5.0	6.7	0.8	4.0	5.0	6.3	0.7	4.0	5.1	6.7	0.8	4.0	5.4	6.3	0.8
Na^+		5.0	6.0	8.0	0.9	5.0	6.0	8.0	0.9	5.0	5.9	7.0	0.8	5.3	5.7	7.0	0.5
$Ca2^+$		46.6	56.0	62.1	4.0	46.6	54.1	61.0	4.3	53.7	60.0	62.1	2.8	51.0	55.6	59.8	2.4
Mg^{2+}		8.6	10.9	12.0	1.0	9.0	10.7	12.0	1.1	9.6	10.9	12.0	0.9	10.0	10.6	11.5	0.4
K^+		0.2	1.0	3.0	0.8	1.0	1.0	3.0	0.9	0.9	1.0	3.0	0.8	1.1	1.3	1.5	0.1
NO_2^-		<0.05	<0.05	0.18	n.a.	<0.01	<0.05	<0.05	n.a.	0.02	0.10	0.18	n.a.	<0.01	<0.01	0.04	n.a.
NO_3^-		0.71	1.56	2.00	0.49	1.44	1.56	1.68	0.17	0.71	1.25	1.79	0.76	1.06	1.45	1.65	0.15
NH_4^+		<0.05	0.05	0.08	n.a.	<0.05	<0.05	<0.05	n.a.	0.05	0.06	0.08	n.a.	<0.05	<0.05	<0.05	n.a.
Fe	**µg/L**	7.5	16.1	55.3	17.4	7.5	31.4	55.3	33.8	12.6	16.1	19.6	4.9	22.8	88.8	313.6	92.1
Mn		<1	2.4	329.0	131.5	<1	18.5	36.0	24.7	1.1	165.1	329.0	231.9	2.5	12.2	85.4	25.8
Al		4.5	14.2	62.6	22.3	6.8	14.1	21.4	10.3	4.5	33.6	62.6	41.1	24.8	105.8	339.3	86.1
Zn		4.3	21.1	172.4	64.2	8.7	90.6	172.4	115.8	15.8	23.2	30.6	10.5	#	#	#	#

Gibbs diagram (Figure 2.7) represents the ratio of $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ as a function of TDS, which is widely used to assess the functional sources of dissolved chemical constituents, such as precipitation dominance, rock dominance, and evaporation dominance (Gibbs, 1970). Our samples fell in the rock–water interaction dominated waters, with limited dispersion, suggesting the strong influence of carbonate minerals common in the catchment bedrock as a major factor controlling water chemistry.

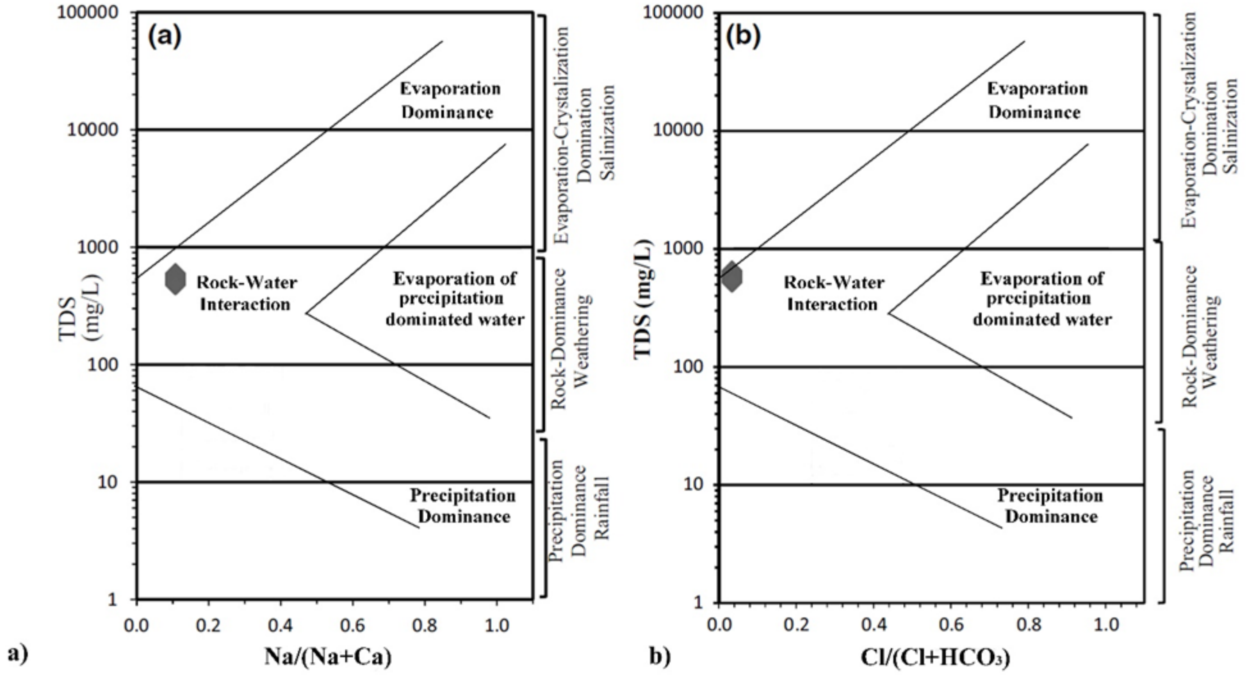


Figure 2.7, Gibbs plots of **(a)** TDS vs Na/(Na + Ca), and **(b)** TDS vs Cl/(Cl + HCO3) showing major processes controlling water chemistry of the Ridracoli reservoir water.

The stratification of the reservoir shown by physical parameters (Figure 2.5 and Figure 2.6) could have an effect on the vertical distribution of several elements (Figure 2.8). Fe and Mn had different behavior compared to Al, K, and Mg, as shown in Figure 2.8. Profiles show surface, middle, and bottom concentrations along the water column in the two periods of the year: October 2015, when the reservoir had the smallest water volume (Figure 2.3) and the anoxic condition at the bottom (Figure 2.6); and April 2016, when the reservoir had at its maximum water storage and no oxygen stratification was recorded.

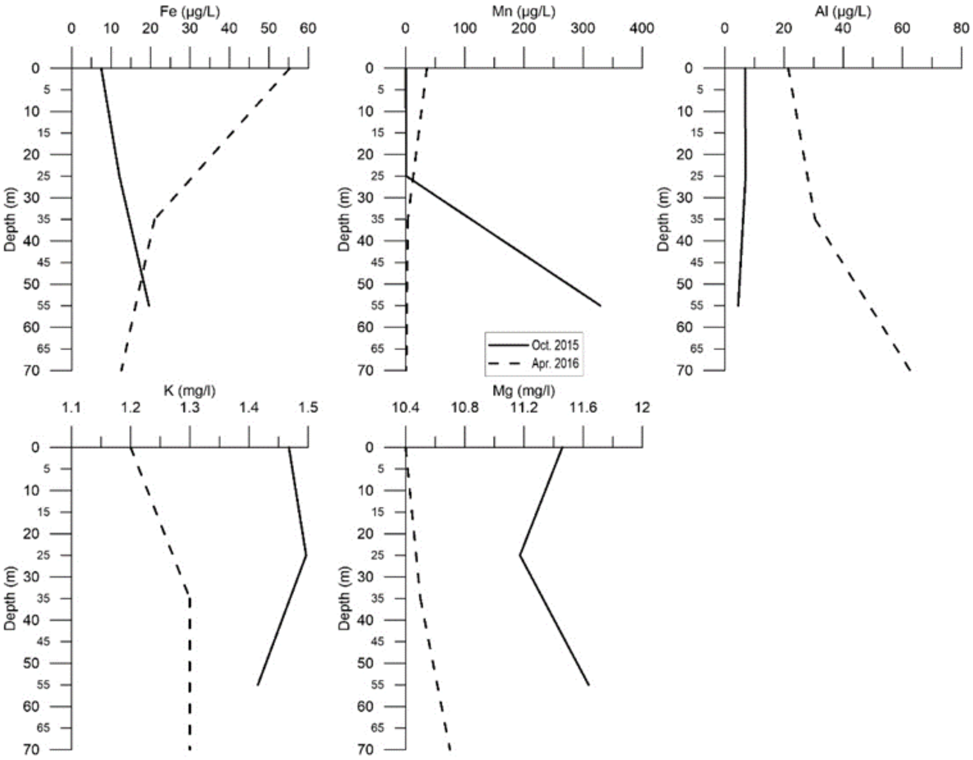


Figure 2.8, Fe, Mn, Al, K, and Mg concentrations along the water column in October 2015 and April 2016 via Niskin bottle sampling.

The pattern for dissolved Fe and Mn elements shows a downward increase in concentration in the late summer observation (October 2015), when water stratification was present, ranging from concentrations of 7.5 µg/L of Fe and <1 µg/L of Mn in surface waters to 19.6 and 329 µg/L to the bottom, respectively. Lower concentrations at the bottom could be found instead when the water column was not stratified (April 2016), ranging from of 55.3 µg/L Fe and 36 µg/L of Mn at the top to 12.6 and 1.1 µg/L, respectively, showing opposite behaviour.

Other elements show different behaviour along the water column and across the year than Fe and Mn. Al concentrations decreased along the column from 6.8 to 4.5 µg/L in October and increased towards the bottom in April 2016, from 21.4 to 62.6 µg/L.

Other elements, such as K, Mg (Figure 2.8), Na, Cl, and Cu (Supplementary material, Table 2.S1) are constant along the water column and during the whole year. Concentrations of as decreased in April when the water column was fully oxygenated, because it was absorbed onto Fe-Mn-oxyhydroxides. In the presence of reducing environment and relative absence of sulphur (2.S2− < 0.1), the high concentrations of Fe^{2+} and Mn^{2+} were in agreement with the presence in solution of As.

Figure 2.9 shows a decrease in NO_3^- concentration (from 1.4 to 0.7 mg/L) in the late summer profile, coupled with the appearance of NO_2^- (from <0.05 to 0.18 mg/L) and traces of NH_4^+ (<0.05-0.1 mg/L) in the deepest water samples. The reduced nitrogen species at the reservoir bottom was linked to the anoxic conditions and degradation of organic matter. On the contrary, when the water column was mixed, their concentrations were constant throughout the water column.

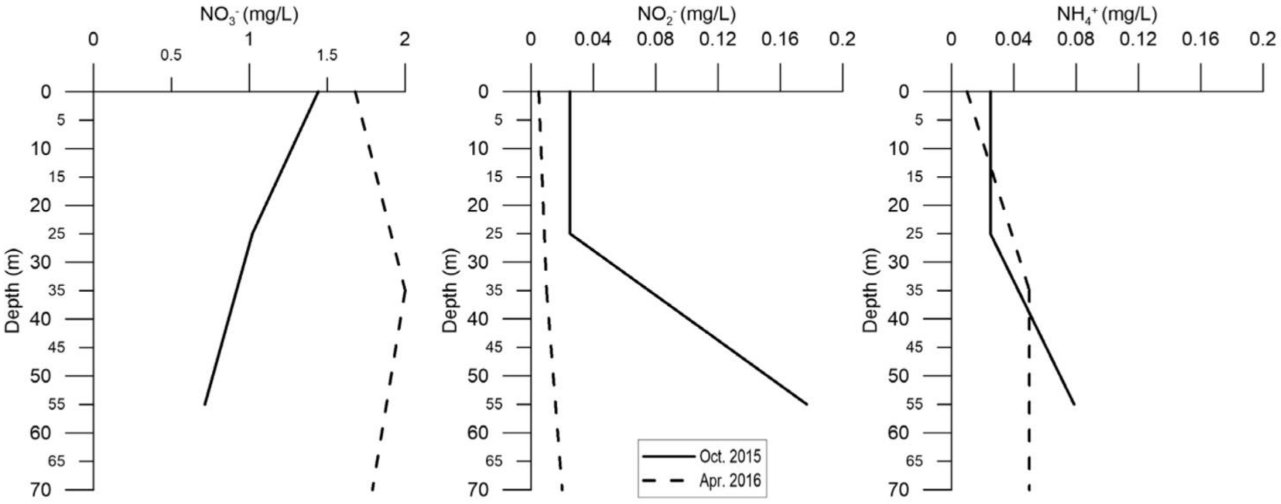


Figure 2.9, NO2−, NO3−, and NH4+ (mg/L) profiles along the water column in October 2015 and April 2016.

These changes in chemistry along the water column across the year affected the quality of water, which reached the water treatment plant in Capaccio. At the treatment plant, the monitored intake water chemistry did not show significant variation in the concentration of the majority of elements analysed during the year, except for Fe and Mn. Both elements show a significant increase in August and September (Figure 2.10). The average Fe concentrations from August to October was 200 µg/L that were more than double the average value of the remaining months (90 µg/L); Mn revealed a similar trend with average of 58 µg/L in late summer against the average value of 12.6 µg/L in the remaining months.

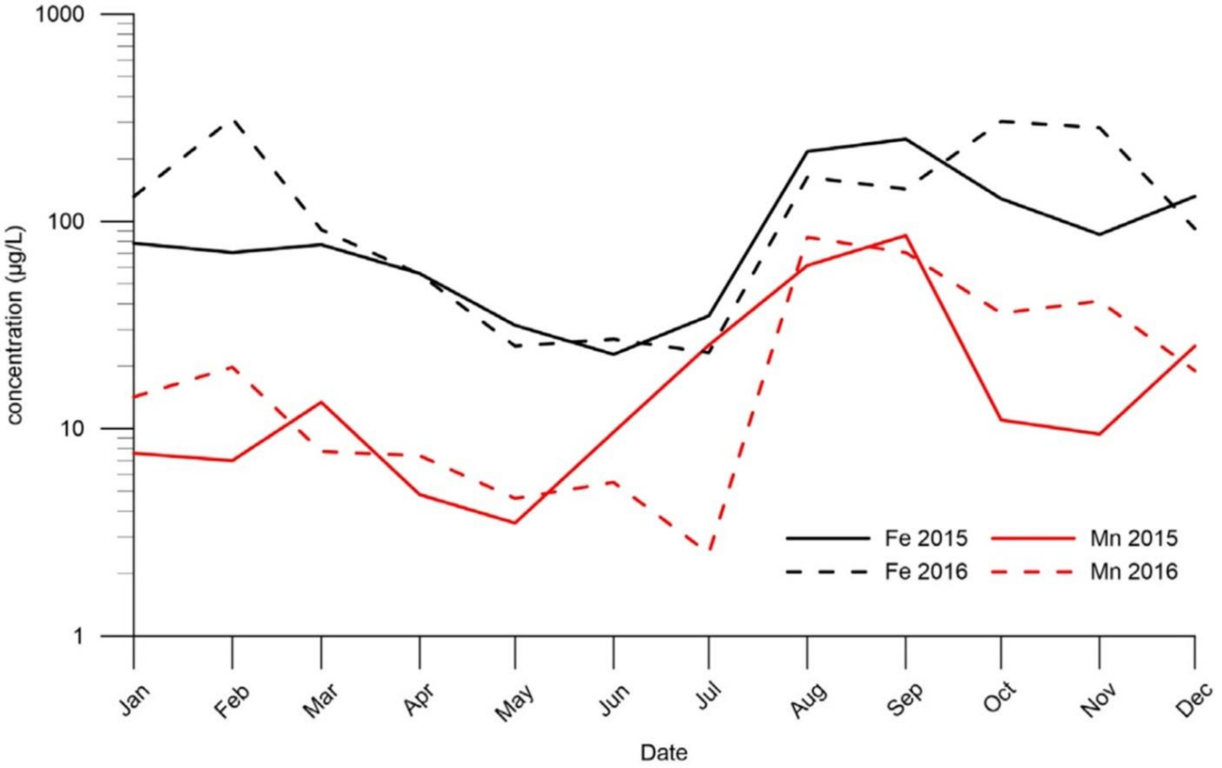


Figure 2.10, FeTOT and Mn (µg/L) concentrations at the water treatment plant at Capaccio in 2015 and 2016.

2.5 Discussion

Overall, water chemistry at the Ridracoli reservoir is controlled by rock weathering of the catchment (Figure 2.7). Weathering of the outcrop of sandstones and marl in the Bidente Catchment (Figure 2.2) is the responsible mechanism for the Ridracoli water chemistry. In addition to Ca^{2+} derived from the weathering of fine-grained lithologies, turbiditic unit of Marnoso-Arenacea formation (MAF), there are also sandstone beds enriched in carbonate (Gandolfi et al., 1983), which have higher content of CaO than other turbiditic sandstone units present in the northern Apennines (Dinelli et al., 1999; Lancianese and Dinelli, 2015).

The Ridracoli water reservoir behaves as a monomictic lake that remains stably stratified through the summer season (July–October) and mixes from top to bottom during the cold season (November–Feburary, winter turnover). Thermal stratification (Figure 2.5) occurs in summer due to the much higher solar heating rate of the surface waters than the bottom waters. 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 water column mixing (Magee and Wu, 2017; Winton et al., 2019) and the diffusion of heat and DO between the epilimnion and the hypolimnion (Burns, 1995). Thermal stratification begins in summer and remains stable throughout autumn until the surface waters cool sufficiently that the homogenization of the water temperature occurs, starting from the top (first 25–30 m). The reservoir becomes isothermal and the water column can fully mix once more. The mechanism for stratification is driven by the temperature that induces density difference between the different layers.

Strong thermal stratification also increases the strength of the thermocline as a barrier to the transport of oxygen from the epilimnion to the hypolimnion, limiting processes of vertical mixing (Hawkins, 1985). Dissolved oxygen (DO) is a key indicator of the "health" of a reservoir (Burns, 1995), with high DO concentrations in both the hypolimnion and epilimnion being associated with good health. During the thermal stratification period, DO concentrations decreased as shown in Figure 2.6, reaching hypoxia and eventually anoxic values (max 0.6 mg/L from CTD probe in October 2015) at the reservoir bottom. During the stratification condition, cold and dense water trapped at the bottom between sediment and an upper less dense layer, alters its chemistry and leaches or absorbs elements (Hawkins, 1985). The occurring additional process at the reservoir bottom is the organic matter degradation that under oxygen depletion occurs using other oxidizing agents, different from oxygen (Berner, 1980). In fact, denitrification processes occur causing a decrease in NO_3^- and an increase in NO_2^- and NH_4^+ concentrations (Figure 2.9), along with depletion of dissolved and freely available oxygen (Jossette et al., 1999; Wall et al., 2005; Xiong et al., 2017). In addition, insoluble metal oxides, such as those of Mn and Fe, can be involved as secondary oxidizing agents during organic matter degradation thus leading to a release of soluble reduced forms in solution (Fe and Mn in Figure 2.8). When the hypolimnion becomes re-oxygenated again, the metal oxides form and precipitate down into the sediment once more. Heavy metal adsorption (e.g., As in Table 2.S1 of Supplementary Material) by insoluble Fe-Mn-oxyhydroxides and precipitations can occur at this stage (Sigg et al., 1987; Balistrieri et al., 1994) and explains the downward depletion in concentrations during homogeneous water column (April) compared to stratification condition (October; Figure 2.8 and Table 2.S1 in the Supplementary Material). Equilibrium is established between the soluble and insoluble components where the soluble component tends to diffuse up along the column, towards the oxygenated water, where it is oxidized to the insoluble form.

These dynamics in the reservoir induce a series of chemical reactions that change water column chemistry through the year and consequently the water reaching the treatment plant (Casamitjana et al., 2003; Elçi, 2008). The cyclic monthly patterns of Fe and Mn concentrations observed at the Capaccio treatment plant (Figure 2.10) is the direct consequence of water column stratification-mixing processes occurring in the reservoir: higher concentrations of soluble reduced forms in solution during late summer and fall, and lower concentration in winter and spring due to water mixing and development of oxic conditions, which cause precipitation of insoluble Fe-Mn-oxyhydroxides.

When reservoir water quality issues affect their resource management, some points need to be considered. The maximum withdrawal of water coincides with the summer season (Figure 2.3), when anoxia is developing and Fe^{2+} and Mn^{2+} concentrations starts increasing. This also coincides with the lowest water level period, when it is no longer possible to withdraw from the upper intake at 540 m a.s.l., but the deepest intake at 490 m a.s.l. has to be used. From April to October the volumes of stored water, is more than halved and the water level significantly decreases from about 557 (78 m deep water column) to about 532 m a.s.l. (55 m deep water column). This decrease affects the intake water chemistry that is withdrawn from the spot close to the bottom layer (sketch in Figure 2.1), enriched in Fe^{2+} and Mn^{2+}.

The Fe and Mn limits for drinking water in Italy are 200 and 50 µg/L, respectively (D. Lgs. 2 February 2001, n. 31; (D. Lgs., 2001)). These thresholds are occasionally exceeded (Figure 2.10) leading to the implementation of further water oxidation, clariflocculation, and filtration processes at the Capaccio treatment plant with an increase in operational costs.

The reservoir water quality can be managed by altering operating regimes, changing water uses, blending waters of varying quality (Gibbs and Kickey, 2020), as well as by diversifying the depths of the withdrawals valves in order to avoid selective draw-induced stratification and create a forced mixing of the water column. In the short time, the installation of new water intakes at different depth to seasonally modify the withdrawal depth and accommodate the intra-annual variability of water quality seems to be the more feasible solution for the studied reservoir.

Other interventions could prevent anoxic water discharge, forcing the artificial mixing of oxygenated upper water with the bottom water or increase the DO in the bottom water thanks to external input of oxygen (Nordin and McKean, 1982; Singleton and Little, 2006). Another alternative is the positioning of floating mats on the water surface by leading vegetables to accumulate the analytes of concern thanks to specific plants (Phillips et al., 1995; Gantzer et al., 2009), even if it seems more suitable for shallow reservoir.

Attention should also be paid on the siltation phenomenon that trapping the sediments at the bottom will fill, over time, the reservoir. The continuous decrease of reservoir depth will bring hypolimnion much closer to the deepest water intake that is used in the summer period. In the future, this phenomenon could lead to a worsening of the water quality reaching the treatment plant.

Finally, it has also to be considered that the water quality assessment of a wide reservoir through only one monitoring site cannot be seen as representative for the entire basin; for this reason monitoring network based on multiple sampling sites would be recommended for the entire reservoir quality assessment.

2.6 Conclusions

The seasonal changes in water chemistry of the Ridracoli artificial basin, the main water reservoir of the Emilia-Romagna region (Northeast Italy) was investigated due to an extended and integrated database of physical and chemical parameters.

First of all, based on the water analysis we could conclude that Ridracoli was a good quality reservoir for drinking water purposes. However, thermal stratification of the reservoir played a central role in water quality throughout the year, with consequent implication for water treatment. Due to thermal stratification, reservoir water quality changed seasonally due to absorption and release processes, equilibrium between soluble and insoluble components (e.g., Fe and Mn), nitrification and denitrification processes, and organic matter degradation.

Two different conditions were identified in the reservoir: (I) a short period (August–November), during which the reservoir had the annual minimum water storage (12–15 × 10^6 m^3) and the water column shows marked thermal stratification and an anoxic layer at the bottom; (II) a long period (December–July) during which the water volume started to increase till its maximum (33 × 10^6 m^3), the stratification totally disappeared and the oxic condition was constant along the water column. In the first condition, a consistent release of Mn^{2+} and Fe^{2+} and an increase in NO_2^- and NH_4^+ concentrations (denitrification) occurred at the bottom water. During the second period, the water column was homogenous in temperature and DO concentration, and the bottom enrichment in Mn^{2+} and Fe^{2+} disappeared due to Fe-Mn-oxyhydroxides precipitation.

From a management point of view, these dynamics affected the quality of water reaching the downflow treatment plant of Capaccio, which purifies and distributes water for about one million of people during the tourist summer season. When the limits of Fe and Mn concentrations are exceeded (after summer season) the treatment plant has to implement further water treatment and purification processes with an increase in costs.

The comprehension of the seasonal stratification and its related effects on bottom water geochemistry will allow one to implement management practices in order to reduce costs of further purification processes. The installation of new water intakes at several depths operating in different periods of the year in order to accommodate the intra-annual variability of water quality seems to be the most feasible solution for the artificial basin. Other alternatives include the use of artificial water column mixing or external input of oxygen to solve the anoxic condition at the bottom. More attention should also be paid on the water monitoring system; considering the reservoir extension, multiple sampling sites, and sediment–water interface monitoring campaigns would be recommended to fully assess the water quality and better characterize the release and absorption processes under different redox condition.

Supplementary materials

The following are available online at https://www.mdpi.com/2073-4441/12/2/581/s1

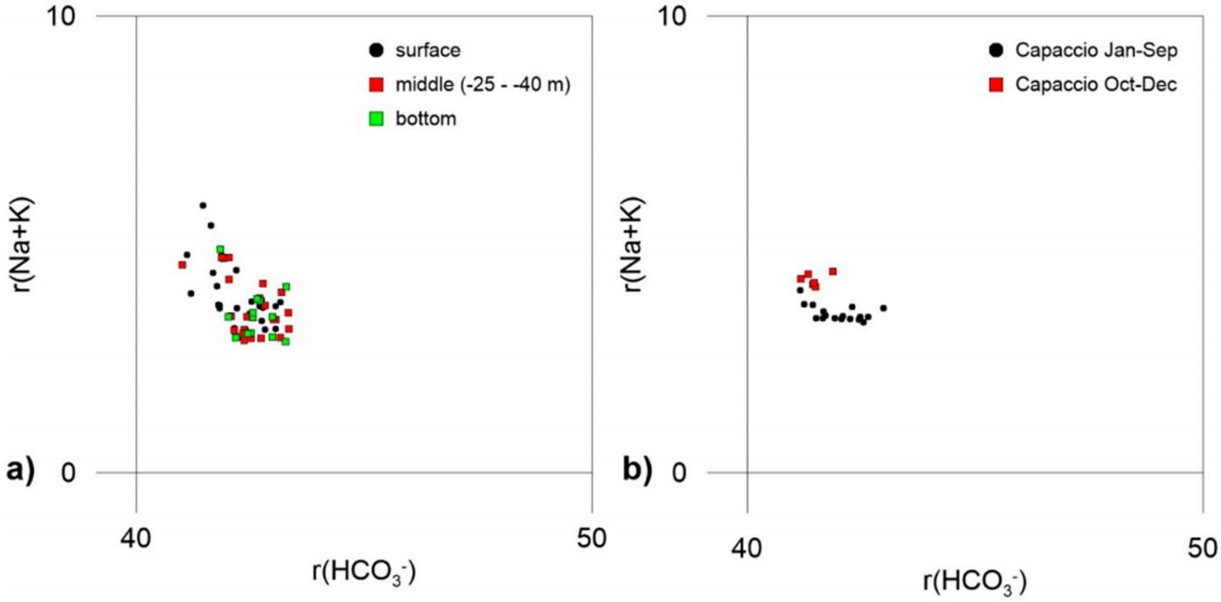
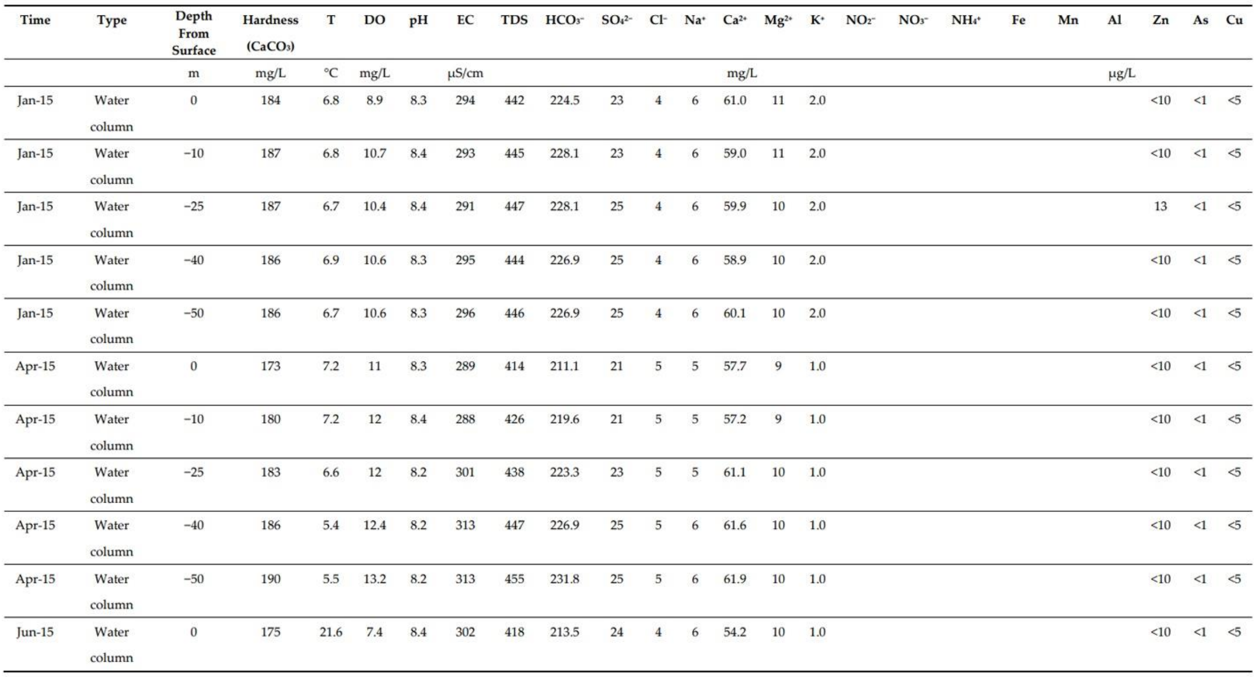
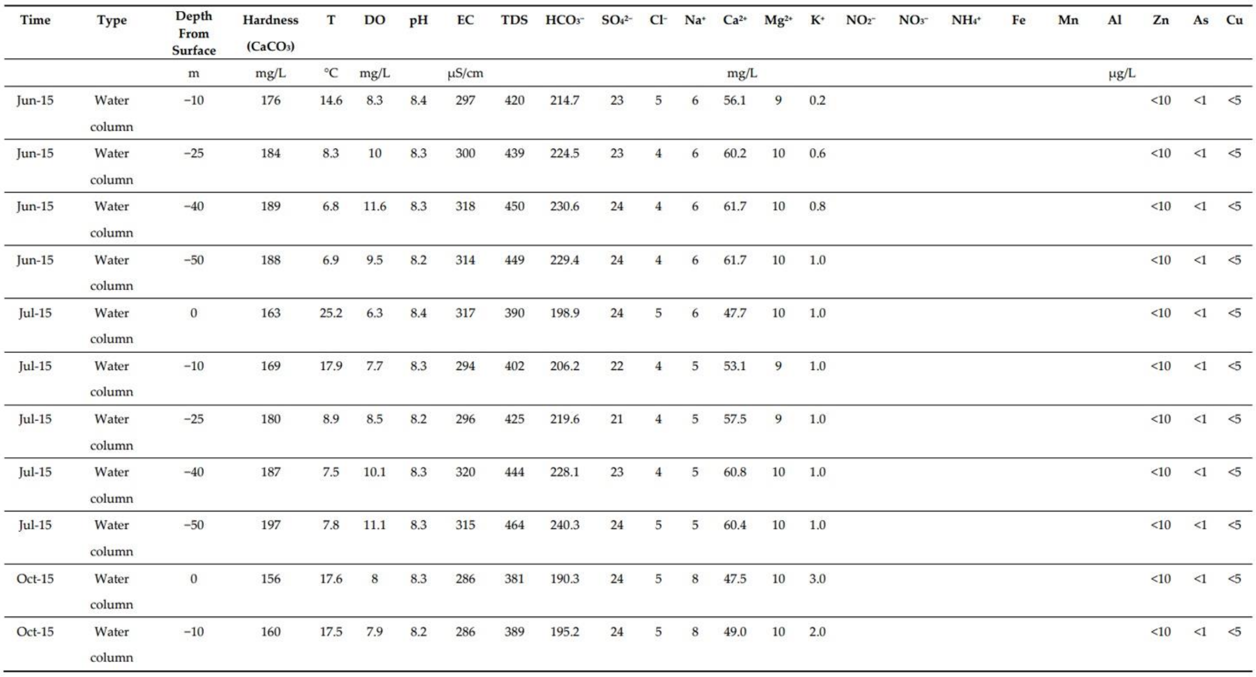


Figure 2.S1, Langelier-Ludwig classification diagrams with respectively: (a) Ridracoli reservoir waters from surface, bottom (−50 m) and middle (−25 and −40 m) water column; (b) Water samples of Capaccio treatment plant at 2 different periods, Jan-Sep and Oct-Dec. To be noted: in order to distinguish the sample dots, the diagram were cut on the bicarbonate-calcium water quadrant.

Table 2.S1, Major and trace element concentrations in water samples collected at the Ridracoli water reservoir and Capaccio water treatment plan.

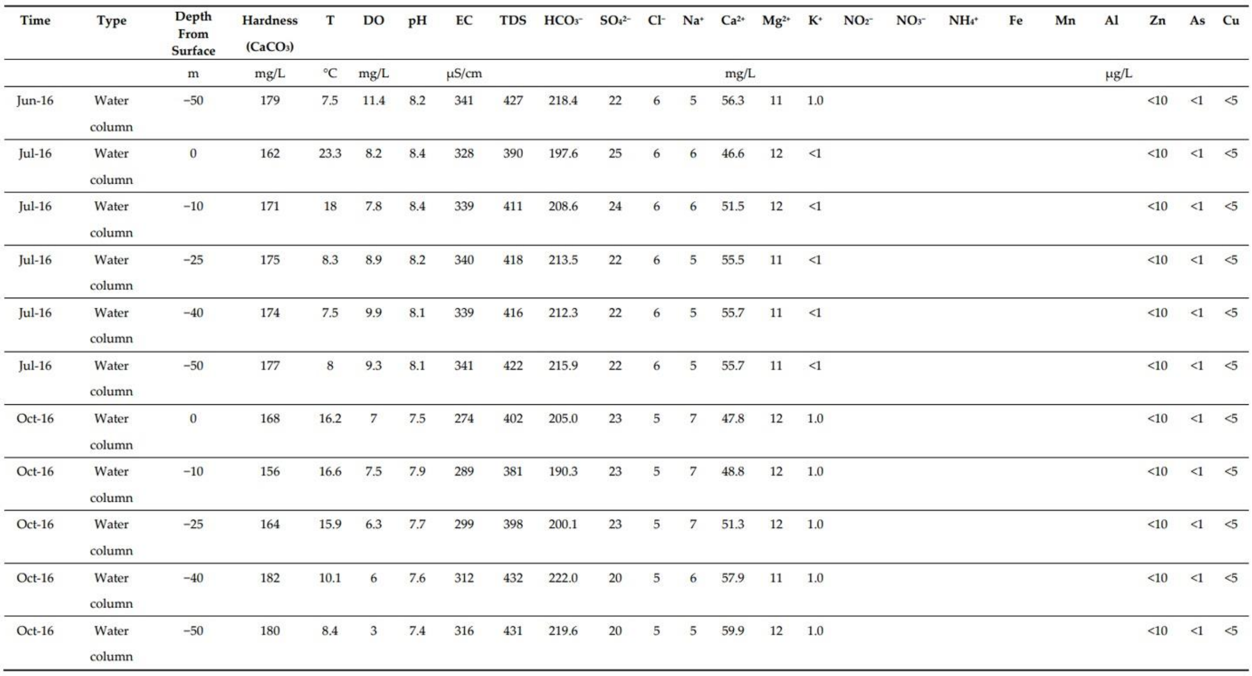


Time	Type	Depth From Surface	Hardness ($CaCO_3$)	T	DO	pH	EC	TDS	HCO_3^-	SO_4^{2-}	Cl^-	Na^+	Ca^{2+}	Mg^{2+}	K^+	NO_2^-	NO_3^-	NH_4^+	Fe	Mn	Al	Zn	As	Cu
		m	mg/L	°C	mg/L		µS/cm						mg/L								µg/L			
Jan-15	Water column	0	184	6.8	8.9	8.3	294	442	224.5	23	4	6	61.0	11	2.0							<10	<1	<5
Jan-15	Water column	−10	187	6.8	10.7	8.4	293	445	228.1	23	4	6	59.0	11	2.0							<10	<1	<5
Jan-15	Water column	−25	187	6.7	10.4	8.4	291	447	228.1	25	4	6	59.9	10	2.0							13	<1	<5
Jan-15	Water column	−40	186	6.9	10.6	8.3	295	444	226.9	25	4	6	58.9	10	2.0							<10	<1	<5
Jan-15	Water column	−50	186	6.7	10.6	8.3	296	446	226.9	25	4	6	60.1	10	2.0							<10	<1	<5
Apr-15	Water column	0	173	7.2	11	8.3	289	414	211.1	21	5	5	57.7	9	1.0							<10	<1	<5
Apr-15	Water column	−10	180	7.2	12	8.4	288	426	219.6	21	5	5	57.2	9	1.0							<10	<1	<5
Apr-15	Water column	−25	183	6.6	12	8.2	301	438	223.3	23	5	5	61.1	10	1.0							<10	<1	<5
Apr-15	Water column	−40	186	5.4	12.4	8.2	313	447	226.9	25	5	6	61.6	10	1.0							<10	<1	<5
Apr-15	Water column	−50	190	5.5	13.2	8.2	313	455	231.8	25	5	6	61.9	10	1.0							<10	<1	<5
Jun-15	Water column	0	175	21.6	7.4	8.4	302	418	213.5	24	4	6	54.2	10	1.0							<10	<1	<5

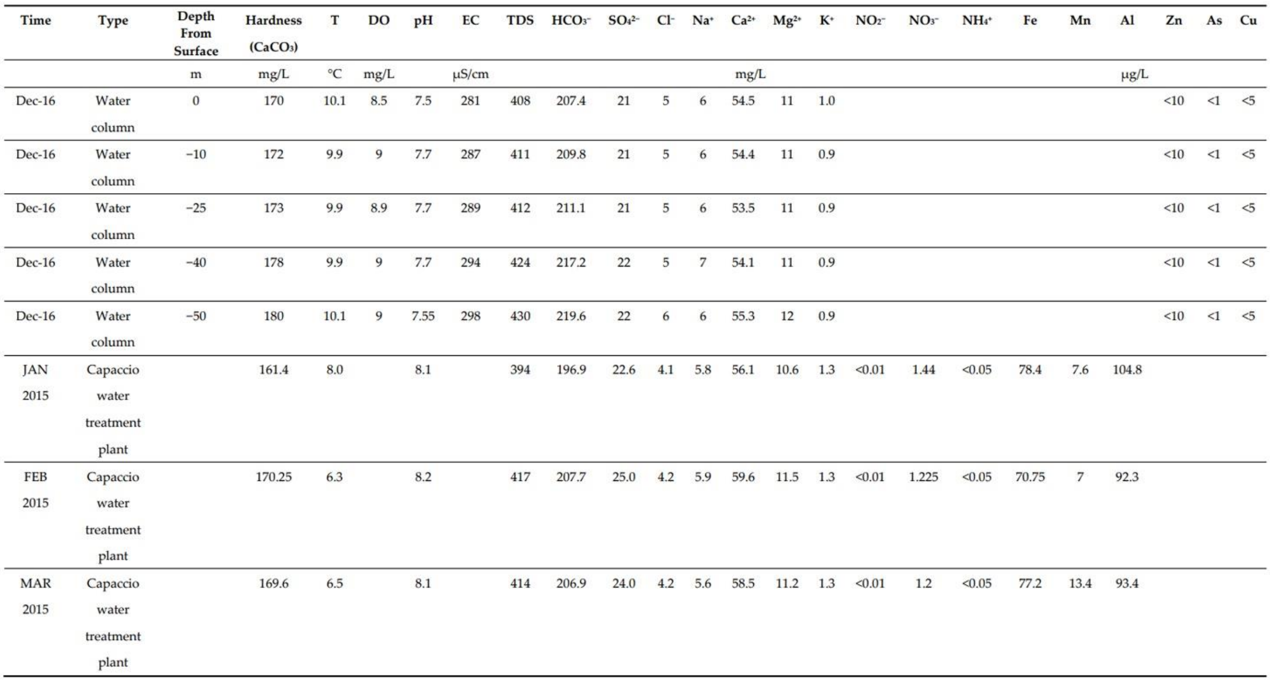


Time	Type	Depth From Surface	Hardness ($CaCO_3$)	T	DO	pH	EC	TDS	HCO_3^-	SO_4^{2-}	Cl^-	Na^+	Ca^{2+}	Mg^{2+}	K^+	NO_2^-	NO_3^-	NH_4^+	Fe	Mn	Al	Zn	As	Cu
		m	mg/L	°C	mg/L		µS/cm						mg/L								µg/L			
Jun-15	Water column	−10	176	14.6	8.3	8.4	297	420	214.7	23	5	6	56.1	9	0.2							<10	<1	<5
Jun-15	Water column	−25	184	8.3	10	8.3	300	439	224.5	23	4	6	60.2	10	0.6							<10	<1	<5
Jun-15	Water column	−40	189	6.8	11.6	8.3	318	450	230.6	24	4	6	61.7	10	0.8							<10	<1	<5
Jun-15	Water column	−50	188	6.9	9.5	8.2	314	449	229.4	24	4	6	61.7	10	1.0							<10	<1	<5
Jul-15	Water column	0	163	25.2	6.3	8.4	317	390	198.9	24	5	6	47.7	10	1.0							<10	<1	<5
Jul-15	Water column	−10	169	17.9	7.7	8.3	294	402	206.2	22	4	5	53.1	9	1.0							<10	<1	<5
Jul-15	Water column	−25	180	8.9	8.5	8.2	296	425	219.6	21	4	5	57.5	9	1.0							<10	<1	<5
Jul-15	Water column	−40	187	7.5	10.1	8.3	320	444	228.1	23	4	5	60.8	10	1.0							<10	<1	<5
Jul-15	Water column	−50	197	7.8	11.1	8.3	315	464	240.3	24	5	5	60.4	10	1.0							<10	<1	<5
Oct-15	Water column	0	156	17.6	8	8.3	286	381	190.3	24	5	8	47.5	10	3.0							<10	<1	<5
Oct-15	Water column	−10	160	17.5	7.9	8.2	286	389	195.2	24	5	8	49.0	10	2.0							<10	<1	<5

Time	Type	Depth From Surface	Hardness (CaCO$_3$)	T	DO	pH	EC	TDS	HCO$_3^-$	SO$_4^{2-}$	Cl$^-$	Na$^+$	Ca^{2+}	Mg^{2+}	K$^+$	NO$_2^-$	NO$_3^-$	NH$_4^+$	Fe	Mn	Al	Zn	As	Cu
		m	mg/L	°C	mg/L		µS/cm						mg/L								µg/L			
Oct-15	Water column	−25	164	16.2	6.4	8.2	290	397	200.1	23	5	7	51.7	10	2.0							<10	<1	<5
Oct-15	Water column	−40	175	13.2	4.3	8.1	297	418	213.5	21	4	6	56.0	10	2.0							<10	<1	<5
Oct-15	Water column	−50	194	8.3	3.6	8.1	318	462	236.7	22	5	7	62.1	11	2.0							<10	<1	<5
Dec-15	Water column	0	171	8.9	9.1	8.5	298	417	208.6	25	5	7	55.8	10	3.0							<10	<1	<5
Dec-15	Water column	−10	170	9	9.7	8.4	297	413	207.4	25	5	7	53.5	10	3.0							<10	<1	<5
Dec-15	Water column	−25	172	9	9.4	8.3	298	419	209.8	25	5	7	55.1	11	3.0							<10	<1	<5
Dec-15	Water column	−40	171	8.9	9.7	8.4	299	417	208.6	25	5	7	55.0	11	3.0							<10	<1	<5
Dec-15	Water column	−50	165	8.9	8.8	8.3	293	403	201.3	24	5	7	53.7	10	3.0							<10	<1	<5
Jan-16	Water column	0	169	6.9	10.2	8.2	326	406	206.2	22	6	5	56.3	9	<1							<10	<1	<5
Jan-16	Water column	−10	169	6.7	11	8.3	325	407	206.2	22	6	5	57.6	9	<1							<10	<1	<5
Jan-16	Water column	−25	169	6.7	10.7	8.3	325	407	206.2	22	6	5	57.4	9	<1							<10	<1	<5
Jan-16	Water column	−40	176	6.6	11.5	8.3	331	423	214.7	22	6	5	60.3	9	<1							<10	<1	<5
Jan-16	Water column	−50	182	6.6	10.5	8.2	340	436	222.0	24	6	5	60.2	10	<1							<10	<1	<5
Apr-16	Water column	0	170	11.2	10	8.6	329	408	207.4	21	6	5	53.9	12	1.0							<10	<1	<5
Apr-16	Water column	−10	170	9.1	10.5	8.3	328	408	207.4	21	6	5	54.5	11	1.0							<10	<1	<5
Apr-16	Water column	−25	173	6.9	10.3	8.3	333	416	211.1	21	6	5	56.0	12	0.8							<10	<1	<5
Apr-16	Water column	−40	175	6.8	10.7	8.3	335	423	213.5	22	6	5	58.1	12	0.9							<10	<1	<5
Apr-16	Water column	−50	170	6.8	11.3	8.4	335	413	207.4	22	6	5	57.3	12	1.0							<10	<1	<5
Jun-16	Water column	0	170	17.3	9.7	8.4	343	411	207.4	25	5	6	52.4	12	1.0							<10	<1	<5
Jun-16	Water column	−10	174	14.3	9.6	8.4	361	419	212.3	24	5	6	55.4	11	1.0							<10	<1	<5
Jun-16	Water column	−25	169	9.3	10.3	8.2	334	406	206.2	21	6	5	54.2	11	1.0							<10	<1	<5
Jun-16	Water column	−40	175	7.3	11	8.2	339	420	213.5	22	6	5	56.5	11	1.0							<10	<1	<5

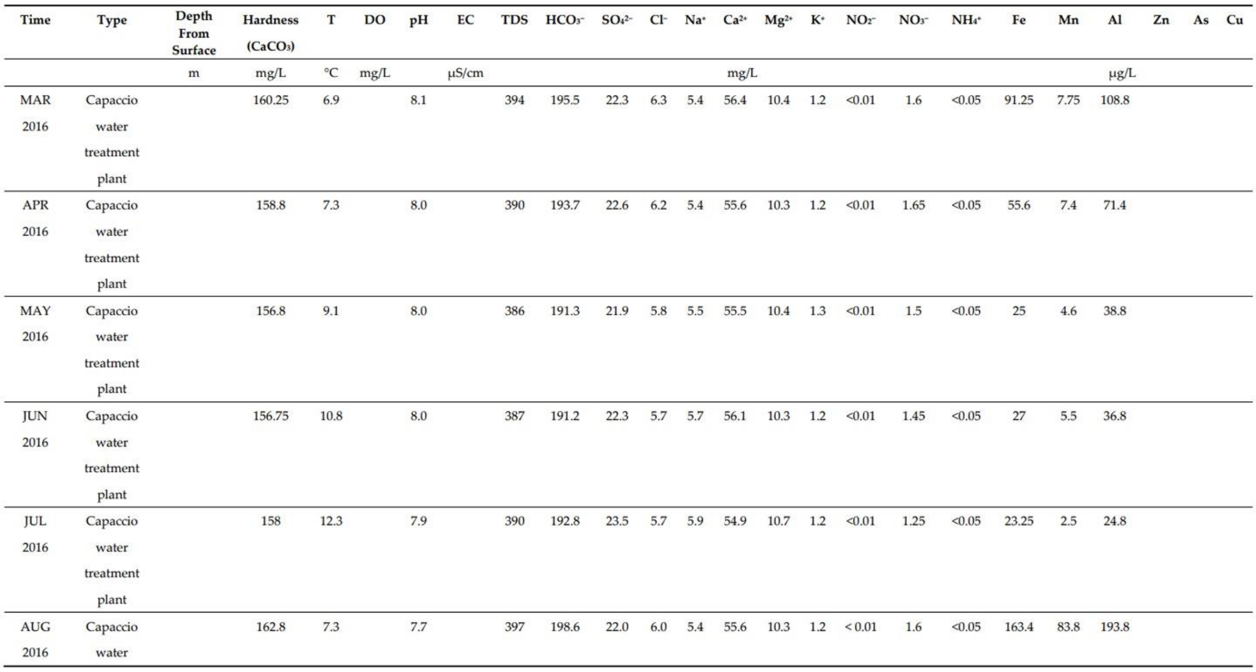


Time	Type	Depth From Surface	Hardness ($CaCO_3$)	T	DO	pH	EC	TDS	HCO_3^-	SO_4^{2-}	Cl^-	Na^+	Ca^{2+}	Mg^{2+}	K^+	NO_2^-	NO_3^-	NH_4^+	Fe	Mn	Al	Zn	As	Cu
		m	mg/L	°C	mg/L		μS/cm						mg/L								μg/L			
Jun-16	Water column	−50	179	7.5	11.4	8.2	341	427	218.4	22	6	5	56.3	11	1.0							<10	<1	<5
Jul-16	Water column	0	162	23.3	8.2	8.4	328	390	197.6	25	6	6	46.6	12	<1							<10	<1	<5
Jul-16	Water column	−10	171	18	7.8	8.4	339	411	208.6	24	6	6	51.5	12	<1							<10	<1	<5
Jul-16	Water column	−25	175	8.3	8.9	8.2	340	418	213.5	22	6	5	55.5	11	<1							<10	<1	<5
Jul-16	Water column	−40	174	7.5	9.9	8.1	339	416	212.3	22	6	5	55.7	11	<1							<10	<1	<5
Jul-16	Water column	−50	177	8	9.3	8.1	341	422	215.9	22	6	5	55.7	11	<1							<10	<1	<5
Oct-16	Water column	0	168	16.2	7	7.5	274	402	205.0	23	5	7	47.8	12	1.0							<10	<1	<5
Oct-16	Water column	−10	156	16.6	7.5	7.9	289	381	190.3	23	5	7	48.8	12	1.0							<10	<1	<5
Oct-16	Water column	−25	164	15.9	6.3	7.7	299	398	200.1	23	5	7	51.3	12	1.0							<10	<1	<5
Oct-16	Water column	−40	182	10.1	6	7.6	312	432	222.0	20	5	6	57.9	11	1.0							<10	<1	<5
Oct-16	Water column	−50	180	8.4	3	7.4	316	431	219.6	20	5	5	59.9	12	1.0							<10	<1	<5

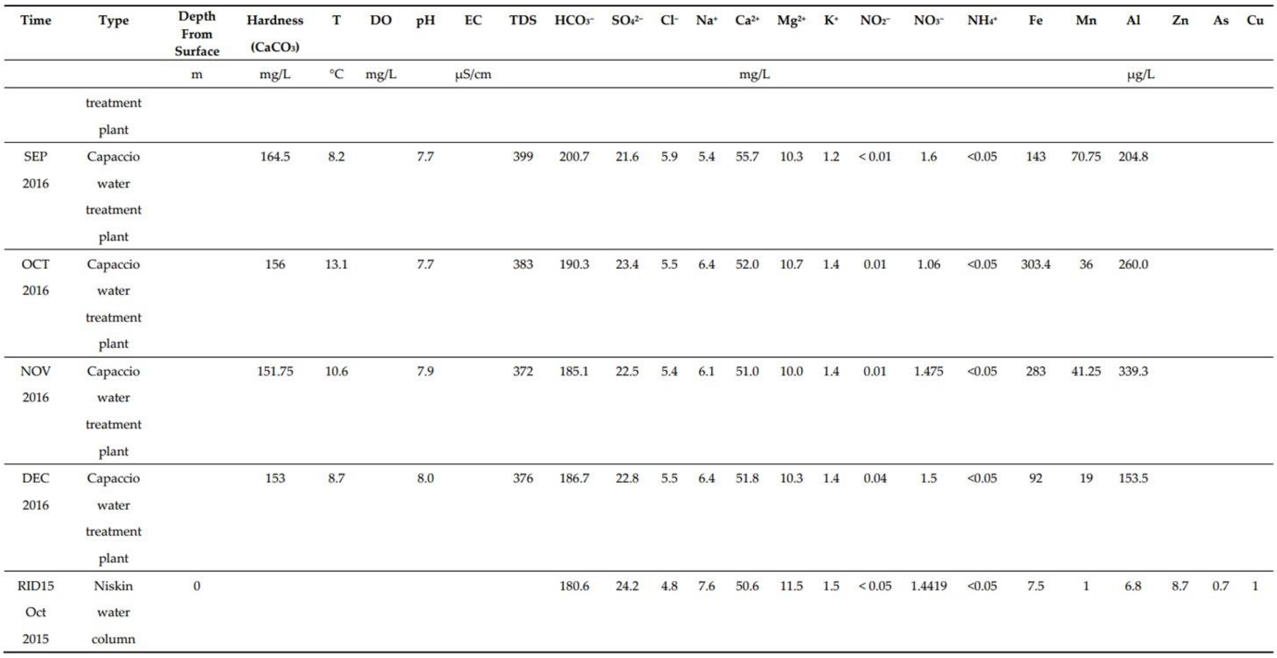


Time	Type	Depth From Surface	Hardness ($CaCO_3$)	T	DO	pH	EC	TDS	HCO_3^-	SO_4^{2-}	Cl^-	Na^+	Ca^{2+}	Mg^{2+}	K^+	NO_2^-	NO_3^-	NH_4^+	Fe	Mn	Al	Zn	As	Cu
		m	mg/L	°C	mg/L		μS/cm						mg/L								μg/L			
Dec-16	Water column	0	170	10.1	8.5	7.5	281	408	207.4	21	5	6	54.5	11	1.0							<10	<1	<5
Dec-16	Water column	−10	172	9.9	9	7.7	287	411	209.8	21	5	6	54.4	11	0.9							<10	<1	<5
Dec-16	Water column	−25	173	9.9	8.9	7.7	289	412	211.1	21	5	6	53.5	11	0.9							<10	<1	<5
Dec-16	Water column	−40	178	9.9	9	7.7	294	424	217.2	22	5	7	54.1	11	0.9							<10	<1	<5
Dec-16	Water column	−50	180	10.1	9	7.55	298	430	219.6	22	6	6	55.3	12	0.9							<10	<1	<5
JAN 2015	Capaccio water treatment plant		161.4	8.0		8.1		394	196.9	22.6	4.1	5.8	56.1	10.6	1.3	<0.01	1.44	<0.05	78.4	7.6	104.8			
FEB 2015	Capaccio water treatment plant		170.25	6.3		8.2		417	207.7	25.0	4.2	5.9	59.6	11.5	1.3	<0.01	1.225	<0.05	70.75	7	92.3			
MAR 2015	Capaccio water treatment plant		169.6	6.5		8.1		414	206.9	24.0	4.2	5.6	58.5	11.2	1.3	<0.01	1.2	<0.05	77.2	13.4	93.4			

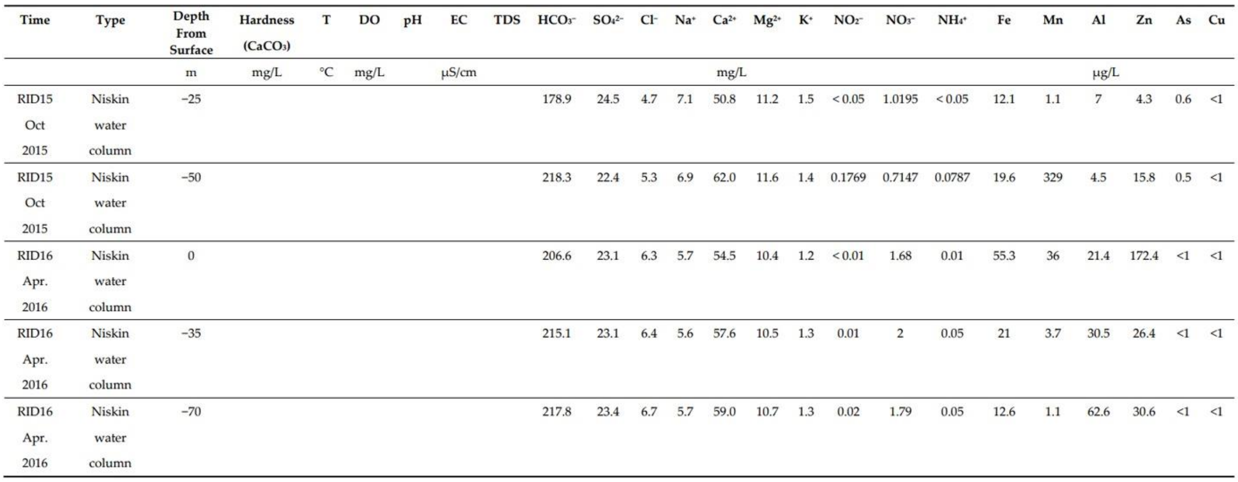
Time	Type	Depth From Surface	Hardness (CaCO$_3$)	T	DO	pH	EC	TDS	HCO$_3^-$	SO$_4^{2-}$	Cl$^-$	Na$^+$	Ca^{2+}	Mg^{2+}	K$^+$	NO$_2^-$	NO$_3^-$	NH$_4^+$	Fe	Mn	Al	Zn	As	Cu
		m	mg/L	°C	mg/L		µS/cm						mg/L								µg/L			
APR 2015	Capaccio water treatment plant		164.4	7.7		8.1		400	200.6	22.2	4.3	5.4	56.6	10.6	1.2	<0.01	1.4	<0.05	56	4.8	84.2			
MAY 2015	Capaccio water treatment plant		163.75	8.5		8.1		396	199.8	21.6	4.3	5.3	55.8	10.3	1.1	<0.01	1.5	<0.05	31.5	3.5	50.3			
JUN 2015	Capaccio water treatment plant		167	9.0		7.9		405	203.7	22.5	4.3	5.6	56.7	10.7	1.2	<0.01	1.44	<0.05	22.8	9.6	28.8			
JUL 2015	Capaccio water treatment plant		176.25	7.6		7.9		427	215.0	24.1	4.4	5.8	59.8	11.4	1.3	<0.01	1.4	<0.05	35	25.25	40.0			
AUG 2015	Capaccio water treatment plant		168	9.3		7.7		407	205.0	22.0	4.2	5.7	57.6	10.8	1.2	<0.01	1.475	<0.05	217.25	61.25	264.3			
SEP 2015	Capaccio water treatment plant		160.4	13.5		7.6		387	195.7	19.6	4.0	5.6	54.0	10.3	1.2	0.01	1.26	<0.05	249.6	85.4	256.0			
OCT 2015	Capaccio water treatment plant		153.25	13.9		7.8		376	187.0	22.5	4.4	6.9	51.5	10.9	1.5	0.02	1.175	<0.05	128.5	11	155.5			
NOV 2015	Capaccio water treatment plant		156	11.1		8.0		386	190.3	24.5	5.0	7.0	53.5	11.1	1.5	<0.01	1.4	<0.05	86.4	9.4	102.2			
DEC 2015	Capaccio water treatment plant		157.5	9.0		8.0		389	192.2	25.0	5.4	6.8	53.0	10.8	1.4	<0.01	1.44	<0.05	132	25	129.4			
JAN 2016	Capaccio water treatment plant		159.8	7.4		8.1		395	195.0	25.3	5.6	6.5	54.6	10.8	1.3	<0.01	1.52	<0.05	131.6	14.2	106.8			
FEB 2016	Capaccio water treatment plant		156.6	7.2		8.2		387	191.1	23.5	6.1	5.8	54.6	10.4	1.3	<0.01	1.58	<0.05	313.6	19.8	167.0			



Time	Type	Depth From Surface	Hardness (CaCO$_3$)	T	DO	pH	EC	TDS	HCO_3^-	SO_4^{2-}	Cl^-	Na^+	Ca^{2+}	Mg^{2+}	K^+	NO_2^-	NO_3^-	NH_4^+	Fe	Mn	Al	Zn	As	Cu
		m	mg/L	°C	mg/L		μS/cm						mg/L								μg/L			
MAR 2016	Capaccio water treatment plant		160.25	6.9		8.1		394	195.5	22.3	6.3	5.4	56.4	10.4	1.2	<0.01	1.6	<0.05	91.25	7.75	108.8			
APR 2016	Capaccio water treatment plant		158.8	7.3		8.0		390	193.7	22.6	6.2	5.4	55.6	10.3	1.2	<0.01	1.65	<0.05	55.6	7.4	71.4			
MAY 2016	Capaccio water treatment plant		156.8	9.1		8.0		386	191.3	21.9	5.8	5.5	55.5	10.4	1.3	<0.01	1.5	<0.05	25	4.6	38.8			
JUN 2016	Capaccio water treatment plant		156.75	10.8		8.0		387	191.2	22.3	5.7	5.7	56.1	10.3	1.2	<0.01	1.45	<0.05	27	5.5	36.8			
JUL 2016	Capaccio water treatment plant		158	12.3		7.9		390	192.8	23.5	5.7	5.9	54.9	10.7	1.2	<0.01	1.25	<0.05	23.25	2.5	24.8			
AUG 2016	Capaccio water		162.8	7.3		7.7		397	198.6	22.0	6.0	5.4	55.6	10.3	1.2	< 0.01	1.6	<0.05	163.4	83.8	193.8			



Time	Type	Depth From Surface	Hardness (CaCO$_3$)	T	DO	pH	EC	TDS	HCO_3^-	SO_4^{2-}	Cl^-	Na^+	Ca^{2+}	Mg^{2+}	K^+	NO_2^-	NO_3^-	NH_4^+	Fe	Mn	Al	Zn	As	Cu
		m	mg/L	°C	mg/L		μS/cm						mg/L								μg/L			
	treatment plant																							
SEP 2016	Capaccio water treatment plant		164.5	8.2		7.7		399	200.7	21.6	5.9	5.4	55.7	10.3	1.2	< 0.01	1.6	<0.05	143	70.75	204.8			
OCT 2016	Capaccio water treatment plant		156	13.1		7.7		383	190.3	23.4	5.5	6.4	52.0	10.7	1.4	0.01	1.06	<0.05	303.4	36	260.0			
NOV 2016	Capaccio water treatment plant		151.75	10.6		7.9		372	185.1	22.5	5.4	6.1	51.0	10.0	1.4	0.01	1.475	<0.05	283	41.25	339.3			
DEC 2016	Capaccio water treatment plant		153	8.7		8.0		376	186.7	22.8	5.5	6.4	51.8	10.3	1.4	0.04	1.5	<0.05	92	19	153.5			
RID15 Oct 2015	Niskin water column	0							180.6	24.2	4.8	7.6	50.6	11.5	1.5	< 0.05	1.4419	<0.05	7.5	1	6.8	8.7	0.7	1



Time	Type	Depth From Surface	Hardness (CaCO$_3$)	T	DO	pH	EC	TDS	HCO$_3^-$	SO$_4^{2-}$	Cl$^-$	Na$^+$	Ca^{2+}	Mg^{2+}	K$^+$	NO$_2^-$	NO$_3^-$	NH$_4^+$	Fe	Mn	Al	Zn	As	Cu
		m	mg/L	°C	mg/L		μS/cm						mg/L								μg/L			
RID15 Oct 2015	Niskin water column	−25							178.9	24.5	4.7	7.1	50.8	11.2	1.5	< 0.05	1.0195	< 0.05	12.1	1.1	7	4.3	0.6	<1
RID15 Oct 2015	Niskin water column	−50							218.3	22.4	5.3	6.9	62.0	11.6	1.4	0.1769	0.7147	0.0787	19.6	329	4.5	15.8	0.5	<1
RID16 Apr. 2016	Niskin water column	0							206.6	23.1	6.3	5.7	54.5	10.4	1.2	< 0.01	1.68	0.01	55.3	36	21.4	172.4	<1	<1
RID16 Apr. 2016	Niskin water column	−35							215.1	23.1	6.4	5.6	57.6	10.5	1.3	0.01	2	0.05	21	3.7	30.5	26.4	<1	<1
RID16 Apr. 2016	Niskin water column	−70							217.8	23.4	6.7	5.7	59.0	10.7	1.3	0.02	1.79	0.05	12.6	1.1	62.6	30.6	<1	<1

Author Contributions

Data curation, Investigation, Methodology, Writing—original draft, S.T.; Formal analysis, S.T., B.M.S.G. and N.G.; Project administration, Supervision, E.D.; Resources, I.V.; Validation, B.M.S.G. and E.D.; Visualization, B.M.S.G.; Writing—review & editing, B.M.S.G., N.G., M.A., and E.D. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

Chapter 3 - Geochemical characterization of surface sediments from the Ridracoli reservoir area and surroundings. Details on bulk composition and grain size.

Abstract

Sediment characterization is central in the environmental assessment of aquatic systems. This study is a characterization work on surface sediments of Ridracoli reservoir and a first attempt to compare with surroundings areas sediments of the Fiumi Uniti catchment in the northern Apennines, Emilia-Romagna, Italy. The study area combines the reservoir catchment, that is part of the Foreste Casentinesi-Monte Falterona-Campigna National Park, formed by the construction of a dam and operates, since 1982, for drinking water storage and electricity production, and the upstream side of Fiumi Uniti catchment that flows into the Adriatic Sea, including also nearby sub-catchments of Ridracoli reservoir, as Corniolo and Pietrapazza.

In this work were collected surface sediments within the area of the reservoir and riverbed sediments of surroundings catchments during a sampling campaign in 2015, analyzing grain size distribution using a sedigraph as well as the total composition including carbon and nitrogen contents by X-ray fluorescence (XRF) and CHNS-O Analyzer, respectively. This work aims to investigate the chemistry and distribution of elements within the area of study, to evaluate the effect of the dam upstream and downstream, and to study the processes that happen in rivers and in the reservoir.

The bulk composition is mainly SiO_2, Al_2O_3, CaO, with high Corg content reflecting the Marnoso Arenacea Formation geology of the area. From the total composition of sediments and relative statistical analysis, it is also possible to note the presence of two main types of sediment, a clayey one and one carbonate. On the reservoir area, the relationship of most of the elements with clay matrix and organic matter, besides iron, induces to suppose on some grain size influence, degradation of organic matter, and precipitation processes. The grain size shows the spatial distribution of silt and clay in the sediment from the bottom of the reservoir and sand which is more present in samples from the tributaries, due to sorting effects, and seems to be directly related to the concentration of metals. Further analysis has taken to include the entire surrounding area database dividing the sampling stations into groups on their chemical composition thanks to cluster analysis. Below has been studied few branches of the same river to investigate the geochemical evolution and the effects of the damming on the area.

Keywords: Geochemistry – Artificial Reservoir – Reservoir Sediments – Stream Sediments – PCA – Cluster analysis

3.1 Introduction

Reservoirs and lakes made by humans for different purposes, usually stop the water of one or more rivers via dam construction and store it creating an artificial lake. This new structure does not only affect the water flow but interferes with sediment transport routes 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 water quality (Ghaleno et al., 2015). Sediment accumulation, dynamics of deposition and movement, and quality are often of concern in reservoirs management, and geochemical tools can be useful to assess the potential risks. Potentially harmful elements (PHEs) can accumulate in sediments exceeding the background concentrations up to several times and this, in turn, may lead to potential hot spots of harmful substances (Milačič et al., 2017). Generally, more than 90% of the PHEs load in aquatic systems is bound to particulates like suspended matter and sediments (Calmano et al., 1993; Bird et al., 2010). The type and stability of elements on these compounds are decisive factors for their potential mobility and bioavailability. Contaminants may be a risk for the quality of resources as water, plants, and aquatic animals to which we are linked by consumption and may have consequent effects on our health. For this reason, the study of sediment characteristics and their pollutant load is of interest and used in environmental studies as indicators (Avila-Pérez et al., 1999; Arnason and Fletcher; 2003, Chen et al., 2008; Zhu et al., 2013; El-Radaideh et al, 2014).

Lakes and reservoirs are studied around the world and their engineering, biological, geological, and geochemical aspects have been extensively investigated. Among the major issues of particular relevance to reservoirs, besides the assessment of their water quality, are the potential public health impacts due to the spread and transmittal of diseases (Wasana et al., 2016; Robert et al., 2016) or the release of contaminant from industries and urban settlements adjacent to the reservoir (García-Ordiales et al., 2016), eutrophication episodes (Yang et al., 2008), the thermal and density stratification and the associated water chemistry deterioration (Elçi, 2008; Zouabi-Aloui et al., 2015; Toller et al., 2020). In reservoirs interested by thermal stratification, the suppression of vertical transport processes at the thermocline normally allows a thermic and oxygen gradient occurrence, which can cause anoxic conditions to develop in the hypolimnion, favouring internal element and nutrient loading at the sediment-water interface layer. This may cause the release of phosphorus (Kim et al., 2003), but also ammonium, iron, and manganese from sediments back into the water column (Munger et al., 2017, 2019) which can affect water quality and requires constant control and eventually actions to manage high concentrations.

Silting of reservoirs due to sediment trapping in the river system, bank and shore erosion, and eventually bank and slope sliding cause a decrease in storage capacity and reservoir lifetime, as well as water availability (Sumi and Kantoush, 2011; Ran et al., 2013), and eventually affect water quality due to turbidity and sediment-associated pollutants (Robert et al., 2016). Further side effects related to the construction of a dam include the supply of sediment to the sea (Mentaschi et al., 2018) and the configuration and morphology of the river channel upstream and downstream (Kondolf et al., 2014). Overall, the entire ecosystem tied to a new human-imposed regime system needs to be monitored for potential variations in chemical and ecological status, temperature, etc. (Ignatius and Rasmussen, 2016).

In order to manage large water reservoirs sustainably and to minimize the occurrence of conditions that interfere with the beneficial uses of their waters, regular collection, and analysis of different types of data are required. Notably, knowledge of the geochemical status of the sediment is of paramount importance for management purposes in the medium- to long-term.

This work investigates the bulk chemical composition of the sediments in Ridracoli artificial basin, the main water reservoir of the Emilia-Romagna region (northeast of Italy), and compare their chemical features with those of the sediments from the surrounding areas, which are part of the upper section of Fiumi Uniti catchment on the northern Apennines. Special emphasis is given to selected trace elements, Cu, Co, Cr, Ni, As, Pb, Zn, named hereafter as PHEs. We recently discussed the seasonal changes in water’s physical and chemical parameters, characterizing seasonal stratification and mixing processes along the water column (Toller et al., 2020). However, further studies on the solid matrix over a larger area are crucial for comprehensive environmental assessment of the Ridracoli reservoir area and its surroundings. The importance of this study relies on the chemical and sedimentological characterization of sediments of the reservoir and the comparison with nearby catchments sediments, providing information on the geochemical effects associated with the dam.

3.2 Material and Methods

3.2.1 Study area and sampling sites

The study area is located on the Northern Apennines in the Emilia-Romagna Region, Italy (Figure 3.1), and is part of Foreste Casentinesi Monte Falterona and Campigna National Park. The Romagna Apennines are crossed by a number of rivers which develop a hydrographical SW-NE drainage network, from the mountain to the plains. In the upper part of their catchments, the rivers cross the members of the Marnoso-Arenacea Formation, then in their closing mountain sections the terrains of the Padano-Adriatic domain and Quaternary alluvial deposits in their plain sections.

In particular, the investigated area includes the Ridracoli reservoir and related and confining basins: Bidente river, tributaries as Bidente di Corniolo, Bidente di Ridracoli and Pietrapazza, and a tributary of Rabbi river, connected to the reservoir by a gutter gallery (Figure 3.1).

The Ridracoli reservoir is located at 480 m a.s.l., it covers an area, calculated at the maximum water surface, of 1.035 km^2. It has a water depth that can reach 82 m and it can store at most 33.06 x 10^6 m^3 of water. The dam collects water from the Bidente di Ridracoli in the southern, and largest part, and from Rio Celluzze to the West, creating the two main branches of the reservoir (Figure 3.1). The total water supply catchment covers an area of about 88 km^2, including the direct basin, and in addition the reservoir receives waters from an indirect catchment of 51.1 km^2, represented by Bidente di Corniolo and Rabbi (Fiumicello) catchments, thanks to a gutter gallery, a channel for carrying waters. The rainfall recorded at the monitoring station of Ridracoli for 2015 and 2016 is 1294 and 1519 mm/year respectively, with the rainiest months from January to May. The reservoir has an irregular shape within its catchment, from a morphological and hydrological standpoint the water body lies within a complicated network of torrents and minor tributaries together with Bidente di Ridracoli and Rio Celluzze. Downstream, the Bidente river arises from the confluence of the Bidente di Corniolo and the Bidente di Ridracoli, rivers in the homonymous valley, reaching the Romagna plain, finally flowing into the Adriatic Sea.

The reservoir is surrounded by broad-leaved and coniferous forests typical of the National Park and of the temperate climate, whose most important effects is to reduce siltation of the basin because of their anti-erosion function and in addition helps to improve water quality because a forest cover promotes the infiltration of rainwater as a pre-treatment step in the context of quality for drinking-water function (Uhlman et al., 2011).

Romagna Acque Società delle Fonti S.p.A. manages the reservoir and the primary use of the reservoir is to supply drinking water to 48 municipalities downstream, in the lowland area of the southeast part of Emilia-Romagna, providing alone 50% of the entire water needs. The secondary function of the dam is the production of hydroelectricity for the surrounding area and Romagna Acque’s facilities.

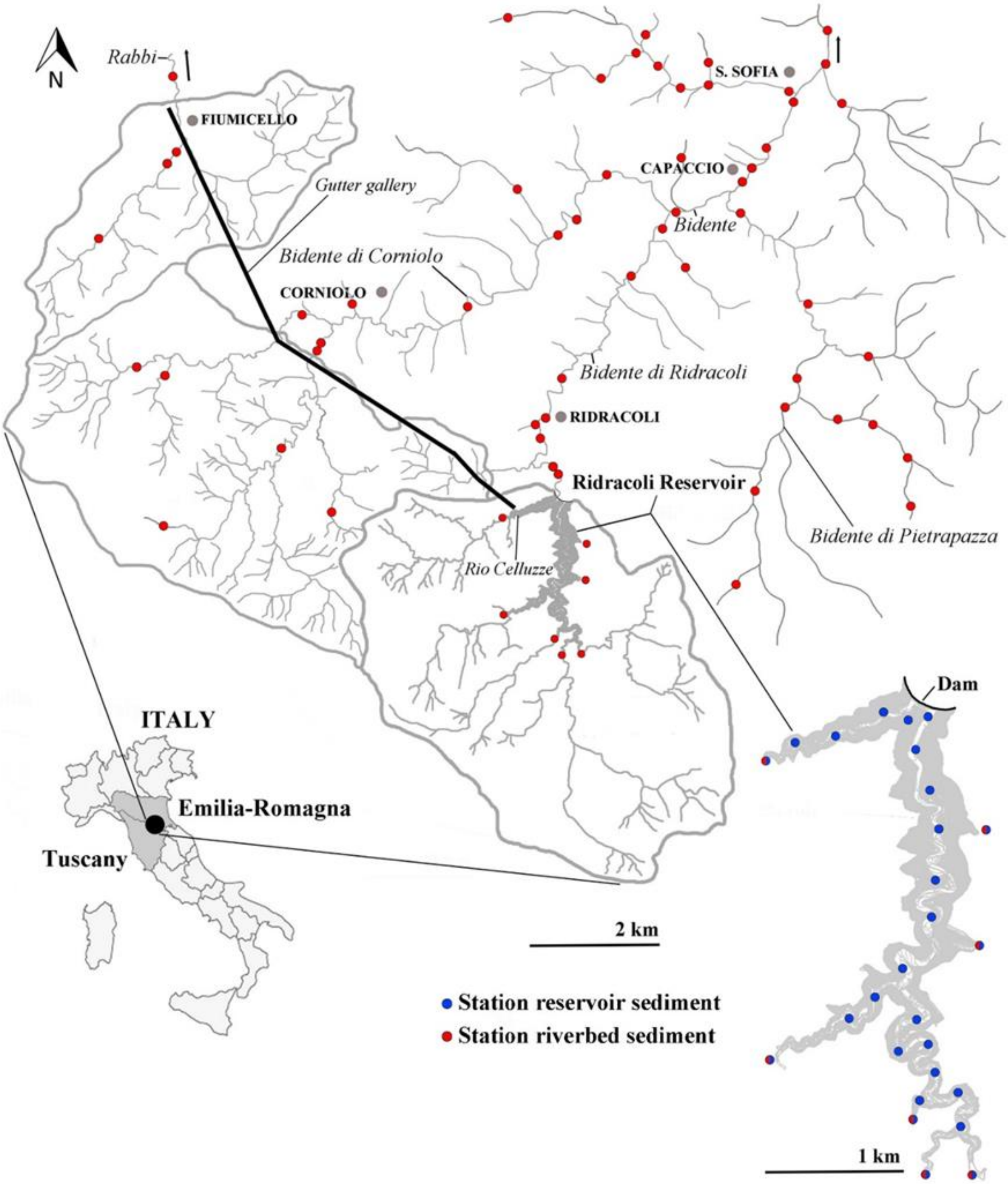

Figure 3.1, Location map of the study area, with a detail on the Ridracoli reservoir. The map includes the location of the sampling sites: stream sediment sampling stations (red circles) and reservoir sediment sampling stations (blue circles). The catchment of the reservoir is indicated, as well as the gutter gallery.

The bedrock geology of the study area includes different units from the Successione Romagnola, which is dated from 20 to 11.6 million years ago (Neogene; Miocene; Burdigalian, Langhian, and Serravallian). In the study area dominates terrains from the Marnoso Arenacea Formation (MAF), an alternation of sandstones and marls (Figure 3.2) that covers 88% of the total surface of the catchment area of the reservoir (Table 3.1). There are other minor units (for a total surface covered of 9%), referred to as the Mount Falterona Formation (FAL) and the Scaglia Toscana Formation (STO). The

MAF is a turbiditic unit deposit in the Tuscan-Umbrian portion of the Inner Periadriatic basin formed during the Miocene epoch (Ricci Lucchi, 1978; Ricci Lucchi and Valmori, 1980), elongated in an NW-SE direction in front of the growing Apennine orogenic wedge (Ricci Lucchi, 1978). In the area of Romagna Apennines, the MAF occurs as a belt which is 90x40 Km and reaches a thickness of up to 3500 m (Cornamusini et al., 2002; Martelli et al., 2005).

This Formation includes 14 members identified according to distinctive parameters as lithology (arenite/pelite (A/P) ratio), the average thickness of layers, the composition of arenites, and stratigraphic position (Benini et al., 2009, a, b) (Table 3.1). The most important member in the area is the Premilcuore member, a predominantly arenaceous unit, that occurs in 41.9 % of the catchment particularly in the upper part and in the dam area. Important for the reservoir is also the more pelitic members of Galeata and Corniolo (Figure 3.2).

Table 3.1, Formations included in the study area with the indication of thickness, age, sandstone/pelite ratio (A/P), and distribution (%) of members included in the Ridracoli reservoir catchment.

Formation	% in Ridracoli catchment	Member	Thickness of the member (m)	Age	A/P ratio
Marnoso Arenacea (MAF)	8.8	Collina	950	Langhian-Serravallian	0.2–0.33
Marnoso Arenacea (MAF)	18.7	Galeata	>400	Langhian-Serravallian	0.33–0.5
Marnoso Arenacea (MAF)	41.9	Premilcuore	150	Langhian-Serravallian	1–2
Marnoso Arenacea (MAF)	15.6	Corniolo	150-200	Langhian-Serravallian	0.33–0.5
Marnoso Arenacea (MAF)	3.0	Biserno	150-450	Langhian-Serravallian	0.2–0.33
Mount Falterona (FAL)	7.7	-	1500	Upper Oligocene-Lower Miocene	Decreases upwards
Scaglia Toscana (STO)	1.3	-	0-100	Upper Eocene-Lower Oligocene	Argillites, marly argillites, and silty marls

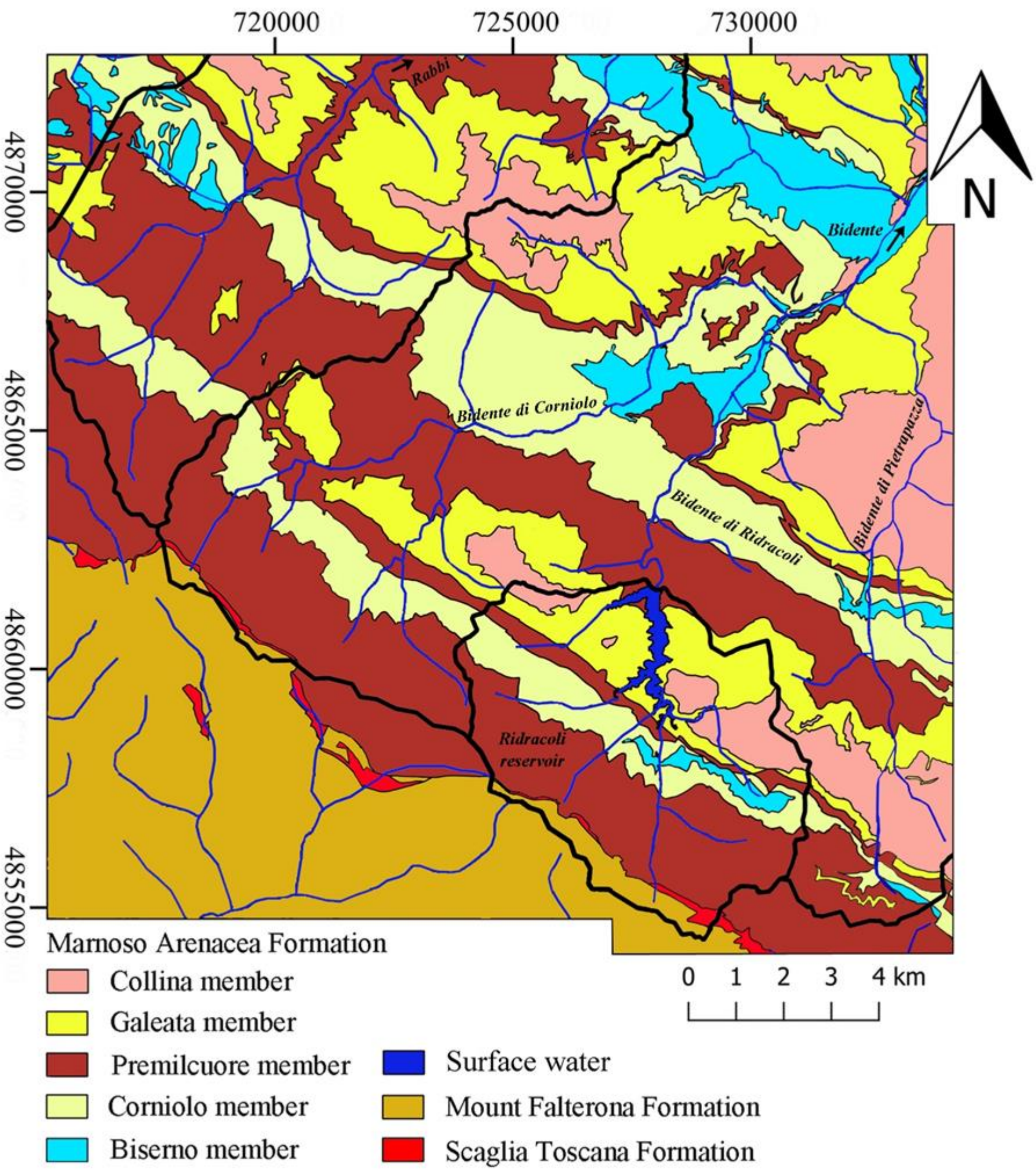

Figure 3.2, Area of study surface geology and Ridracoli reservoir, map coordinate system WGS84-UTM zone 32 N (modified data from Geoportale Regione Emilia-Romagna).

3.2.2 Analytical procedures

3.2.2.1 Sediment sampling and preparation

During the sampling campaign, carried out in Autumn 2015, samples included sediments from the bottom and tributaries of the reservoir, and from creeks and rivers outside the reservoir. Surface sediment samples, of a thickness of about 15 cm, were collected with a Van Veen Grab. Sampling included a total of 27 stations within the reservoir: 7 at the inlet of the main tributaries at a water depth of about 1 m and 20 stations were distributed within the Ridracoli reservoir's main body at water depths ranging from 71 m to 8 m. The grab was opened in a plastic box, the sediment collected with a spoon, stored in a plastic jar, and kept in a refrigerator until analysis. Stream sediments were sampled either in the tributaries, close to the inlet within the Ridracoli catchment, and in stations downstream the dam and from nearby catchments (Figure 3.1, red dots). The stream sediments were collected with a spoon, sieved directly in the field, and the fraction < 180 µm retained for analysis. The filtered slurry was stored in PET bottles, allow to settle, and prepared for analysis.

For the geochemical characterization, an aliquot of the reservoir bottom and the stream sediments sample was oven-dried at 60 °C for 48 h, followed by homogenization and milling in an agate mortar. To implement the database, additional stream sediment stations, studied by Lancianese and Dinelli (2016), were considered, comparable for sampling and analytical techniques applied.

3.2.2.2 Analytical procedures

The analyses of major (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5; expressed as their oxides) and trace (As, Ba, Ce, Co, Cr, Cu, La, Nb, Ni, Pb, Rb, S, Sr, Th, V, Y, Zn, Zr) element concentrations were performed using X-ray fluorescence (XRF) spectrometry at the XRF laboratory of BiGeA Department, Bologna, using a Panalytical Axios 4000 wavelength dispersive equipped with a Rh tube. The analysis was performed on pressed powder pellets. The reproducibility of the major elements was generally better than 5%, while it was better than 10% on average for trace elements. The absolute accuracy of the certified values of International Reference Material was generally within the reproducibility range (details can be found in Lancianese and Dinelli, 2015). The Loss On Ignition (LOI), was gravimetrically estimated after 12h heating at 950 °C in a muffle furnace (Heiri et al., 2001). The results depend on the contribution of humidity, organic matter, water present in the lattice of clay minerals, and carbon dioxide in carbonate. Analysis with a CHNS-O Analyzer in Ravenna, a Thermo Fischer FLASH 2000 Organic Elemental Analyzer CHNS-O, was conducted to evaluate concentrations of Carbon, Hydrogen, and Nitrogen in sediments, according to the standard method ISO 10694. The process of Dynamic Flash Combustion works oxidizing the sample forming the analysed components (CO_2, NO_2, H_2O, SO_2). For the granulometric analysis, only on the samples of the reservoir, a sediment aliquot of each sample was pre-treated by sieving at 63 µm, sonication for 20 minutes before analysis, carried out thanks to the addition of a sodium hexametaphosphate $(NaPO_3)_6$ (Calgon) in solution. For the analyses we used a Micromeritics SediGraph 5100 at Ravenna Campus for Environmental Sciences to collect the grain size and derive the percentages of clay, silt, and sand in the sample sediments, exploiting the X-ray sedimentation technique.

3.2.2.3 Elaboration

Data collection and elaborations were done using Microsoft Excel software, GCDkit 5.0 in R 3.4.3 (Janoušek et al., 2006), R studio and Past4.0 (Hammer et al., 2001) suites, whereas QGIS 3.12 Bucarest was used for map production and spatial analysis.

Descriptive statistical data analysis (mean, median, minimum, maximum, and standard deviation) was used to summarize the variability of data among the investigated sites for the total database and subgroups of samples. In order to obtain a better indication of the geochemistry of sediments and eventually discuss the presence of trace metals at contaminant levels, several tools are proposed and discussed. Multivariate statistical approaches performed were a principal component analysis (PCA) and a cluster analysis on all the variables considered and on the area of study, in sequence to identify a group of variables that are correlated and to enable the interpretation of geochemical data (Reimann et al., 2008; Templ et al., 2008).

A multivariate PCA was performed to summarize and visualize information on the dataset of the Ridracoli reservoir. The purpose was to identify the hidden pattern and the correlated variables within the sediment. The dataset has been analysed on all the available data of 27 sample stations of the catchment including the total composition of inorganics, organic matter, and grain size, to identify differences and behaviors of elements in the reservoir area (Reinmann et al., 2008). PCA was executed considering results only with eigenvalue higher than 1, following the Kaiser Criterion.

According to the chemical composition, cluster analysis is used to explore the similarities between sites. To classify sampling stations, we used a Past 4.0 multivariate clustering analysis practicing Ward's algorithms. The dendrogram given by this method is based on the complete geochemical database of the total composition of samples by XRF and was handled to assess the grouping of elements. The organization of scenarios by classes of similarity, the hierarchical agglomerative clustering based on the Ward algorithm (Ward, 1963), was used as the more representative of the dataset. The Ward formulation ensures that the overall heterogeneity is minimized at every clustering interaction and that the separation between the different classes defined by clustering analysis is maximized.

3.3 Results and Discussion

3.3.1 Ridracoli catchment and reservoir

Ridracoli catchment is the direct basin of 36.9 km^2 area where the Ridracoli reservoir is located (Figure 3.1). In this paragraph will be presented and discussed the results concerning the texture and geochemical features of the reservoir.

3.3.1.1 Grain size within the reservoir

A summary of the results is presented in Table 3.2 along with granulometric analysis for the Ridracoli reservoir and catchment. The single sample results are described using the Shepard's classification scheme (Shepard, 1954) by red triangles for the bottom sediments of the reservoir and black circles for the tributary ones (Figure 3.3a). The majority are classified as clayey-silt, whereas those along the inlets range from silty-sand to sand. The spatial distribution of grain size for each sampling station is reported as pie charts (Figure 3.3b) and suggests that a prevalence of silts characterizes the Ridracoli reservoir's main branch, reaching percentages > 70% in the uppermost part. The North-West branch of the reservoir ("Rio Celluzze", Figure 3.1) is prevalently sandy probably for morphological (steeper slopes compared to the N-S trending branch of the reservoir, shorter extension) and geological features (relative importance of sand-rich members). As a fact, the member of Premilcuore (Figure 3.2, Table 3.1), the bedrock of the "Rio Celluzze" branch is predominantly sandy (Arenite/Pelite ratio ranging 1-2), whereas the member of Galeata (characterizing the upstream catchment) has a lower ratio of 0.33-0.5, indicating the finer grain size for the latter (Magalhaes and Tinterri, 2010). The short distance from the dam and the combination of morphology and geological feature could not favor the deposition of fine-grained material. Besides, the presence of the mouth of the gutter gallery might contribute to sediment resuspension, leaving the coarse-grained fraction in place. The sample taken from the sampling station on the intersection between the two main branches of the reservoir is dominated by sand, this is probably due to its particular position: during the construction of the dam a steep slope was created in front of the dam for safety and operational purposes, and at present, this site receives only limited amount of sediments.

The distribution of grain size can be justified by the high energy deposition system that can be found in the peripheral sampling stations, Figure 3.1 and Figure 3.3b, based on the reservoir morphology, that let only the coarse matrix to deposit and favor transport in the main body of the reservoir of the finer fraction, producing a sorting effect downstream towards the dam (Uhlman et al., 2011).

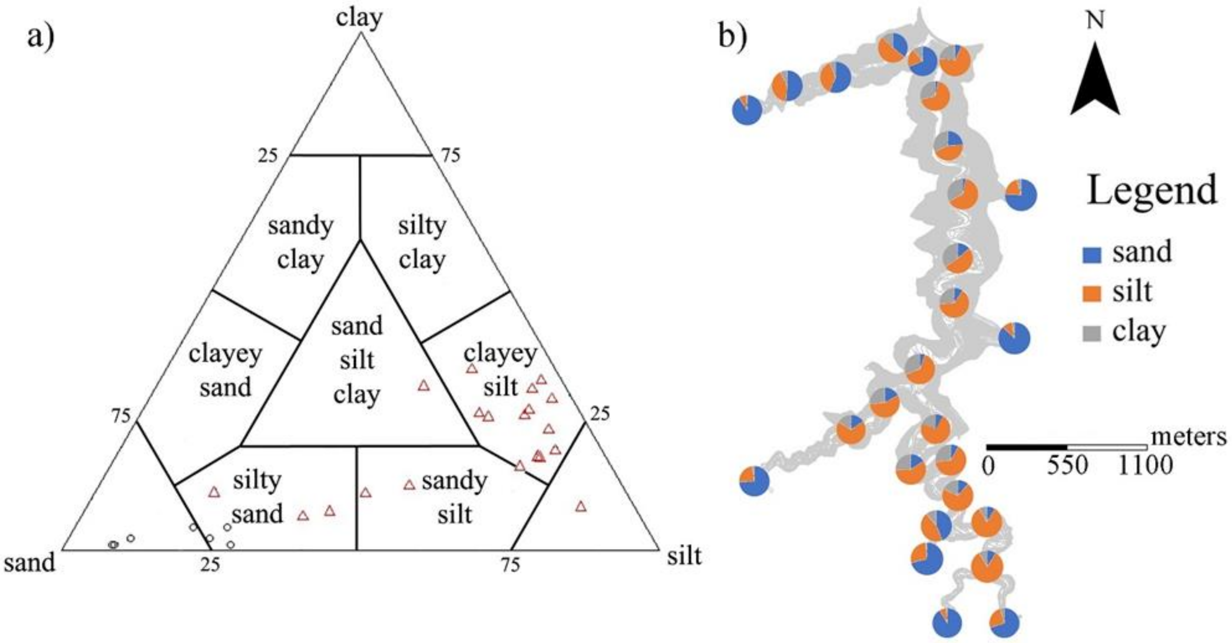

Figure 3.3, a) Shepards's classification diagram, red triangles for the bottom sediments of the reservoir and by black circles for the tributary ones, and b) grain size distribution within the reservoir area, pie charts with relative sand (blue, 0.06-2 mm), silt (orange, 0.002-0.06 mm) and clay (grey, <0.002 mm).

3.3.1.2 Major and trace abundances in sediments of the study area

Descriptive statistics as median (Med), mean (M), standard deviation (SD), and minimum and maximum (min and max) were used to summarize the variability of the dataset for the study area (Table 3.2). To better understand the variability of the complete dataset in its entirety but grasping the different nuances is useful to divide the data population into samples upstream the dam (Ridracoli catchment, n = 27) and downstream or surroundings (External areas, n = 57). A further division was then also made within the area of the Ridracoli catchment between samples taken from the areal surface of the reservoir (Reservoir, n = 20) and those recovered at the major inlets (Tributaries, n = 7). The choice of grouping the total dataset in sub-datasets was made considering the variability of the data, their different environments and geological substrate, and the data coming from the grain size.

Table 3.2, descriptive statistics of the sediment chemical composition

	Ridracoli catchment (n=27)					**Reservoir (n=20)**					**Tributaries (n=7)**					**External areas (n=57)**				
wt%	**Min**	**Med**	**M**	**SD**	**Max**	**Min**	**Med**	**M**	**SD**	**Max**	**Min**	**Med**	**M**	**SD**	**Max**	**Min**	**Med**	**M**	**SD**	**Max**
SiO_2	38.9	46.0	45.5	3.2	51.5	39.6	45.1	45.2	2.6	49.7	38.9	48.1	46.4	4.6	51.5	19.4	35.6	35.8	8.5	58.1
TiO_2	0.35	0.64	0.62	0.08	0.70	0.59	0.66	0.66	0.03	0.70	0.35	0.53	0.52	0.08	0.59	0.32	0.45	0.46	0.07	0.61
Al_2O_3	8.6	13.0	12.8	1.4	15.2	12.0	13.3	13.3	0.8	15.2	8.6	11.7	11.4	1.7	13.3	7.2	9.5	9.7	1.6	14.2
Fe_2O_3	3.8	5.9	5.7	0.7	6.5	5.3	6.0	6.0	0.4	6.5	3.8	5.0	4.9	0.8	6.0	2.9	4.0	4.1	0.8	5.8
MnO	0.07	0.09	0.10	0.01	0.12	0.07	0.10	0.10	0.01	0.12	0.08	0.08	0.09	0.01	0.12	0.07	0.11	0.11	0.02	0.16
MgO	2.88	4.36	4.30	0.70	5.65	2.88	4.46	4.49	0.57	5.65	2.96	3.64	3.77	0.81	5.36	2.65	3.46	3.43	0.44	4.84
CaO	2.7	8.1	7.9	3.0	17.7	3.5	8.0	7.8	1.9	10.6	2.7	8.6	8.0	5.1	17.7	2.7	23.3	21.2	6.5	30.5
Na_2O	0.52	0.74	0.79	0.26	1.59	0.52	0.63	0.70	0.16	1.06	0.58	1.11	1.07	0.33	1.59	0.48	0.79	0.84	0.25	1.58
K_2O	1.72	2.56	2.49	0.28	2.88	2.30	2.61	2.59	0.16	2.88	1.72	2.18	2.19	0.33	2.61	0.92	1.68	1.70	0.30	2.54
P_2O_5	0.13	0.15	0.15	0.01	0.18	0.13	0.15	0.15	0.01	0.18	0.13	0.16	0.16	0.01	0.17	0.02	0.12	0.11	0.05	0.26
LOI	14.3	19.7	19.6	3.3	26.7	14.3	17.6	18.9	3.3	25.4	18.5	21.3	21.6	2.5	26.7	12.1	22.4	22.5	5.1	32.0
Corg	1.0	2.3	2.6	1.1	6.4	1.4	2.3	2.4	0.8	4.0	1.0	3.0	3.1	1.7	6.4	0.5	1.5	1.6	0.7	2.8
N	0.0	0.3	0.4	0.2	0.9	0.2	0.4	0.5	0.2	0.9	0.0	0.2	0.2	0.1	0.3	0.0	0.1	0.1	0.1	0.3
ppm	**Min**	**Med**	**M**	**SD**	**Max**	**Min**	**Med**	**M**	**SD**	**Max**	**Min**	**Med**	**M**	**SD**	**Max**	**Min**	**Med**	**M**	**SD**	**Max**
As	5	6.1	6.1	0.7	8	5	6.3	6.3	0.7	8	5	5.8	5.7	0.5	6.	< 3	4.0	4.8	3.1	15
Ba	245	327	328	39	397	281	332	339	32	397	245	297	294	40	363	231	306	318	53	449
Ce	35	57.8	57.5	8.4	70	48	59.2	59.9	6.9	70	35	51.8	50.6	9.1	63	21	43.0	42.5	9.5	65
Co	8	17.1	16.4	2.8	20	13	17.6	17.4	1.8	20	8	14.2	13.6	3.5	17	2	8.5	8.4	3.0	18
Cr	64	145	138	23	182	118	148	147	13	182	64	120	111	23	129	63	93	94	18	175
Cu	18	34.9	33.1	5.1	41	27	35.7	34.7	3.4	41	18	27.9	28.5	6.5	36	14	26.0	27.2	6.8	44
La	14	31.1	30.2	6.7	43	22	32.1	32.0	5.9	43	14	27.3	25.0	6.2	31	2	22.0	21.0	6.7	35
Nb	8	12.3	12.1	1.8	15	11	13.3	12.9	1.4	15	8	10.5	10.0	1.3	11	4	7.0	7.3	1.7	12
Ni	38	78	74	12	87	62	80	78	7	87	38	60	60	12	72	31	62	61	12	113
Pb	15	20.2	20.0	1.8	23	17	20.2	20.2	1.5	23	15	20.5	19.1	2.5	22	2	13.0	12.1	5.8	26
Rb	66	107	104	15	121	91	113	110	9	121	66	95	88	16	107	48	77	78	13	116
S	270	560	631	241	1130	270	500	561	202	980	560	730	831	245	1130	360	800	877	364	1962
Sr	120	212	218	61	423	133	211	211	35	279	120	244	238	108	423	149	473	464	131	690
Th	< 3	5.4	5.1	2.5	9	< 3	6.2	5.8	2.3	9	< 3	2.0	3.1	2.4	6	3	9.0	18.1	17.0	73
V	46	85	86	15	107	74	95	92	11	107	46	67	67	12	85	45	69	67	9	89
Y	16	24.0	23.6	3.3	28	21	25.9	24.7	2.4	28	16	20.0	20.4	3.4	25	8	17.0	16.4	4.0	26
Zn	50	83	83	14	100	72	91	88	10	100	50	68	69	15	96	46	75	77	16	111
Zr	99	124	123	12	144	99	127	124	12	144	100	124	121	12	140	2	89	88	47	222
%	**Min**	**Med**	**M**	**SD**	**Max**	**Min**	**Med**	**M**	**SD**	**Max**	**Min**	**Med**	**M**	**SD**	**Max**					
sand	3.3	17.0	36.2	31.5	91.2	3.3	12.7	20.9	19.5	69.0	70.0	75.8	80.0	9.3	91.2					
silt	7.8	51.9	47.7	22.6	82.7	20.0	63.5	58.3	15.0	82.7	7.8	19.8	17.5	8.6	27.7					
clay	1.0	16.1	16.0	11.4	35.0	6.5	21.2	20.8	9.2	35.0	1.0	2.3	2.4	1.5	4.6					

In the reservoir SiO_2, LOI, Al_2O_3, and CaO are the most abundant component of the sediment matrices, averaging 45.5, 19.6, 12.8, and 7.9 wt.%, respectively. The relative abundance of SiO_2, Al_2O_3, and CaO are presented in the ternary diagram in Figure 3.4a to represent the clay mineral fraction along the SiO_2/Al_2O_3 side, a quartz-rich fraction on the SiO_2 vertex, and a fraction dominated by carbonatic materials (CaO vertex). In samples of the Ridracoli catchment, CaO has lower concentrations, about 7.9 wt.%, in comparison to the sediments from the inlets representing the surrounding catchments (about 21.2 wt.%, Table 3.2). Most samples plot along a carbonate-clay mixing line (dotted black line) but slightly on the Al_2O_3 side for ones from the bottom of the reservoir compared to average pelite, samples from tributaries are slightly shifted to the SiO_2 side, likely reflecting the different grain size already noticed. Samples from tributaries have a lower Al_2O_3 content and plot on the mixing line or on a clayey composition. The ternary plot in Figure 3.4b allows us to extract information about the organic matter using the ratio between LOI and CaO. Samples show a rather variable distribution and, compared to those lying at about the carbonate-clay mixing line, a LOI enhancement, which suggests a relative abundance in organic matter to the detriment of carbonate-rich phases.

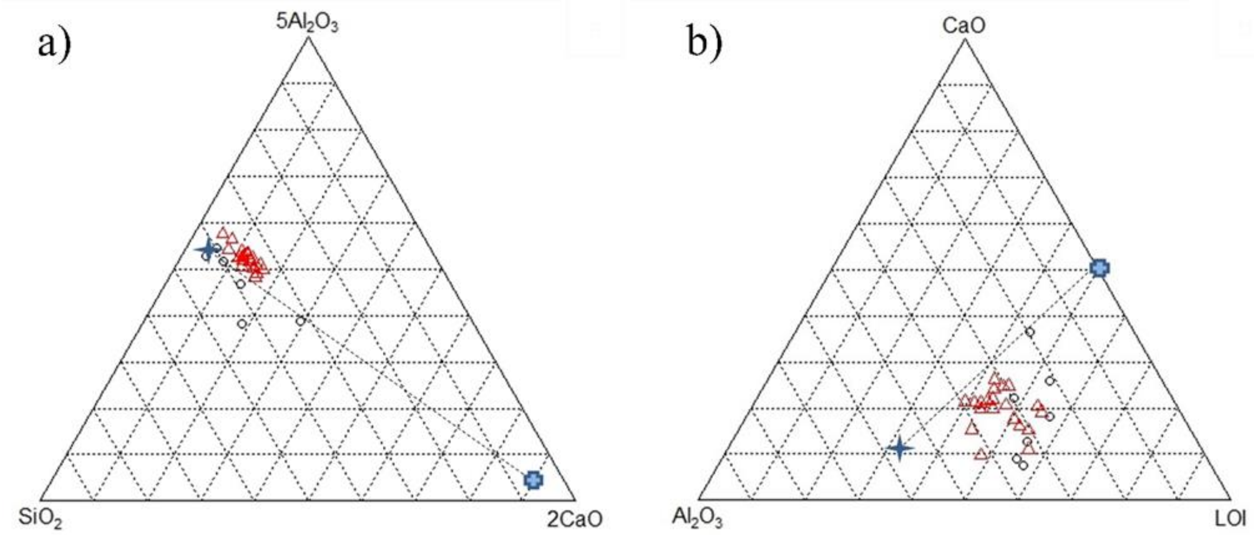

Figure 3.4, samples from the reservoir (red triangles), from tributaries (black circles), average pelite (thin blue cross), and average carbonate (big blue cross) (composition from Turekian and Wedepohl, 1961) plotted on ternary diagrams.

Another important component of the sediment is represented by Corg and N, which show a wide range of concentrations throughout the entire area. The results show concentrations of Corg from a minimum of 1 to a maximum of 6.4 wt.% with a distribution that identifies two groups: one with relatively lower concentrations of organic carbon including sediments from the bottom of the reservoir (1.4-4 wt.%; M=2.4, SD=0.8) at greater depth, and a second group of with relatively higher values (1-6.4 wt.%; M=3.1, SD=1.7) basically including the samples from the inlet areas.

Corg concentrations show a median of 2.3 wt.% which is consistent with the average values found in the literature for water reservoirs (about 2%, Mulholland and Elwood, 1982; Ritchie and Hill, 1989). The highest values are attributable to the significant amount of debris from the abundant vegetation that surround the shores of the reservoir, that is immediately ringed by the forest, which acts as a direct source of organic matter. Materials that can accumulate high levels of organic carbon can be found in shallow water where there are no currents so that organic matter is easily trapped. The N-W branch of "Rio Celluzze" has higher values than the S-E one, and the trend decreases towards the dam in both cases. Organic carbon originates from the complex mixture of lipids, carbohydrates, proteins, and other organic matter components produced mostly by plants present nearby the reservoir since, for this site, it can be supposed the unlikely presence of external sources of organic matter. The importance of organic matter, once deposited, is that once buried undergoes degradation, either aerobic and anaerobic with possible effects on water chemistry.

In general, organic matter sources can be classified into autochthonous, such as plankton and bacterial production, and terrestrial load, including soil organic matter or material from terrestrial plant input. These sources could be distinguished for example by C:N ratio (Park et al., 2009; Nazneen and Raju, 2017). In this study, the ratios between tributaries and external areas are 15.5 and 16, respectively, typical of terrestrial sources, and the ratio of samples from the reservoir is 4.8, indicated for an autochthonous provenance and index of bacterial activity.

The major elements, Fe_2O_3 and MnO, were of interest in a previous study in this reservoir (Toller et al., 2020). In sediments, Fe_2O_3 averages 5.7 wt.% in the reservoir catchment increasing up to 6.0 wt.% at the bottom of the reservoir. Overall, those concentrations are higher than continental crust average (5.04 wt.%, Rudnick and Gao, 2014), and iron content in MAF (from 3.4 to 4.3 wt.%, Lancianese and Dinelli, 2016) and riverbed sediment of surrounding catchments (4.1 wt.%, Table 2). The MnO content in sediments shows low values, ranging about 0.1 wt.%, similar to literature (Lancianese and Dinelli, 2016).

As regards other analytes, some elements are transported by rivers and trapped at the bottom of the water body because of the absence of natural transport outwards, that is typical of a reservoir system, PHEs have similar behaviour to chemical compounds to which they bound (Zahra et al., 2014) and, in general, their distribution shows a higher concentration in sediments from the bottom of the reservoir than ones from tributaries. Different concentrations of metals can be seen between coarser sediment and finer sediments, which promote adsorption processes (Audry et al., 2004).

Trace element distribution highlights different concentrations between samples from peripheral areas and the main body of the reservoir as well as enrichment for some components and depletion for others can be noted in Table 3.2. Comparing the reservoir and tributaries sediments, elements like Ba (297 to 332 ppm), Cr (120 - 148 ppm), Cu (28.5 - 35.7 ppm), Ni (60 - 80 ppm), and Rb (95 - 113 ppm) show a slight enrichment in bottom ones, while V (67 - 95 ppm) and Zn (68 - 91 ppm) show the most marked enrichment. Instead, other analytes such as S (730 - 500 ppm) and Sr (244 - 211 ppm) are more enriched in the tributary samples, with the latter element showing a moderate concentration enhancement.

Enrichments can be due to sorting in a high energy environment like the one of tributaries with respect to the main body of the reservoir that has a lower one, and therefore high energy environments allow sandy sediments to deposit earlier and fine sediments to be transported to the center. The same processes of enrichment of Cr can involve other elements, like Cu, Ni, Rb, V, Y, and Zn, which in general are linked to clays (Chen et al., 2016). The higher concentration of Cu and Zn in sediments at the bottom may be explained by the process of adsorption on clay minerals, Fe, Mn, Al hydroxides, or organic matter (Ettler et al., 2012), Cu and Zn are also usually used as indicators of pesticides or inputs from industrial activities (Lyngby and Brix, 1987), but not in this range of concentration.

3.3.1.3 Inter-element relationship in sediments using Principal Component Analysis (PCA)

To better understand the relationship between elements five principal components were extracted and reported in Table 3.3 along with relative eigenvalues, variance explained, and component loadings for the variables investigated, considering samples within the reservoir. They were selected with an eigenvalue > 1 and explain a total of 84% of variance.

Table 3.3, the top five Principal Components and relative loadings per analyte based on the geochemical dataset of sediments from the Ridracoli reservoir. Values lower than |0.20| are omitted, and higher than |0.50| are in bold.

	PC 1	**PC 2**	**PC 3**	**PC 4**	**PC 5**
SiO_2		**-0.78**	-0.37	0.22	0.33
TiO_2	**0.93**				
Al_2O_3	**0.83**	-0.43			
Fe_2O_3	**0.76**	**0.51**	-0.22		
MnO	0.45	0.23	-0.42	**0.53**	
MgO	**0.60**	-0.43	-0.22		
CaO	-0.33	**0.88**	-0.22		
Na_2O	**-0.68**	-0.43			0.47
K_2O	**0.86**	-0.37	-0.20		-0.20
P_2O_5		-0.32	0.33		-0.34
LOI	-0.37		**0.72**		-0.27
Corg	**-0.50**	0.31	0.25	**0.55**	
N	**0.52**	-0.24		-0.44	0.48
As	**0.61**	0.38		0.31	
Ba	0.24	**0.66**	-0.31	-0.29	-0.33
Ce	**0.86**			0.23	
Co	**0.91**	-0.28			
Cr	**0.95**				
Cu	**0.89**				-0.22
La	**0.73**		-0.32	0.25	
Nb	**0.91**		0.24		0.25
Ni	**0.97**				
Pb	**0.70**	-0.22	**0.59**	0.25	
Rb	**0.92**	-0.27			
S	**-0.50**		**0.62**		-0.38
Sr	-0.39	**0.87**			
Th	**0.62**	**0.55**	0.20	0.26	0.33
V	**0.92**	0.29			
Y	**0.84**	0.27	0.37		0.20
Zn	**0.86**		0.21		
Zr			**0.62**		**0.54**
sand	**-0.77**	-0.24	0.11	0.48	-0.13
silt	**0.73**	0.17	-0.01	**-0.54**	0.16
clay	**0.69**	0.32	-0.29	-0.25	0.03
Eigenvalue	16.71	5.00	3.03	1.99	1.84
% variance	49.14	14.71	8.92	5.85	5.42

PC1 explains 49.14 % of the total variance, it is characterized by high positive loadings of TiO_2, K_2O, Al_2O_3, Fe_2O_3, MgO, N, As, Ce, Co, Cr, Cu, La, Nb, Ni, Pb, Rb, Th, V, Y, Zn, silt, clay, and significant negative loadings for sand, Na_2O, Corg, S (Table 3.3). This association can be interpreted to reflect a general opposite behaviour between a fine-grained (silt and clay) fraction and a coarse-grained sandy fraction. The list of chemical elements with significant positive loadings includes major elements commonly forming clay minerals (e.g. Al_2O_3, Fe_2O_3, MgO, K_2O) and trace elements controlled by the clay mineral fraction (Singh et al., 1999; Dinelli et al., 2007; Chen et al., 2016). These trace elements, mainly credited by PHEs, are controlled via substitution or surface adsorption by grain size (Filipek and Owen, 1979), as can be seen in Table 3.3 for Cu, Co, Cr, Ni, As, Pb, Zn. For Fe_2O_3 and related, the iron oxides usually can control the behavior of other elements as Cu, Pb, Zn, and many trace elements bound to it with co-precipitation processes (Verplanck et al., 2004). Fe_2O_3 and MnO furthermore, are of concern in this site and both have positive values but one higher (+0.76) and one lower (+0.45). This behaviour is due to processes of formation and precipitation of oxides and hydroxides which differ in terms of methods and times (Krueger et al., 2020).

The negative loadings are dominated by sand, and a number of chemical elements, that actually could be explained by a combination of contribution: the first, represented by Na_2O likely controlled by the abundance of plagioclase, common in sandy fractions of the sandstone beds of bedrock geology (Gandolfi et al., 1983); the second referable to a contribution of organic matter which provenance is directly from the surrounding environment.

The spatial distribution of the factor scores (Figure 3.5a) indicates the tributaries as those controlled by the sand/organic matter rich contribution, whereas positive factor scores are generally observed along the major branch of the reservoir. This distribution pattern of positive and negative values can be related to the one of grain size (Figure 3.3b), indicating that the first principal component is mainly controlled by this component.

PC2 accounts for 14.71 % of the total variance and includes among the parameters with positive loadings CaO, Fe_2O_3, Sr, Ba, and Th, whereas among the negative ones SiO_2 shows the only significant loading, although other elements such as Al_2O_3, Na_2O, K_2O, and MgO display important negative loadings, close to the $|0.50|$ threshold. The positive loadings can be associated generally with the influence of carbonate minerals, particularly abundant in the lower members of the MAF (Lancianese and Dinelli, 2016) that characterize the southern portion of the reservoir catchment (Figure 3.5b). The linking of Fe_2O_3 with this group could suggest some kind of reprecipitation of siderite in the bottom sediment (Sapota et al., 2006; Jiang and Tosca, 2019) or present as clastic contribution considering that siderite is reported as the cement in sandstones of the MAF (Fontana et al., 1986). The group of elements CaO, Sr, Ba, and Fe_2O_3 which can be related to the carbonate and terrigenous behavior, depends on the source as sandstone and pelites from the MAF, which usually provides calcium for carbonates (Lancianese and Dinelli, 2016). CaO in this area is likely present in calcite and not in silicate minerals (e.g., plagioclase), because of the poor correlation between CaO-Na_2O, CaO-Al_2O_3. A second and minor factor in this component could be represented by Corg, As, V and MnO, although with lower loadings group elements that can be controlled by the presence of organic matter within the sediment.

PC3 explains 8.92% of the total variance. It shows positive loadings for LOI, Pb, S, and Zr, and lower for Corg, P_2O_5, Nb, Th, Y, and Zn. Negatives loadings, but to a less extent lower than |0.50|, were indicated for the remaining major elements, Ba and La. PC3 seems to be representative of organic matter and shows a positive correlation with the volatile component (LOI), S, Corg, P_2O_5. LOI values do not include only the organic carbon, but also water in clay minerals or hydroxides and CO_2 from carbonates (Heiri et al., 2001), the distribution of factors follows the concentration behaviour of Corg, but the stronger loading value for this principal component (+0.72, LOI; +0.25, Corg) may induce to consider with a certain weight also the others components. Also, the occurrence of P_2O_5 in this component can be likely explained by its association with organic matter, as observed elsewhere (Randall et al., 2019). The occurrence of positive factor scores indicates sites along the main branch of the reservoir (Figure 3.5c) mostly in the deeper stations. A second group of elements with positive loadings includes Pb, Zr, and with lower values Nb, Th, and Y, which are usually low-mobility elements, often associated with heavy minerals that contribute to the positive signal observed.

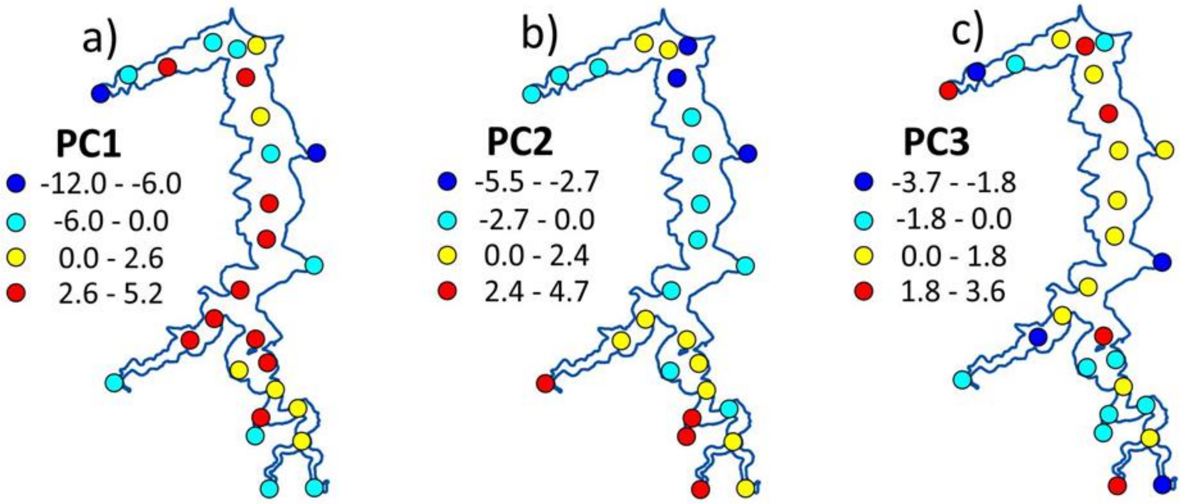

Figure 3.5, factor's maps of every station for the first three principal components, **a)** PC1, **b)** PC2, and **c)** PC3. The positive and negative values are respectively shown in red and yellow and dark and light blue.

The second principal component that takes into account the organic matter, but in a different way, is PC4 (accounting for 5.85% of total variance) which shows positive contributions of Corg, MnO, and the sand grain size. This fourth principal component takes into account the behavior of manganese cycling related to anaerobic degradation of organic matter, which also affects the behaviour of As, Ce, La, Pb, and Th into the sediment.

PC1, PC2, and PC3 show an important controlling factor for metals in sediments given by the grain size (Li et al., 2007) and, in particular, finer particles can control the destiny of PHEs likely stored via sorption (Krishna and Mohan, 2013). Particle size plays a significant role in the accumulation of PHEs, therefore it needs to be carefully considered (Arnason and Fletcher, 2003). Any variation of environmental parameters, like pH or redox potential, can be of concern and can involve metal release into the water-phase. Manganese usually has similar chemical behavior to iron (Young and Harvey, 1992), to which it is usually correlated, but not in PC4, they are both controlled mainly by the redox state (Herndon et al., 2018).

PC5 shows positive loadings for Zr, N, Na_2O, SiO_2, Nb, Th, and Y, and slight negative loadings for K_2O, P_2O_5, LOI, Ba, Cu, and S. SiO_2, Nb, and Zr are typically considered non-reactive because of their low solubility, as already seen in PC3. A further element correlated positively is Na_2O, which is usually associated in sedimentary rocks with detrital minerals, feldspars, or clay minerals, as seen in PC1, sodium can be adsorbed in clays because of cation exchange capacity.

3.3.2 Cluster Analysis results

In this section, we compare the data of the reservoir with those referring to nearby catchments (Corniolo, Pietrapazza, and Bidente, Figure 3.1), a population of 57 sediment samples on a larger area. The comparison was made using a cluster analysis approach and the results of the analysis divide into four main clusters (A, B, C, D) related to chemical behaviour and location of the sampling stations, clearly seen in Figure 3.6.

The first cluster (A, white) is the smallest identified from cluster analysis. The stations are located in the northern part of the study area, on the main branch of the Bidente river. Two further stations are located just downstream of the dam (Figure 3.6). Group A is characterized by relatively high CaO and low SiO_2 and Al_2O_3 as more abundant major elements composition. Compared to the other clusters, this is characterized by intermediate values (Figure 3.7) except for the high S and Sr and low Ni and Rb.

The second cluster (B, violet in Figure 3.6) includes samples from three different sources: tributaries of the Ridracoli reservoir, in general the peripheral stations of the water body; four samples from the Bidente di Corniolo area near its confluence with the Bidente di Ridracoli and two scattered samples along the Bidente river at the closing part of the study area. The second group B displays an aluminum silicate composition with high concentrations SiO_2, Al_2O_3, and other elements generally related to a clay mineral fraction (e.g. Fe_2O_3, Co, Cr, Nb, Pb) and also S, whereas the CaO content is intermediate to low (Figure 3.7).

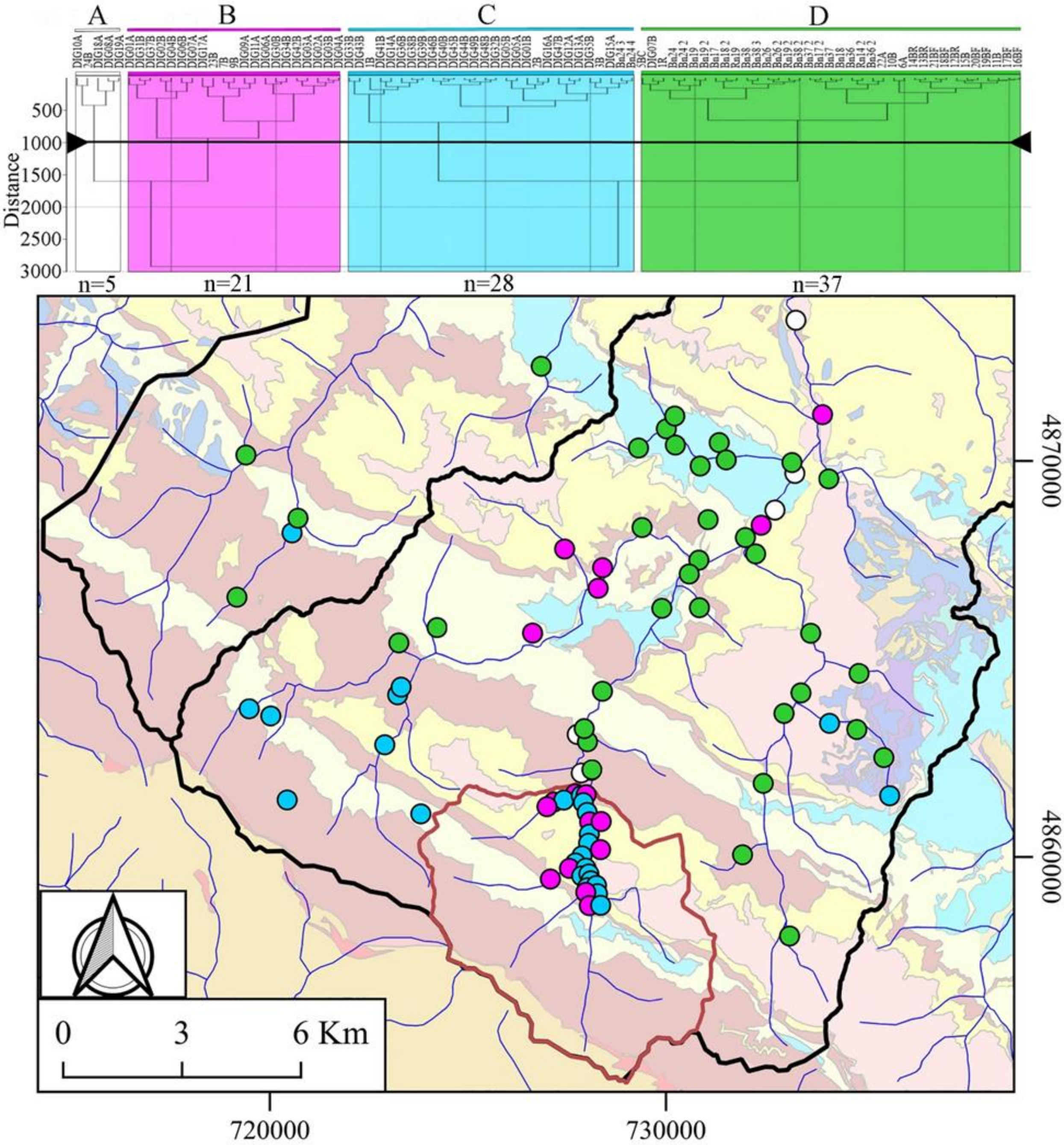

Figure 3.6, sample stations of the area of study grouped by colors (A, white; B, violet; C, blue; D, green) according to the results of cluster analysis. Background is the simplified geology of Figure 3.2.

The third cluster (C, blue) includes samples from the bottom of the Ridracoli reservoir and of riverbed sediments taken from the most upstream part of the nearby catchments (Figure 3.6). Group C shows features in common with group B, a main composition of SiO_2- Al_2O_3, with high TiO_2, Fe_2O_3, and MgO; similar Na_2O, K_2O, P_2O_5 values, and presents the lowest volatile component (LOI). This group has the highest values for many trace elements, as Co, Cr, La, Nb, Ni, Rb, V, Zn, and Zr and the lowest for S and Sr (Figure 3.7). It has to be noted that boxplots of group C (blue) have the largest range between minimum and maximum for a lot of analytes taken into account, which makes this group less defined.

The fourth cluster (D, green) is the largest one by the number of samples and covered area (Figure 3.6), it is characterized by the highest values of CaO and lowest of SiO_2, TiO_2, Fe_2O_3, MgO, K_2O, P_2O_5. Trace elements have lower values of As, Ba, Co, Cr, Nb, Pb, Y, and Zr and high of Sr and Th (Figure 3.7). The sampling stations belonging to this group do not directly have a relation with the reservoir and its western external contribution (Figure 3.6). They include samples downstream of the dam and from the confining catchment to the East.

It is interesting to note the fact that samples from the reservoir catchments are included in two clusters (B and C), both including also stream sediment samples, likely showing relation with bedrock geology. In particular cluster C, which grouped the largest number of bottom reservoir sediments, also included many stream sediment samples, on the western catchments, draining similar bedrock (Premilcuore, Galeata, and Corniolo members of MAF, Figure 3.2 and Table 3.1). Cluster B, in the reservoir grouping mostly sediment from the tributaries, also includes some stream sediments draining the Corniolo and Galeata members of the MAF.

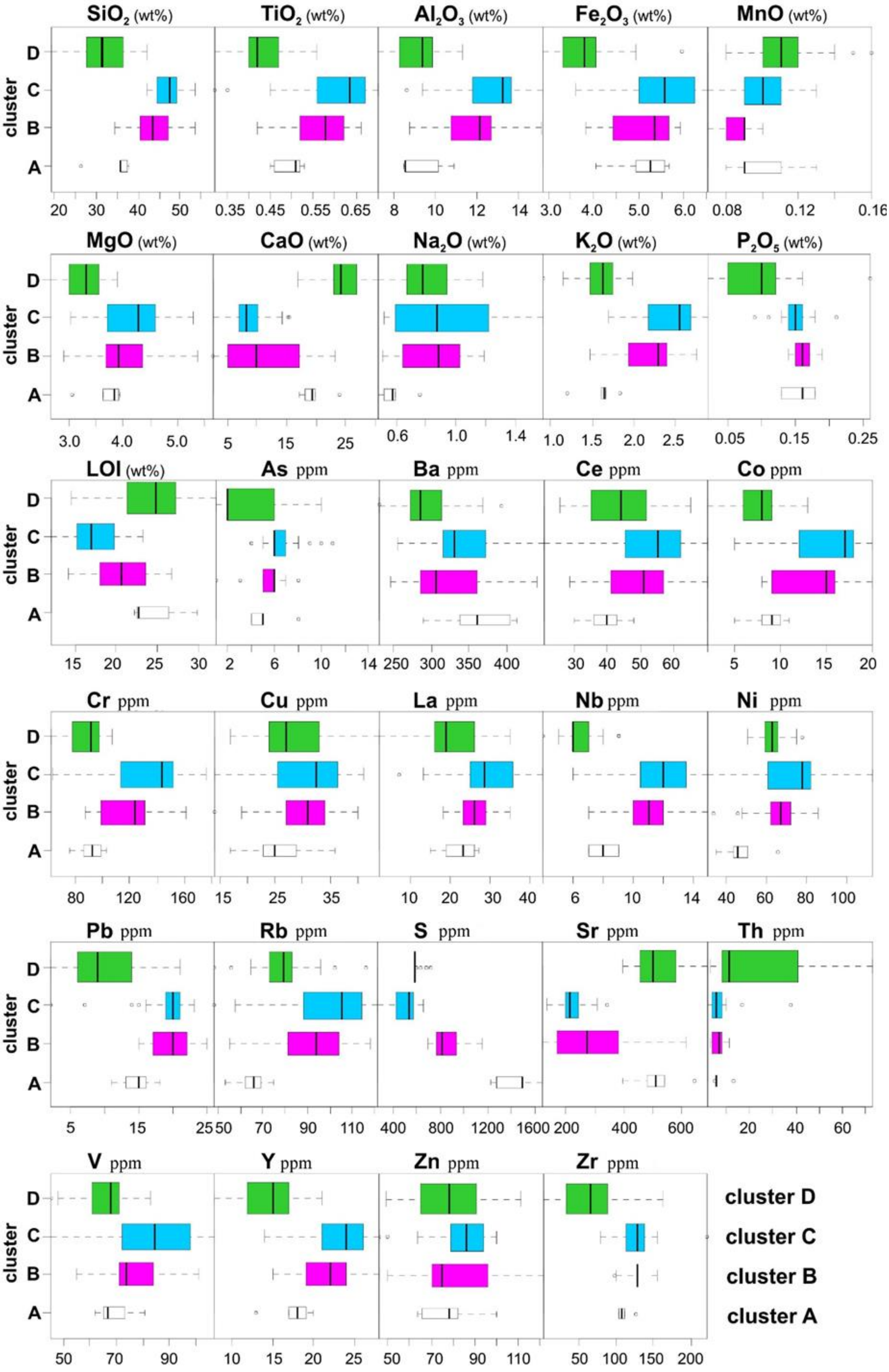

Figure 3.7, boxplots of elements according to the four groups identified from cluster analysis.

3.3.3 River branches chemistry and evolution of PHEs

To stress even more if there are differences caused by the presence of the dam, we focus on the geochemical evolution of three of the river branches of the Bidente river in its upland sector, Bidente di Corniolo, Bidente di Ridracoli, and Bidente di Pietrapazza (Figure 3.1). Each branch is part of three different mountainous sub-catchments that join to form the Bidente river a few kilometers southwest of the Village of Santa Sofia. They have similar development and length, but the bedrock geology is partially different, particularly in the Bidente di Pietrapazza where the Collina Member of the MAF is extensively outcropping (Figure 3.2). The concentration/distance profiles for selected elements are presented in Figure 3.8 and Figure 3.9, with reference to the furthest sampled site downstream comparing the three river rods almost parallel to each other.

The reported parameters (CaO, Sr, TiO_2, V, Co, Cr, Ni, and Zn) display similar concentrations in their sections, and in the case of the Bidente di Ridracoli downstream of the dam.

In agreement with cluster analysis, the downstream part of Bidente di Ridracoli (orange) seems to be affected by the presence of the barrier, showing different patterns upstream and downstream the dam, between samples from 12,500 m of distance downstream the dam and ones in the 12,500-17,000 m range. Furthermore, is possible to see a jagging pattern downstream when compared to the nearby catchments of Corniolo (grey) and Pietrapazza (blue), due to the stability of the signal provided by the concentrations in sediments which for the other two rods are in equilibrium and for the Bidente di Ridracoli one is more inconstant, and will be regularized only after the confluences.

CaO and Sr, which represent the terrigenous signal, show similar patterns for Corniolo and Pietrapazza and a more unstable for Ridracoli. They show similar patterns and constantly increase downstream, but both show strong differences upstream and downstream of the dam because of the lithology.

Elements as TiO_2 and V, which are usually tied to sediment transport but less reactive, show a swinging trend for the Ridracoli (orange) river rod likely due to the dam influence on the river regime while this trend is more stable for Corniolo (grey) and Pietrapazza (blue) rods. However, both TiO_2 and V display high concentrations within the reservoir, reflecting the enrichment in fine-grained sediment fraction.

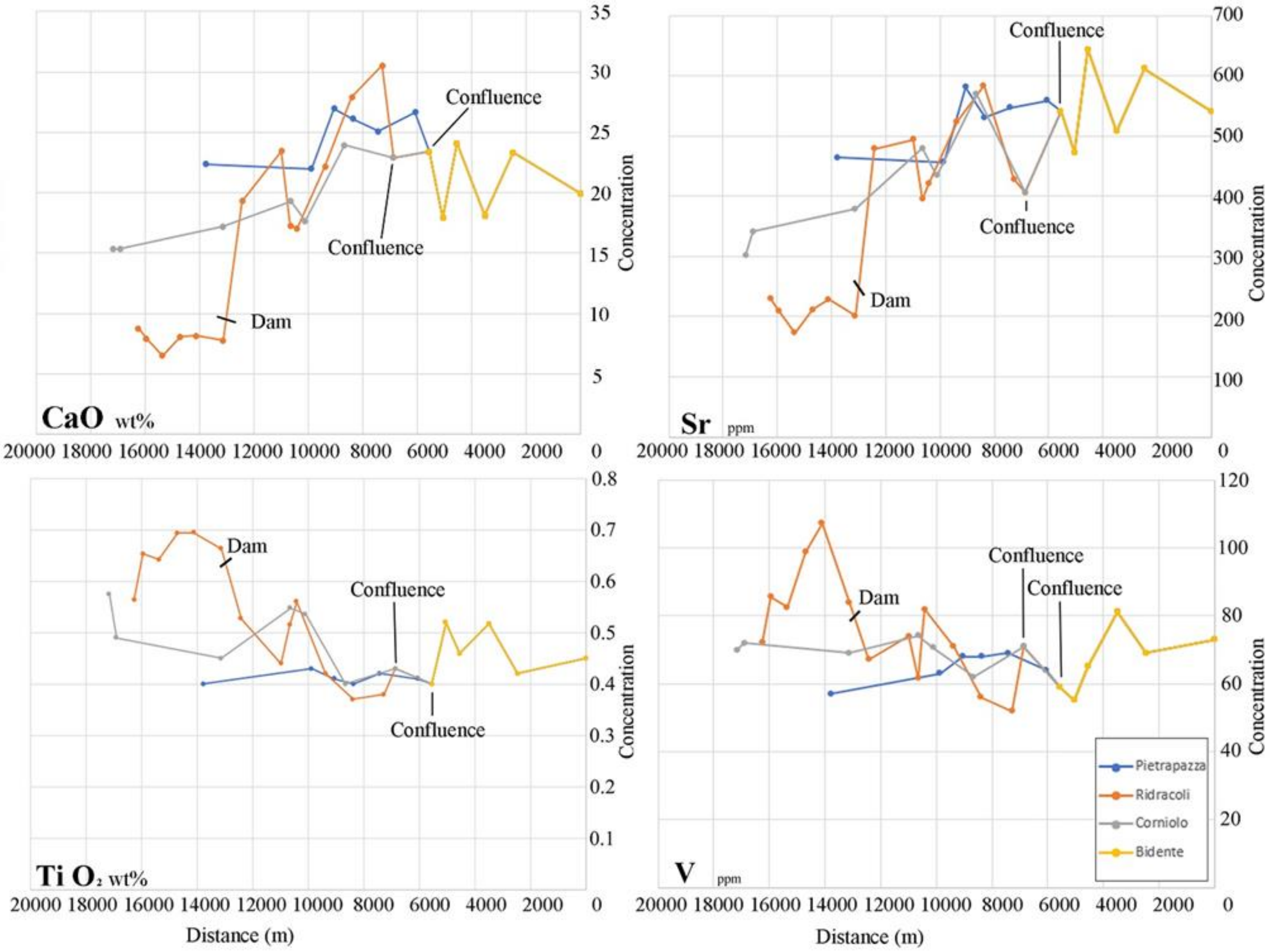

Figure 3.8, Concentration in sediments of CaO, Sr, Ti2O, and V, along Bidente di Pietrapazza (blue), Bidente di Ridracoli (orange), Bidente di Corniolo (grey) and in the final part of Bidente river (yellow).

Four more analytes have been selected to represent the trends of some PHEs in the considered branches (Figure 3.9). Co, Cr, Ni, and Zn show similar patterns for Corniolo and Pietrapazza and one more inconstant for Ridracoli, as already stated. Based on the trends and concentrations of the stations in the reservoir, all show differences upstream and downstream of the dam.

For TiO_2, V, Co, Cr, and Ni, it is possible to identify the effect of the dam, as it concentrates these elements mostly associated with the silt-clay fraction of the sediment. It is important to remember that the stream sediment included a fine-grained sediment fraction (< 180 µm) but clearly did not obtained a similar enrichment. It is interesting to note that the upstream sample within the reservoir is generally similar to the Bidente di Corniolo data for the similar bedrock geology, but then for the elements a convex shape appears (Figure 3.9), suggesting the enrichment. Stream sediment down-stream the dam along the Bidente di Ridracoli are quite comparable to the other branches draining the area suggesting what could be a local background for these elements.

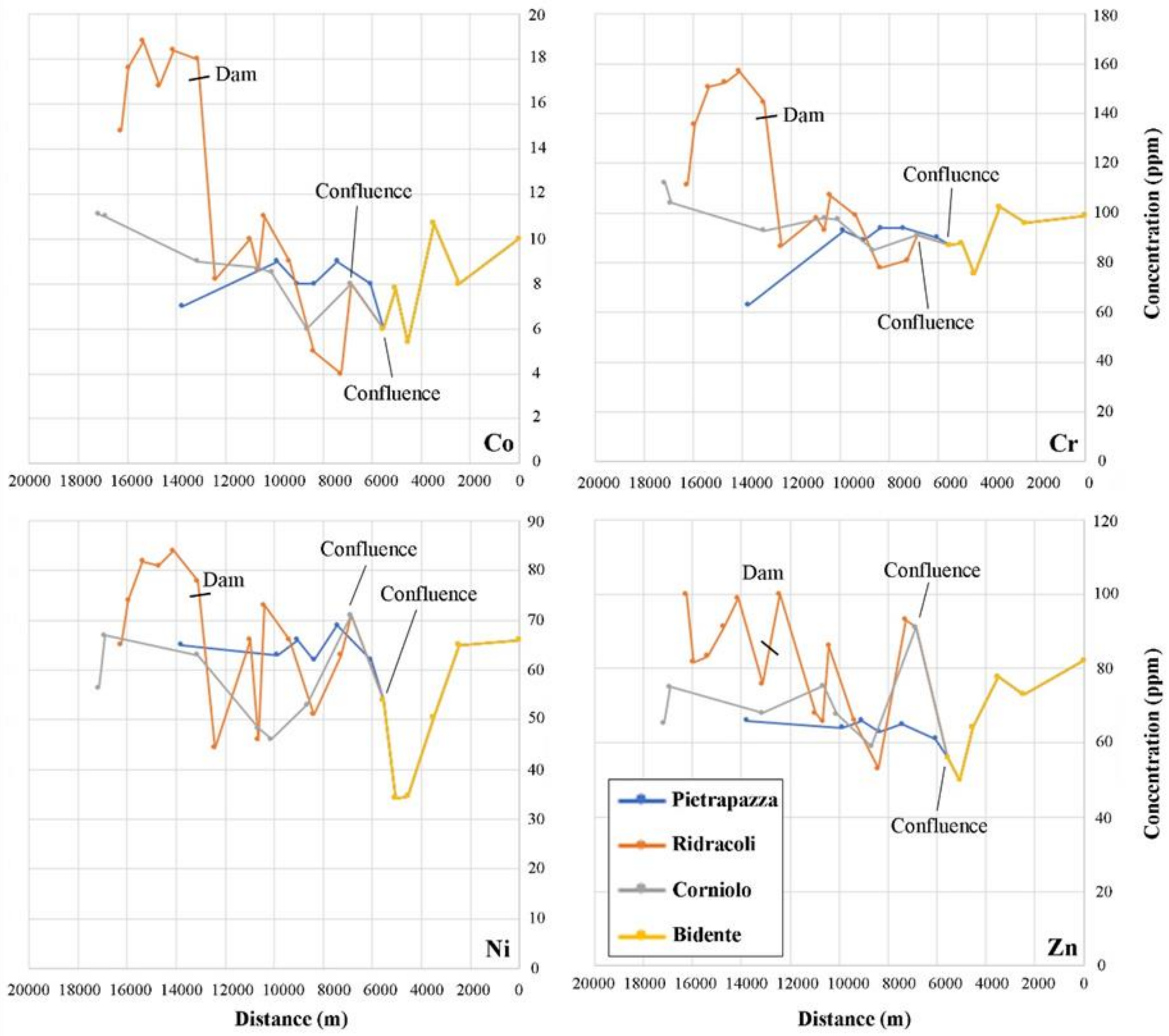

Figure 3.9, Concentration in sediments of Co, Cr, Ni, and Zn, along Bidente di Pietrapazza (blue), Bidente di Ridracoli (orange), Bidente di Corniolo (grey) and in the final part of Bidente river (yellow), in ppm.

3.4 Summary and Conclusions

In this work, we described the bulk sediment geochemistry of sediments from the Ridracoli reservoir and compared it with local stream sediments.

The sediments of the Ridracoli reservoir are mostly clayey-silt, reflecting a common sorting effect, with coarser textures in spot sites within the basin and at the inlet of the tributaries. The difference in grain size is also reflected in changes in composition which, in turn resulted from the mixture of carbonate and silicate material with abundant organic matter.

The PCA results reveal well known geochemical associations for sediments suggesting that a large number of elements are strongly linked to the clay silt fraction of the sediment (TiO_2, K_2O, Al_2O_3, Fe_2O_3, MgO, N, As, Ce, Co, Cr, Cu, La, Nb, Ni, Pb, Rb, Th, V, Y, Zn). Although the role of organic matter remains virtually undefined, the PCA suggests that As, V, MnO and Pb can be sensitive to the organic component in this area.

The comparison of the reservoir sediment with stream sediment from surrounding areas identified similarities between sediments with similar geological background, but it also identified the effect of the dam basically involving the elements listed above. They are markedly enriched in the reservoir compared to the external areas and the inlet points, suggesting the importance of sorting effects in controlling the total geochemical composition of the sediments from the reservoir and the role of the dam in trapping fine-grained sediments quantitatively.

The list above includes many PHEs, but their strong association likely suggests stability within the sediments at least from the total content perspective, being present as absorbed into or forming various clay minerals. It is necessary however to further investigate the geochemistry of this site, applying other analytical approaches to better evaluate the geochemical status of the sediments, in consideration of its strategic importance.

Acknowledgements

This paper is the product of the work done thanks to the collaboration between Romagna Acque - Società delle Fonti S.p.a. and the University of Bologna (BiGeA). The Authors wish to dedicate this paper to the memory of the late Ing. Andrea Gambi who promoted, supported and inspired the geochemical investigation in the Ridracoli reservoir, first as CEO then as General Manager of Romagna Acque - Società delle Fonti S.p.a.

This chapter consists of a paper by Toller S., Funari V., Vasumini I., and Dinelli E., submitted and accepted with revisions at the Journal of Geochemical Exploration.

Chapter 4 - Aqua regia results of surface sediments from a Large Dam reservoir. Environmental assessments on element mobility, degree of extractions, and enrichment factors.

Abstract

The impact of heavy metal pollution and elements accumulation on reservoirs is a matter of concern worldwide. In the Ridracoli reservoir on the northern Apennines in Italy, water is stored for potable purposes and its importance has increased considerably in time as a matter of maintaining its quality. In previous studies we assessed the chemical compositions of the water body and seasonal changes along the water column and characterized the sediments from Ridracoli catchment and surrounding areas. As a further step of the investigation, we explored the pseudo total contents of sediments after aqua regia digestion from 42 samples that were collected and analysed for Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Hg, 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. In general, sediments composition was found to be consistent with a mixture of carbonate and clay, in agreement with the background composition. Some exceptions were found in some samples from the tributaries, enriched in organic matter (OM), and from the external area of Ridracoli catchment, richer in carbonate and with a slightly different characterization.

The aims of this work are; I) to study relationships among elements by applying statistical methods; II) to evaluate the extractability degree concerning the total content and understand element mobility between solid and liquid phases in the reservoir; and III) to better understand the environmental relevance of some elements in the study area, comparing pseudo-total contents to values from recent scientific literature, calculating enrichment indexes (EFs) and ones provided by Italian legislation and environmental guidelines.

Keywords: Geochemistry – Sediments – Reservoir – Aqua Regia – Degree of Extraction – Enrichment factor

4.1 Introduction

Pollution of natural environments by trace elements is a dispute that can be found all over the world. Deriving from natural sources, such as weathering of soils and rocks, erosion, forest fires or volcanic eruptions, or sources as anthropogenic pollution, industrial activities, mining, agricultural uses or atmospheric deposition, trace elements, and heavy metals enter continuously and constantly in aquatic environments, arranging serious environmental issues (Yang and Rose, 2005; Ip et al., 2007; Davutluoglu et al., 2011).

In rivers, lakes, reservoirs, and wetlands the solid phase as rock surfaces and deposited sediments are of concern because of the interaction between solid and waters that may release or absorb metals. At present, the presence of potentially harmful elements (PHEs) in bottom sediments is one of the major secondary pollution issues due to the potential hazard and effects on organisms, plants, animals, and human health (Linnik and Zubenko, 2000; Armiento et al., 2011). In this group of elements, heavy metals are the main contaminants and the most persistent in the aquatic environment since their resistance to decomposition and accumulation in this kind of system (Li et al., 2015; Yang et al., 2016). Lakes, and in particular reservoirs, are a physical trap for sediments which deposit at the bottom (Ran et al., 2013; Kondolf et al., 2014) and have been recognized as an important sink for inputs of trace elements, especially heavy metals (Jernström et al., 2010). The sediments of the bottom, which act as an important deposit of metals in water bodies, are formed by the sedimentation of suspended particles from the water column and inputs from tributaries and surroundings. Sediments can be considered as the last destination of heavy metals since solid substances are trapped over time inside the reservoir and soluble forms in contact with water can precipitate, flocculate, adsorbed, agglomerated, complexed, or assimilated into organic compounds (e.g. intake by organisms), going to the bottom and settling (Salomons and Förstner, 1984). Heavy metals tend to accumulate and cannot be chemically or biologically easily eliminated except by remediation (Song et al., 2017). The dissolution of metals from sediments occurs less frequently under natural circumstances, but this effect cannot be excluded if equilibrium change and physicochemical conditions vary. Many are the parameters that regulate the metal adsorption process on sediment particles: physicochemical parameters of metals, pH, redox conditions, and mineralogical composition of the suspended material. Metals are not perpetually linked to the solid fraction when deposited, but seasonal changes of the environment can determine the re-mobilization of the accumulated PHEs. In this way, the sediment on the bottom of a lake or reservoir, which changes its characteristics over time, can be considered as a source of metal contamination. However, the mobility of the elements is linked to their chemical forms. To study the different shapes and possible associations of the metals in the sediment, and the potential mobility of elements total and pseudo total compositions (Quevauviller, 1998) can be useful to clarify which elements are more linked to the solid phase and which more to a release, as a good estimate of the bioavailable fraction of heavy metals (Borghesi et al., 2016; Frémion et al., 2017).

Especially in a reservoir which has functions of accumulation of drinking water, essential for the regional potable water network, the assessments on harmful elements are essential to understand the system and preserve it. In Chapter 3 sediments of a larger scale area on the Apennines has been characterized focusing on the geochemical total composition, grain sizes, and the relationship among elements. Here (Chapter 4), instead, we investigate more deeply the behaviour of elements inside the reservoir and critically observe the concentrations found, with the aims to I) study the relationships among elements by applying statistical methods and principal component analysis on the pseudo total composition of sediments; II) evaluate the extractability degree concerning the total content and understand element mobility between solid and liquid phases in the reservoir (Taraškevičius et al., 2012; Borghesi et al, 2016); finally III) compare the pseudo-total contents of this site to values from recent scientific literature, calculating enrichment indexes (EFs) and to ones provided by Italian legislation and environmental guidelines, to better understand the environmental relevance of some elements in the study area (Zhang and Liu, 2002; Karageorgis et al., 2009; Zhu et al., 2013; Palma et al., 2015).

4.2 Material and Methods

4.2.1 Study area description and sampling sites location

The study area is part of Casentinesi-Campigna National Park, located between Emilia-Romagna and Tuscany regions on the Northern Apennines in Italy. The Ridracoli reservoir is at 480 m a.s.l., has an irregular shape, and an area of about 1 km^2 of water surface, a depth that can reach about 80 m and it can store a maximum of 33x10^6 m^3 of water. The Ridracoli catchment, closed by the dam built in the 80s, is 37 km^2 wide and is fed besides from an indirect catchment thanks to a gutter gallery for a total drainage basin of about 87 km^2 which ensure a complete water supply. From a hydrological standpoint, the reservoir lies within a complicated network of torrents and minor tributaries filling the nearby valleys with the stored water. The reservoir is located on the mountainous area upstream one of the tributaries that feed the Bidente and Fiumi Uniti rivers which flows East until to reach the Romagna plain and the Adriatic Sea.

The primary use of the reservoir is to store drinking water for the supply of Romagna and surroundings, for a maximum of one million people during summer, and its second function is of electricity production, which allows the entire system of monitoring and water treatment at Capaccio to self-sustain. The reservoir is the most important in the area and is managed by Romagna Acque Società delle Fonti S.p.A., the sole manager of drinking water resources in Romagna, thanks to reservoirs and wells it can make the most of the water resource without waste and preserving the groundwater of Romagna plain, which exploitation has been a cause of subsidence of the area.

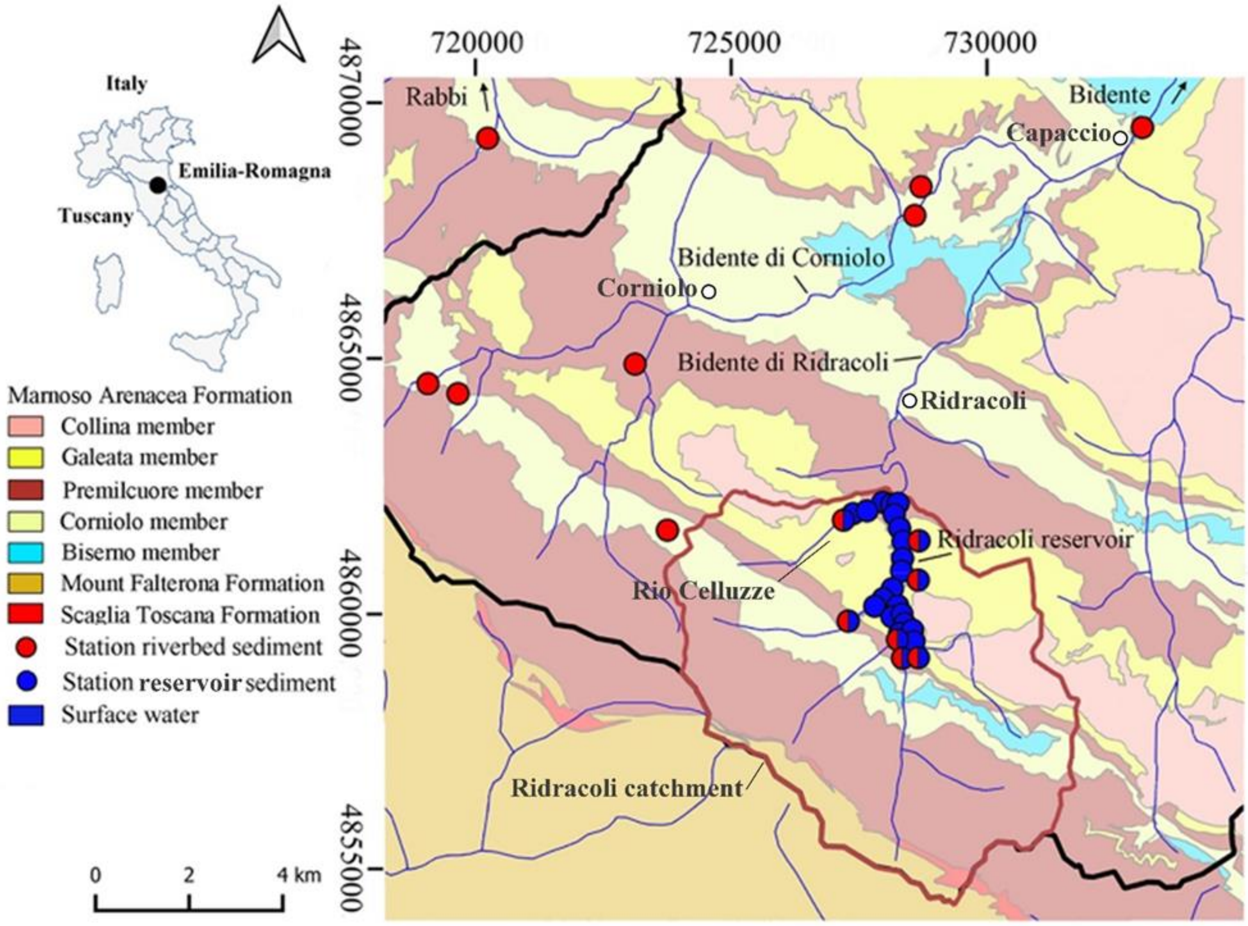

Figure 4.1, Ridracoli reservoir sampling stations (red and blue circles), topographical and river names, and simplified map of the geology of the study area (map coordinate system: WWGS84-UTM zone 32 N, modified data from Geoportale Regionale Emilia-Romagna).

The geology of the area presents units from the Successione Romagnola (Figure 4.1), dated from 20 to 11.6 million years ago (Neogene; Miocene; Burdigalian, Langhian, and Serravallian) and includes an alternation of sandstones and marl called Marnoso-arenaceous formation (MAF). This formation is a thick turbiditic unit deposited in the Tuscan-Umbrian portion of the Inner Periadriatic basin formed during the Miocene (Ricci Lucchi, 1978; Gandolfi 1983). This deposit includes 14 members that differ according to lithology criteria as arenite/pelite ratio (A/P), the average thickness of arenaceous levels, the composition of arenites, and stratigraphic position (Cornamusini, 2002). In the Ridracoli catchment area outcrop mainly Member of Premilcuore, together with Member of Galeata and member of Corniolo, and with a lower percentage Members of Collina and Biserno (41.9, 18.7, 15.6, 8.8, and 3.0% respectively). The surroundings are also part of MAF with the same 5 Members that cover the area, together with Mount Falterona Formation and Scaglia Toscana Formation.
The main characteristics of the sampling site object of study from a hydrological, geological, or managerial point of view, have been already discussed in previous works (Chapters 2 and 3).

4.2.2 Analytical procedures

4.2.2.1 Sediment sampling and preparation

The sampling campaign was carried out in 2016, were collected sediments from both tributaries and Ridracoli reservoir main water body and samples from surrounding stream sediments. Samples were taken selecting 27 sampling stations to cover the whole area of the water surface, whose ground spanned from a maximum depth of 71 m to a minimum of 1 m, collecting the upper 10 cm of sediment using a Van Veen grab. More samples were taken from tributaries (7) and streams and rivers inside the catchments and external areas (15), collected at a maximum depth of 1 m below the surface.

The primary samples were collected by a spoon, cleaned from coarse vegetable remains, stored in plastic bottles, and, finally, sealed before being analysed, for a total of 42 stations.

For granulometry and bulk composition, two rates of each sample were taken and analysed at the University of Bologna laboratories by Sedigraph and XRF respectively, and a further aliquot of the primary samples of about 15g each was oven-dried at 60 °C for 48h, followed by homogenization and milling in an agate mortar, before shipping to Vancouver laboratories for ICP-MS analysis.

The pseudo-total composition was evaluated thanks to a modified aqua regia digestion composed of a mixture of concentrated HNO_3 (16 M) and HCl (12 M) in a volume ratio of 1:3, this solution shows a dissolving power stronger than HNO_3 alone, due to the complexing power of the Cl^- combined with the catalytic effects of free Cl_2 and NOCl (Hu and Qi, 2014), each sample was made up to volume with dilute HCl before analysis.

4.2.2.2 Chemical analysis

The concentrations of 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) were determined by Inductively coupled plasma mass spectrometry (ICP-MS) at the Bureau Veritas Minerals (BVM) of AcmeLabs laboratories in Vancouver (Canada). Among all elements, Ge, Hg, Hf, In, Pd, Pt, Re, Ta, Te were not taken into account in the statistical analysis of this work because of their concentrations that were found to be below the limit of detection (D.L.) in some or all analysed samples.

Through this analysis, we obtain a pseudo-total concentration of the elements, as the aqua regia dissolves only a part of silicates, carbonates, clay minerals, and organic matter, leaving for the analysis the more stable analytes. The matter of this type of procedure lies in the type of matrix and the strength of the solvent itself, which is unable to dissolve silicates and aluminum and iron oxides to which some metals may be bound.

To evaluate the role of these sediment components including their total composition, we included in the elaboration also SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, LOI, Corg, H and N values, derived from the XRF and CHNO-S analysis for major components, already elaborated in Chaper 3.

X-ray fluorescence spectrometry (XRF) data were performed by a PANalytical, Axios spectrometer at the Department of Biological, Geological and Environmental Sciences (BiGeA), in Bologna and the volatile content, defined as total Loss On Ignition (LOI), was gravimetrically estimated after 24h heating at 950 °C in a muffle furnace (Heiri et al., 2001). This process includes the evaluation of humidity, organic matter concentration, water present in the lattice of clay minerals, and carbon dioxide in carbonate. A CHNO-S analyzer, Thermo Fischer FLASH 2000 CHNS/O, was conducted to evaluate concentrations of Carbon, Hydrogen, and Nitrogen in sediments, according to the standard method ISO 10694 at Ravenna Environmental Campus.

4.2.2.3 Elaboration

Descriptive data analysis, including arithmetic mean (M), median (MED), minimum and maximum (MIN, MAX), relative standard deviation (SD), and the number of samples (n) were used to explore the concentration of the analytes within the investigated site.

To better understand relationships among elements a multivariate statistic approach was used to perform a Principal Component Analysis (PCA) on all the considered parameters, to identify groups of variables that are correlated and to assist the interpretation of geochemical data (Filzmoser et al., 2005; Templ et al., 2008; Reimann et al., 2011). PCA was executed considering only the eigenvalues higher than 1, following the Kaiser Criterion, and giving a cumulative variance for the first 6 principal components of about 88.5%. Statistical analyses and graphs (descriptive statistics, PCA and map studies) were carried out using Past 4.0, GCDkit, and QGIS Budapest (Janoušek et al., 2006).

For those elements analysed both by ICP-MS for pseudo total composition and by XRF for total composition on different rates of the same sample, the mean degrees of extractability have been calculated. The theme of comparison between aqua regia contents and real total contents not only adds information compared to what is given by the single method, but it is also topical in international scientific research (Reimann et al., 2008).

A comparison between data of the total composition, acquired by XRF analysis, and the pseudo-total, from an aqua regia digestion and ICP-MS, shows different results of concentrations on several analytes. The disparity can be found because digestion by aqua regia does not completely mineralize the sample but affects carbonates, clay minerals, organic matter, and only partially silicate minerals present in the sample.

The degree of extraction for each sample is calculated like DE=100*[(Ci ARM)/(Ci RTM)] where Ci ARM is the aqua regia value and Ci RTM is the real total concentration of the same analyte i. To better show differences between the two concentrations can be useful to calculate the degree of extraction (DE) as a percentage and its relative deviation (SD).

Most trace elements, especially those of relevant environmental concern, are summarized and discussed concerning the outcomes of the previous elaborations and taking into account several other references: column A and B values of 152/2006 Italian Decree on environmental regulations, and background/baseline values across Italy from scientific literature, the latter values were published in 2015 (Cicchella et al. 2015) referring to agricultural soils and can be an useful tool of comparison to evaluate the natural variation. We are aware that between sediments and agricultural soil differences could exist in terms of distribution for certain elements, related to peculiarities in the geochemical features of the two matrices. Being a nationwide study and because of this an extensive sampling results of Cicchella et al 2015 are driven by lithological variability, while sediments in our case are strongly influenced by the local influences being part of a reservoir and specific of the Marnoso-Arenacea formation (MAF) geological background.

Enrichment factor (EF) is used to estimate the degree of anthropogenic heavy metal pollution or the status of environmental contamination (Zhang and Liu, 2002; Zhang et al., 2007), in this case of study we tried to use as a tool to assess enrichments and depletions of elements respect to a standard or a reasonable background value to quantify metal enrichment in aquatic sediments. The central concept is to produce a numerical result comparing the metal content of each sample with a background level, here related to values proposed by Cicchella, the ideal alternative would be to compare concentrations between contaminated and non-contaminated sediments, looking for similar mineralogy (Covelli and Fontolan, 1997; Dung et al., 2013; Sakan et al., 2015), in this case, a national database was preferred to calculate EF, remaining aware of the sources.

The EF values were calculated as follows:

$$EF=(\text{metal}/\text{Al})_{\text{sample}}/(\text{metal}/\text{Al})_{\text{background}}.$$

Enrichment factor (EF) is a geochemical approach based on the assumption that there is a linear relationship between a reference element, as data from the literature and the measured element.

Normalization of element contents against an immobile element is a common practice to accommodate grain size effects and dilution by phases such as quartz and carbonates. Currently, aluminum (Al) is the most frequently used geochemical normalization in fluvial, estuarine and coastal sediments, based on the assumption that Al is held exclusively in terrigenous aluminosilicates (Chen and Kandasamy, 2008; Karageorgis et al., 2009). Because Al is inert in the migration process, originates mainly from natural lithogenic sources, is a conservative element and a major constituent of clay minerals, and was selected also in this case of study as element for normalization.

4.3 Results and Discussion

4.3.1 General descriptive statistics on Ridracoli reservoir

To characterize the sediment of Ridracoli reservoir by trace elements and identify indicators at contaminant levels, several tools are proposed and discussed, in this paragraph summary statistics, divided in inside Ridracoli Reservoir samples and Bed Sediments samples from external areas, is present in Table 4.1. Parameters derived from screening values from the literature for Italian soils (Cicchella et al., 2015) and Italian legislation (D. Lgs 152/2006) may provide a good standard of direct comparison to better values the found concentrations, the complete dataset is reported in supplementary materials.

Major element oxides of all 42 sampling stations, obtained by XRF and CHNO-S, are together with trace elements by ICP-MS in Table 4.1.

Table 4.1, shows median (MED), arithmetic mean (M), standard deviation (SD), minimum and maximum (Min, Max), and the number of samples (n), for each parameter. Median from Cicchella et al., 2015 have been entered, together with elements of environmental concern from the Italian Legislative Decree n. 152 of 2006 on environmental standards, Column A (sites for public or private green and residential) and Column B (sites for commercial or industrial use).

	Ridracoli Reservoir (n=27)					Bed Sediments (n=15)					Cicchella 2015	D.lgs 152/2006	
wt%	**Min**	**Med**	**M**	**SD**	**Max**	**Min**	**Med**	**M**	**SD**	**Max**	**Med**	**A**	**B**
SiO_2	38.9	46.0	45.5	3.2	51.5	36.5	47.1	47.0	5.9	53.6			
TiO_2	0.35	0.64	0.62	0.08	0.70	0.46	0.58	0.57	0.05	0.66			
Al_2O_3	8.6	13.0	12.8	1.4	15.2	8.8	12.1	11.7	2.0	15.1			
Fe_2O_3	3.8	5.9	5.7	0.7	6.5	4.1	5.4	5.2	0.5	5.8			
MnO	0.07	0.09	0.10	0.01	0.12	0.07	0.09	0.09	0.01	0.11			
MgO	2.88	4.36	4.30	0.70	5.65	3.02	4.02	4.07	0.48	4.84			
CaO	2.7	8.1	7.9	3.0	17.7	5.8	10.0	10.5	5.5	19.3			
Na2O	0.52	0.74	0.79	0.26	1.59	0.64	1.03	1.00	0.25	1.46			
K_2O	1.72	2.56	2.49	0.28	2.88	1.47	2.27	2.17	0.37	2.75			
P_2O_5	0.13	0.15	0.15	0.01	0.18	0.14	0.16	0.16	0.02	0.19			
LOI	14.3	19.7	19.6	3.3	26.7	12.1	17.3	17.5	4.3	26.4	12.8		
Corg	0.4	1.8	1.9	1.4	6.4	0.5	2.0	2.2	1.2	4.3	1.3		
N	0.0	0.3	2.1	2.6	7.2	0.0	0.1	0.1	0.1	0.3	2.58		
ppm	**Min**	**Med**	**M**	**SD**	**Max**	**Min**	**Med**	**M**	**SD**	**Max**	**Med**	**A**	**B**
Ag	0.05	0.10	0.11	0.04	0.24	0.05	0.10	0.10	0.02	0.16	0.05		
Al	10800	20100	18889	3738	24100	8100	14800	14493	2979	18400	17200		
As	2.5	4.3	4.2	0.7	5.7	2.2	4.0	3.9	0.7	4.9	7.6	20	50
Au	0.0012	0.0020	0.0021	0.0005	0.0032	0.0012	0.0024	0.0030	0.0015	0.0071	0.0022		
B	6.0	10.0	10.3	3.9	28.0	4.0	8.0	8.3	1.8	11.0	5.3		
Ba	84	114	112	17	138	64	102	101	21	139	110		
Be	0.5	0.9	0.8	0.2	1.2	0.4	0.7	0.7	0.2	0.9	0.8	2	10
Bi	0.14	0.35	0.32	0.07	0.40	0.12	0.28	0.27	0.07	0.35	0.28		
Ca	16100	55600	53796	21331	118900	18900	66500	70833	38184	138200	28860		
Cd	0.10	0.23	0.22	0.04	0.28	0.10	0.22	0.21	0.07	0.34	0.26	2	15
Ce	20.5	29.7	29.0	3.6	34.1	17.8	26.1	25.1	3.4	29.9	28.7		
Co	8.0	11.9	11.6	1.3	13.8	5.4	10.5	10.3	2.4	13.8	11.8	20	250
Cr	29.7	53.7	50.4	8.5	60.9	22.4	42.2	45.1	15.9	93.8	33.6	150	800
Cs	0.93	1.24	1.31	0.27	1.79	0.77	1.15	1.16	0.24	1.70	1.55		
Cu	11.5	24.9	23.1	4.1	26.9	9.4	21.3	20.3	4.8	28.1	32.0	120	600
Fe	11470	24850	23056	4087	26940	9390	21300	20296	4772	28050	24263		
Ga	3.60	6.10	5.78	0.99	7.20	2.30	4.70	4.51	1.08	6.00	4.72		
K	1900	3100	2974	498	3800	1300	2200	2240	461	2900	2136		
La	9.0	12.8	12.4	1.3	14.6	7.7	10.7	10.6	1.4	12.7	13.9		
Li	17.3	31.1	28.9	5.3	35.7	13.6	25.1	24.2	4.9	31.5	19.1		
Mg	7500	13000	12319	1730	14800	8200	12000	12120	1935	16300	6005		
Mn	446	655	622	114	840	307	535	528	107	741	664		
Mo	0.34	0.46	0.47	0.07	0.62	0.32	0.55	0.52	0.09	0.68	0.59		
Na	70	100	107	25	200	110	140	141	22	190	117		
Nb	0.24	0.58	0.59	0.18	1.06	0.18	0.43	0.48	0.19	0.90	0.65		
Ni	35.2	61.7	58.5	9.4	71.9	29.3	52.7	54.5	17.9	108.8	31.5	120	500
P	400	560	557	65	660	490	610	606	55	700	663		

Pb	10.3	16.6	16.2	2.2	19.6	6.7	15.7	14.0	4.2	21.3	22.1	100	1000
Rb	14.6	25.0	24.5	3.9	29.6	11.3	20.3	19.5	3.8	24.6	20.7		
S	300	600	696	238	1300	400	900	827	212	1200	191		
Sb	0.14	0.19	0.19	0.04	0.28	0.11	0.19	0.19	0.04	0.25	0.32	10	30
Sc	3.30	6.00	5.61	1.00	6.80	2.90	4.90	4.62	0.68	5.30	3.74		
Se	0.30	0.60	0.61	0.13	0.90	0.40	0.70	0.67	0.13	0.80	0.41	3	15
Sn	0.50	1.00	0.94	0.17	1.20	0.50	0.80	0.77	0.17	1.10	1.03	1	350
Sr	63.2	177.1	174.6	63.4	383.1	118.4	240.1	233.2	124.0	452.4	62.3		
Th	3.0	5.1	4.8	0.8	5.8	2.9	4.2	4.1	0.5	4.6	4.6		
Ti	60	130	130	48	220	80	140	143	36	210	119		
Tl	0.09	0.21	0.20	0.04	0.25	0.08	0.17	0.16	0.04	0.23	0.18	1	10
U	0.70	0.80	0.77	0.07	0.90	0.60	0.80	0.78	0.09	0.90	0.98		
V	23.0	40.0	37.7	5.7	44.0	19.0	33.0	31.6	6.2	41.0	34.2	90	250
Y	7.7	13.1	12.7	1.8	15.6	7.3	10.7	10.4	1.3	12.4	10.1		
Zn	39.2	72.7	67.9	12.1	82.6	31.7	65.8	70.0	24.9	118.8	61.7	150	1500
Zr	0.40	0.60	0.59	0.11	0.80	0.30	0.50	0.50	0.11	0.80	2.45		
%	**Min**	**Med**	**M**	**SD**	**Max**						**Med**		
sand	3.3	17.0	36.2	31.5	91.2						39.5		
silt	7.8	51.9	47.7	22.6	82.7						33.9		
clay	1.0	16.1	16.0	11.4	35.0						22.5		

The characterization of analytes in weight percent (wt%) and grain size data were already summarized and described in Chapter 3 and have been included herein Table 4.1 to restate and provide the total composition of samples. SiO_2, LOI, Al_2O_3, and CaO are the most abundant component in percentage, accounting in descending order for a median of about 87% of the total composition of sediments in the Ridracoli reservoir. They represent the clay mineral fraction and carbonate composition, figuring an important role for LOI, representative of an organic matter, water present in the lattice of clay minerals, and/or carbon dioxide in carbonate abundance. Inorganic major components have median values of 46.0, 13.0, and 8.1 respectively, and LOI has 19.7 wt%, of which Corg 1.8 wt%.

Inside the Ridracoli catchment can be seen slight differences in total composition between sediments that come from the bottom and ones that come from tributaries, this is due to the grain size and processes of deposition and accumulation that happens in the reservoir (Chapter 3). The sedimentation system is ruled by the transport energy which regulates the deposit of sediments due to the size, allowing the coarser sediments to settle in the peripheral areas and the finer ones to be transported to the bottom.

In this Chapter on Aqua Regia results, all the 27 samples inside the reservoir are used as representative once and a comparison is made between sediments inside and outside the catchment (Table 4.1).

Ridracoli reservoir shows in descending order for trace elements in ppm: Ca, Fe, Al, Mg, K, Mn, S, P, Sr, Ti, Ba, Na, Zn, Ni, Cr, V, Li, Ce, Rb, Cu, Pb, Y, La, Co, B, Ga, Sc, Th, As, Cs, Sn, Be, U, Se, Zr, Nb, Mo, Bi, Cd, Tl, Sb, Ag, and Au. The main composition is Ca, Fe, Al, Mg (>10000 ppm), consistent with one of the majors and one made of carbonates and clay minerals. S and P are steady with the presence of volatiles in the sediments, Mg, Sr, and Ba are usually bounded to carbonates, and K and Na (>100 ppm) are related to feldspars and plagioclases. Al and Fe are part of clay minerals, which are linked to Mn and other analytes as Zn, Ni, Cr, V, Li, Ce, Rb, Cu. Between values of 20 and 10 ppm can be found Pb, Y, La, Co, and all others are below, reflecting concentrations found in literature. Samples that come from bed sediments show a lower concentration in Al (MED=14800 and 20100 ppm respectively), but a higher one in Ca (MED=66500 and 55600 ppm), reflecting the clayey composition of sediment inside the reservoir and the more carbonate one of the surrounding areas, highlighting a similar but slight different source of background material, depending on the members of MAF that mainly outcrops and impact on the geochemistry of sediment and confirming results obtained from the majors but from the residue fraction. Two more parameters quite abundant are Fe and Mn, which have already been highlighted on this site as a cause of concern, are enriched in the samples inside the reservoir, respectively 24850 and 21300 ppm for Fe and 655 and 535 ppm for Mn. This behavior is due to an accumulation and enrichment in the solid phase of precipitated Fe-Mn oxides and hydroxides in the bottom sediments.

In Table 4.1, for trace elements in ppm most of the analytes show a higher concentration in Ridracoli reservoir sediments (Al, Fe, K, Mn, Pb, and Rb), some slighter (As, B, Ba, Bi, Ce, Cu, Ga, La, Li, Nb, Ni, Sc, Sn, Th, Tl, V, Y, and Zr), and some others show similar concentrations (Ag, Be, Cd, Co, Cr, Cs, Mg, Mo, Sb, Se, U) to the Bed Sediments group. Only a few analytes show higher values in sediments from external areas and are Ca, Au, Na, P, S, Sr, Ti, and Zn.

Trace elements are, by definition, less present in samples, usually in ppm (part per million), and their content variations are relevant for understanding the behaviours of some element of concern, like heavy metals, potentially harmful elements (PHEs) and elements considered by the limits by law (D. Lgs 152/2006).

Higher concentrations of a conspicuous number of trace elements in the Reservoir group are due to sediments trapped at the bottom of the reservoir in 40 years of physical accumulation since the construction of the barrier, and consequent selection of stable elements that have not been removed in the above water column. Most of the analytes from this group of course are part of the the geological major components of clay minerals (Al), or Fe-Mn oxides-hydroxides (Fe and Mn), as already written, and associated elements. Elements as Fe, Mn, and Al are also linked to secondary minerals, by chemical processes of precipitation and deposition of new phases included in the solid phase. In riverbed environment, sediments show higher concentrations in Ca and Sr due to the geological background, which is always part of MAF but in particular outcrops mainly Corniolo and Premilcuore members, rather than Galeata. A further analyte richer in external areas is S, which may be affected by the stable environment not affected by the oxic and anoxic dynamics of the reservoir (Chapter 2), that can let sulfur to accumulate in the solution and not in the stable solid phase as in stream sediments, aqua regia results come from digestion of the sample, which extracts the bioavailable elements and let only the more stable to be analysed.

In Table 4.1 can be done a further comparison with median values proposed by soils of Italian background (Cicchella et al., 2015) and values laid down by the National Decree n. 152 of 2006.

Differences between values proposed by Cicchella for Italian soils and ones of Ridracoli reservoir are found in higher values of Ag, Al, B, Ca, Cr, Ga, K, Li, Mg, Ni, S, Sc, Se, Sr, Ti, Zn, and lower of As, Cs, Cu, Nb, Pb, Sb, U, and Zr respectively. Other remaining analytes, Au, Ba, Be, Bi, Cd, Ce, Co, Fe, La, Mn, Mo, Na, P, Rb, Sn, Th, Tl, V, and Y, show similar concentrations.

In comparison to values proposed on a national scale for soils, we can find in the site sediments richer in LOI and Corg, emphasizing the importance of organic matter in the dynamics of this area. N is lower but depends on the type of site, in soils nitrogen presents higher concentrations due to nitrogen cycle and nitrogen inputs, in comparison to lakes and reservoirs where N is usually at lower concentrations. As regards the grain size, the database of the Ridracoli reservoir is composed mainly of silt, and one of the considered soils more equally balanced with a coarser component of sand at 39.5%, this comparison is however strongly influenced by the scale and matrices taken int consideration.

Lastly, it can be found that all the values of this study are below the limits by law, even more, no maximum value of each sample is above the limits. Only Sn has median and mean below the limit of Column A, but a maximum slightly higher, but it is in accordance with values found by Cicchella and far below the limit proposed by Column B.

Thanks to descriptive analysis it can be established an enrichment of some analytes in reservoir sediments that at the time of this study do not interest levels of concern.

4.3.2 Principal Component Analysis on pseudo-totals, Loadings and Factors

Loadings of the considered sediment samples, from the area of the reservoir, are shown in Table 4.2. Six factors were selected with a cumulative variance of 88.5%, loadings are hereafter abbreviated with L.

Table 4.2, Principal Component Analyses (PCA) on pseudo total compositions by ICP-MS, Loss on ignition (LOI), CHNO-S analysis, and grain size. Eigenvalues and percentage of variance are at the bottom of each principal component column. Loadings are shown by values, stronger than ±0.50 are in bolder, and ones lower than ±0.20 are omitted.

Ridracoli	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
Ag	**0.63**				0.24	**0.59**
Al	**0.96**	-0.22				
As	**0.82**	-0.32			0.32	
Au	**0.59**	0.30				0.48
B	0.42			**0.51**	-0.26	
Ba	**0.84**	-0.21				0.25
Be	**0.86**	-0.23			-0.22	
Bi	**0.98**					
Ca		**-0.51**	**0.78**			
Cd	**0.84**	0.34				0.21
Ce	**0.92**			0.20	0.20	
Co	**0.90**				0.24	
Cr	**0.98**					
Cs	0.44	**0.56**	0.26	0.39		-0.23
Cu	**0.96**					
Fe	**0.96**					
Ga	**0.96**					
Hg	**0.70**	**0.50**	-0.21			
K	**0.92**					
La	**0.86**	0.24		0.29		
Li	**0.97**					
Mg	**0.76**		**0.51**	-0.20	-0.20	
Mn	**0.72**	-0.20		-0.32	0.24	
Mo		**0.65**		**-0.50**	0.36	
Na	**-0.55**	-0.44	0.41			0.35
Nb		**0.90**	-0.25			
Ni	**0.98**					
P	0.48	**0.63**	0.44			
Pb	**0.88**	0.27			0.28	
Rb	**0.94**					
S	-0.38	**0.57**	0.38	0.29		
Sb		**0.92**		0.22		
Sc	**0.98**					
Se	**0.59**	0.28	**0.53**		-0.28	
Sn	**0.94**					
Sr		**-0.55**	**0.73**		0.25	
Th	**0.93**	-0.24				
Ti	**-0.50**	**0.81**			-0.25	
Tl	**0.89**	0.37				
U		0.40	**0.62**	-0.31	-0.29	0.40
V	**0.96**					
Y	**0.89**	-0.20		0.20	0.25	
Zn	**0.94**					
Zr	**0.85**			0.31		
LOI	-0.28	**0.52**	0.43	0.38		
Corg	-0.25	0.48	0.29	-0.28	**0.51**	-0.22
N	0.46	0.33	0.20	**-0.54**		-0.35

sand	**-0.89**	0.13	-0.15	0.18	0.18	0.09
silt	**0.78**	0.12	0.23	-0.30	-0.20	-0.16
clay	**0.82**	-0.43	0.00	0.03	-0.11	0.04
Eigenvalue	28.5	6.9	3.4	2.2	1.7	1.5
% variance	57.0	13.8	6.9	4.4	3.4	3.0

A PCA on a dataset is generally used to explore and make the data much easier to understand. In geochemistry and environmental studies the principal component analysis allows to understand which process or component rules a pattern of elements and which kind of weight has within the system. In the following paragraphs, we try to combine by principal components the analytes explain which elements can be grouped together.

PC1 is the most representative component and accounts the 57.0% of the variance. Positive L higher than +0.9 are found for Al, Bi, Ce, Co, Cr, Cu, Fe, Ga, K, Li, Ni, Rb, Sc, Sn, Th, V, Zn, always positive for Ag, As, Au, Ba, Be, Cd, Hg, La, Mg, Mn, Pb, Se, Tl, Y, Zr, and the finer grain size, *silt* and *clay*, finally slightly positive for B, Cs, P, and N. Negative values instead are found for the *sand* coarser grain size, Na, S, Ti, LOI, and Corg. This first principal component represents elements of similar origin, controlled by clay minerals, oxides, and secondary species involving Al, Fe, Mg, K, and Mn. Fe and Al seem to strongly control the contents of many metals, having all >+0.5 L and at some extent, B, Cs, P, and N. Lithogenic origin, processes of early diagenesis, and processes between water-sediment interface, like absorption and release of elements, are the key factor of this group, which is also similar to the group previously detected (Chapter 3), enriched in Ridracoli catchment. A further controlling factor for this PC1 seems to be the grain size and the finer fraction, in particular clayey and silty once, both in positive agreement. This chemical association of positive L can be related to the fine grain size, of siliciclastic fraction, dominated by clay minerals according to the positive L distribution of factors (Figure 4.2, PC1).

Cu and Zn are usually key parameters of anthropic pollution, and in this case, showing a very strong relationship with this factor, express a strong relation to clay minerals, as it is expected in an uncontaminated area (De Vivo et al., 2004; Alloway, 2013). The strong positive L of Fe, Mg, and Mn, suggests that something happened at the water-sediment interface modifying the concentration of oxides or hydroxides of secondary formation in relation to other trace elements, possibly leading all the considered analytes to a similar behaviour controlled by the same processes that take place on the bottom of the reservoir. In opposition, negative values can be found for different analytes, which appear to be related to the coarser fraction of the sediment, volatiles, and organic matter. More thoroughly Na, S, Ti, LOI, and Corg show negative values in samples, indicating that sulfur, volatiles, and organic matter have the opposite behaviour to most of the tracers. Na and *sand* parameters are both negative and can lead to a composition of the sandy fraction controlled by the presence of plagioclase, from the bedrock geology. Ti may reflect an abundance of a heavy minerals, as titanium, and together with Na agree in negative values with the coarser grain size. The correlation with other heavy minerals elements, such as Zr, Th, or REE, however show an opposition, suggesting that instead is a fine-grained fraction of the sediment which is associated with accessory minerals.

PC2 shows positive L values for Au, Cd, Cs, Hg, La, Mo, Nb, P, Pb, S, Sb, Se, Ti, Tl, U, LOI, Corg, N, *sand* and *silt*, and negative ones for *clay*, Al, As, Ba, Be, Ca, Mn, Na, Sr, Th, Y, with a total variance of 13.8%. This principal component is ruled by the organic matter component, by LOI and Corg, and organic matter degradation processes in the coarser fraction. This group of elements shows also interesting values depending on the sample group considered, in samples from Ridracoli catchment the organic matter seems to be dominated mainly by *silt* grain size, and in agreement with N, S, and P, which are elements that usually are involved by organic matter. As highted in Chapter 3 the finer grain size is mainly found in sediments at the bottom of the reservoir. Although P can also have a detrital source that cannot be distinguished from the organic one through this type of analysis. Elements such as S and Mo are also present in this group since they have a high affinity with organic compounds (De Vivo et al., 2004). On the contrary, Ca and Sr control the group of analytes with negative L, representing the carbonate fraction (Kim et al., 1999). This group is of great importance in the finer grain size (*clay* fraction), and are in accordance with Al, As, Ba, Be, Mn, Na, Th, and Y.

PC3 shows positive L values for Ca, Cs, Mg, Na, P, S, Se, Sr, U, LOI, Corg, N, and *silt*, and negative for Hg, Nb, and *sand*. It has a total variance of 6.9% and, similar to the previous component PC2 but here with positive L this fraction is controlled by carbonate minerals, whereas S is related both to sulfate minerals and to organic matter. Carbonates are abundant in the lower members of Biserno and Corniolo more than Collina or Galeata (Figure 4.1).

Principal Components 4, 5, and 6 explain together the 10.8% of the variance, a little variability, and do not contribute with additional information. PC4 is positive for B, Ce, Cs, La, S, Sb, Y, Zr, LOI and *sand*, and negative for Mg, Mn, Mo, U, Corg, and N and *silt*. PC5 is positive for Ag, As, Ce, Co, Mn, Mo, Pb, Sr, Y, Corg, and *sand*, negative for B, Be, Mg, Se, Ti, U, *silt*, and *clay*. Finally, PC6 is positive Ag, Au, Ba, Cd, Na, U, *sand* and negative Cs, Corg, N, and *silt*.

Since the majority of data variability, of about 77.7 %, is explained by the first three factors, their combination can be used to define the main features of the sediments of Ridracoli reservoir.

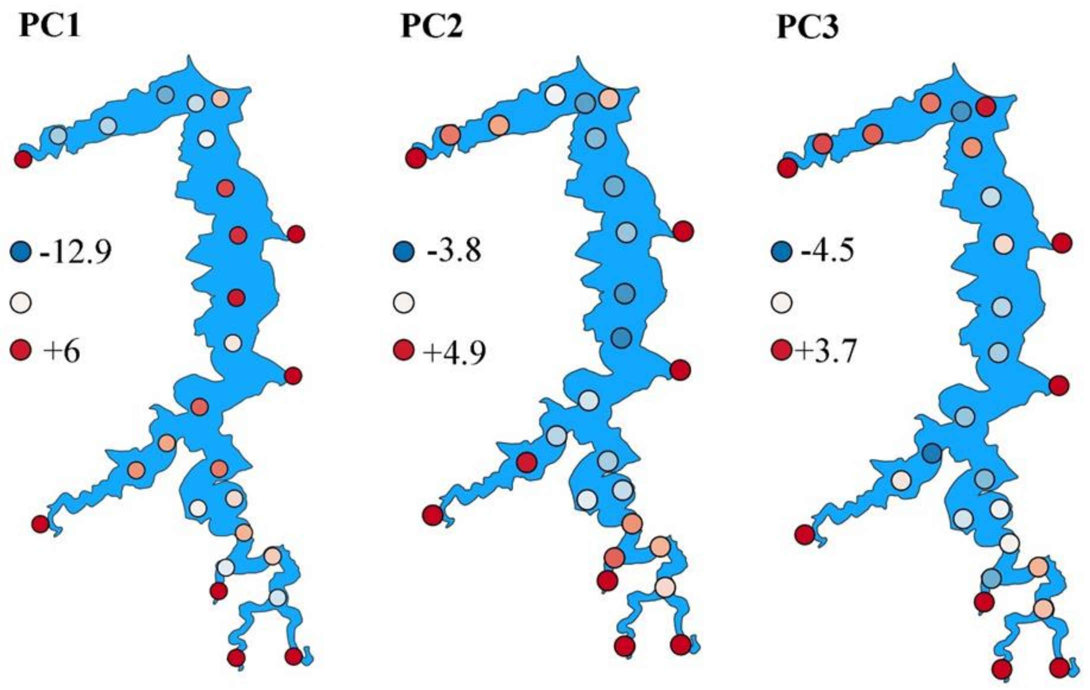

Figure 4.2, Ridracoli reservoir factors of the three principal components, values in red are with positive L and in blue with negative ones.

Factors of each sample are reported in Figure 4.2, combined with the topographic map of the reservoir's area: positive values for clay mineral, corresponding to PC1; organic matter and feldspathic sands, comparable to PC2; carbonates, reciprocal to PC3. The map highlights areas of Ridracoli reservoir with a dominant composition of sediments. In particular, the external areas of tributaries display strong positive values for each considered PC. For clay minerals is also shown a dominant sector in the center of the reservoir, while organic matter rule especially in the peripheral areas and where the depth of the sample station is near the coast and in shallow water. Organic matter shows only one station with positive factors at the bottom of the reservoir near the dam and may suggest a singular situation for the deepest station, probably due to degradation processes. Carbonates of PC3 are focused in the northwest sector of the catchment on the Rio Celluzze branch. Overall, the three groups show similar patterns with tributaries with strong positive values, but with PC1 with positive ones distributed also in the main branch of the reservoir, PC2 with negatives inside the reservoir except for the station near the dam, and PC3 with positives on the Rio Celluzze branch and near the dam.

4.3.3 Element mobility and extractability by aqua regia compared to the total content

In this study, the degree of extraction (DE) for the elements are arranged and grouped in percentage ranges as follows: 100-70% Ca, S, Mn, Th, P, Zn, Pb, N, Sr; Co; 70-30% Cu, As, Fe, Y, Ce, Mg, V, La, Ga, Cr, Ba; and 30-0% U, Al, Sn, Cs, Rb, K, Nb, Ti, Na, Zr. DE suggests which element is more stable in the crystalline structure and which is weakly bound to the sediment and can be extracted, so elements with high values of percentage are ones more easily removable and ones with low percentages are most persistent in the solid fraction. The aqua regia process causes the oxidative action capable of extracting metal electrons from their outermost surfaces and thus migrating to the solution in an ionic state. The analysed elements in descending order of percentage of extraction with relative deviation bars are shown in Figure 4.3. A large DE, on left, suggests that elements can be almost completely extracted thanks to aqua regia digestion, suggesting a relation with sediment phases that can be unstable if sediment environmental conditions change (e.g. oxidation states promoted by re-suspension or burial, changes in pH).

Moving right, are analytes more stable and less mobile. Ca, S, Mn, Th, P, Zn, Pb, N, Sr, Co display DE values >70%, rather easily extracted and mainly part of weak bonds and on the outer layers of solid particles. This group includes elements that can easily be traced back to the carbonate fraction (Ca, Sr). The high DE of P is related to its association to organic matter, whereas that of S could likely be related to the occurrence of small quantities of sulfides formed in the bottom sediment after sulfate reduction reactions involving organic matter degradation. Even these two sediment components affect the behaviour of the listed PHEs.

Cu, As, Fe, Y, Ce, Mg, V, La, Ga, Cr, and Ba have DE between 70 and 30, are in the middle of the graph (Figure 4.3), suggesting that these elements tend to be related to other mineral phases, less, but not entirely, affected by the aqua regia extraction.

The last group of elements, the one on the right with the lowest DE values (<30), includes U, Al, Sn, Cs, Rb, K, Nb, Ti, Na, and Zr. These elements could be related to feldspars (Al, K, Na) or heavy minerals (Ti, Zr), only partially affected by the aqua regia digestion, far stable in a large range of environmental conditions and usually part of the stable crystalline structure of minerals.

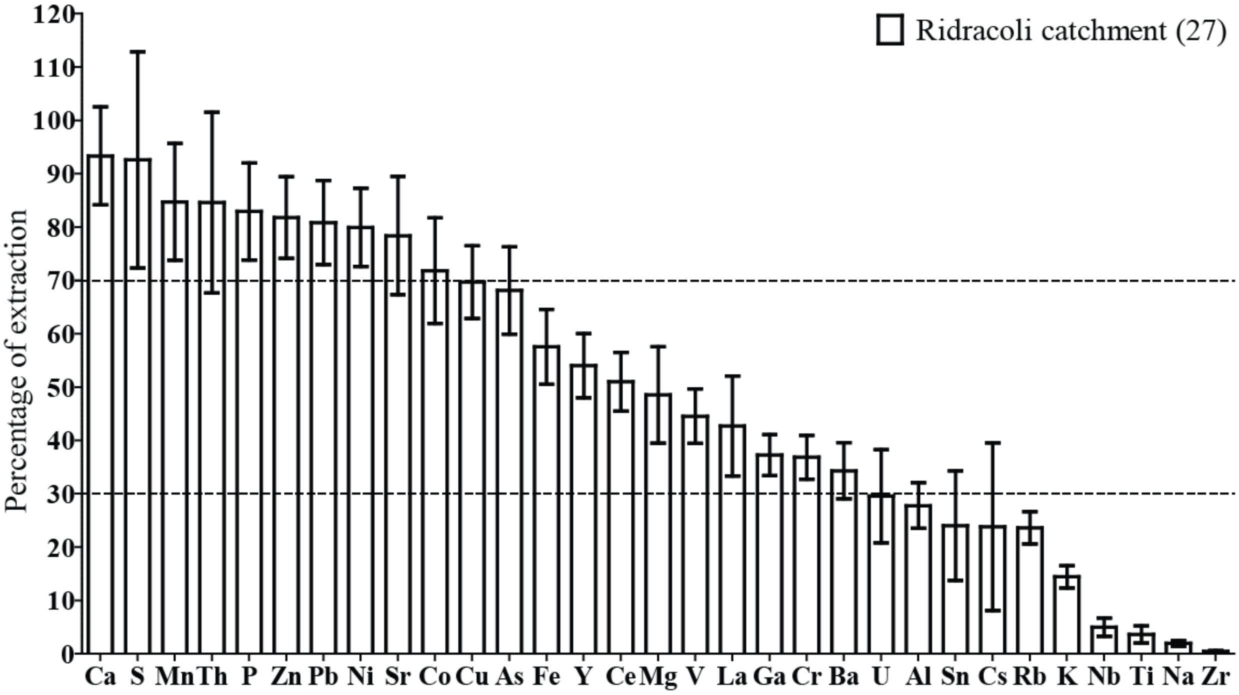

Figure 4.3, Percentages of extraction for Ridracoli catchment samples, in descending order of percentage and relative standard deviation for sediments of Ridracoli reservoir.

Reservoirs of this size may undergo water stratification and mixing (turnover) periods during the year (Toller et al., 2020), leading to periodic variations of oxygen concentration in the bottom water from completely anoxic during the stratified period to oxic during the rest of the year. The redox conditions strongly affect the iron and sulfur cycles and, therefore, the bioavailability of associated trace elements (Berner and Raiswell, 1984; Audry et al., 2004).

The comparison between the pseudo total and total concentration indicates high extractability (>60%) for selected PHEs, Zn, Pb, Ni, Co, Cu, As, which are all elements of concern also present in the Italian Decree 152/2006.

An extractability in the range of the one of Fe and Mn, can be attributable to oxy-hydroxides colloidal phases. Mn (85%) and Fe (58%) are representative of Fe and Mn oxy-hydroxides and several PHEs (e.g. Th, Zn, Pb, Ni, Co, Cu, As). Fe and Mn oxides can contain variable amounts of As, Pb, Cu, and Cr as adsorbed and co-precipitated (Alpers et al., 1994; Casiot et al., 2003) in water reservoirs; the particulate materials are incorporated into the sediment, where biogeochemical transformations might occur depending on the organic carbon supply and redox conditions. P is found to be easily extractable because of organic matter and/or apatites, and S, easily extractable because associated with sulfides, which are affected by oxidation.

Further studies, such as those applying sequential extraction, could be useful to disentangle these first indicative results.

Aqua regia content of the main hazardous pollutants Zn, Pb, and Cu in environmental samples usually do not much differ from real total contents obtained by digestion with HF (Sastre et al. 2002). A values estimation of the degree of extractability (DE) of many harmful elements are listed in normative documents of several countries (Taraškevičius et al., 2012). On a general view the trends of percentages found in the literature in soils are Cu (91%) > Mn (89%) > Zn (89.5%) > Ni (88%) > Co (86%) > Pb (79%) > V (61%) > Cr (56%) > Ba (20.5%) (Taraškevičius et al., 2012), and in a wetland sediments study as Cu (106%; 100–109%), Co (103%; 99–113%), Zn (80%; 75–89%), Ni (76%; 70–79%), Pb (63%; 33– 91%), Mn (58%; 53–66%), Cr (53%; 46–61%), V (33%; 30–36%), and Ba (20%; 17–28%), (Borghesi et al., 2016). Compared to values found in this study, Mn (84.7%) > Zn (81.8%) > Pb (80.8%) > Ni (79.9%) > Co (71.8%) > Cu (69.7%) > As (68.1%) > V (44.5%) > Cr (37.3%) > Ba (34.3%) > Sn (24%), they seem to agree in the general order of extractability with only few differences. Our data confirm that Mn is highly dissolved by aqua regia and shows a higher percentage of extraction in samples from the reservoir (84.7%) concerning riverbed samples (78.7%), due to ions present on the surface of sediments, loosely bound at the bottom and easily removable. The extractability of Zn is high, but there are no enrichments of this element due to industries or anthropogenic, since the reservoir is located far away from any urban area. Pb, Ni, Co seem to be mobile elements in this environment, displaying similar percentages of Th, P, Zn, and Sr, in agreement with literature. Cu and As have similar percentages in both reservoir and riverbed sediments, with a lesser removable degree of Cu respect to wetlands samples of Taraškevičius, indicating a greater stability in this area. Cr, unexpectedly slightly less extracted, does not show high concentrations, both for reservoir and riverbed, and appears not very accessible to mold attack and consequently of low concern for organisms or water content. A further element that reveals limited mobility is V, which together with Ba, shows similar values to ones from literature. At least, another element of concern for the Italian legislation is Sn, which is the most stable in the sediment and consistent with the highest values close to the proposed limits by law.

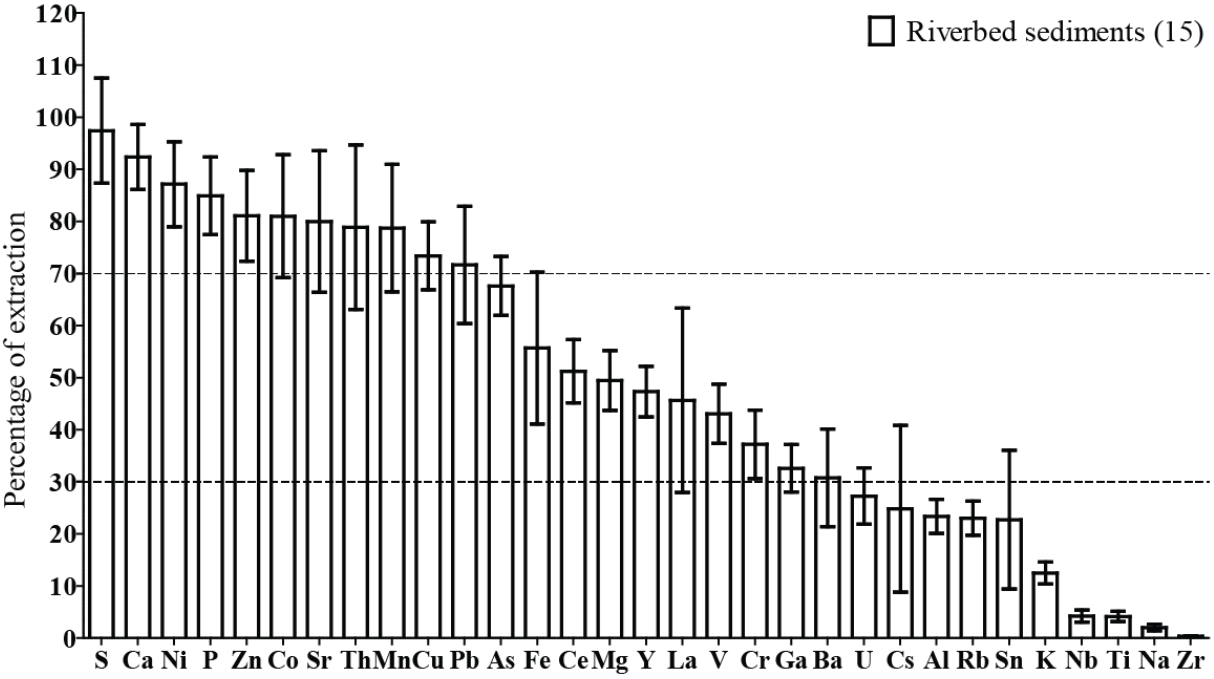

Figure 4.4, Graph showing the percentages of extraction for bed sediment samples, in descending order of percentage and relative standard deviation.

A comparison between the elements considered for the Ridracoli reservoir (Figure 4.3) and samples from riverbed sediments (Figure 4.4) can be done to highlight elements that show minor mobility and which a more mobile depending on environmental characteristics. Mn shows higher values in Ridracoli (84.7%) and lowers in external areas (78.7%), as well as Pb (80.8%) and (71.7%). Ni and Co, instead, display an opposite behaviour, with, respectively, 79.9% and 71.8% in the reservoir and in the tributaries, and 87.2% and 81.0% in riverbed sediments.

In addition to the already described parameters, other element percentages have been analysed, as for U, Al, Cs, Rb, K, Nb, Ti, Na, Zr, very little dissolved by aqua regia digestion. Moreover, among rare earth elements (REEs) V, La, Ga, are slightly extracted in the range between 30% and 45%, resulting more mobile than other elements associated to clay minerals. Iron and manganese should significantly participate in the pseudo-total contents as hydroxides and colloids, influencing the fate of other elements, and, for this reason probably more extractable. All these analytes in sediments are preferably firmly bounded in clays (Al) or immobilized in insoluble heavy minerals to aqua regia (Ti, Zr).

4.3.4 Evaluation of sediment concentrations: Enrichment Factors

Figure 4.5 provides values of EF calculated from 27 samples from Ridracoli reservoir analysis, compared to data reported by Cicchella et al 2015 based on 121 collected samples from ploughed or grazing soils. Ag, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Hg, 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, Zr, LOI, Corg, and N, were taken into account for this comparison.

A first interpretation state of EF values between 0.5 and 1.5 suggests that trace metals may be derived entirely from background materials or natural weathering processes, whereas values greater than 1.5 mean that a significant portion of trace metal delivered from anthropogenic sources (Zhang and Liu, 2002). A second different explanation on different criteria considers EF<1 as "no enrichment", 1<EF<3 as "minor enrichment", and 3<EF<5 as "moderate enrichment", EF 5-10 "moderately severe enrichment", EF 10-25 as "severe enrichment", and EF=25-50= is "very severe enrichment" and would seem to be a more sensible scale (Costa et al., 2015; Zalewska et al., 2015).

Since any anthropogenic source and agricultural or industrial activity are present in this area, elements enrichments are presumably due to the natural accumulations that occur in the sediments of the reservoir. Overall, our results provide a further step towards understanding the natural accumulations in this area and the effects of the dam.

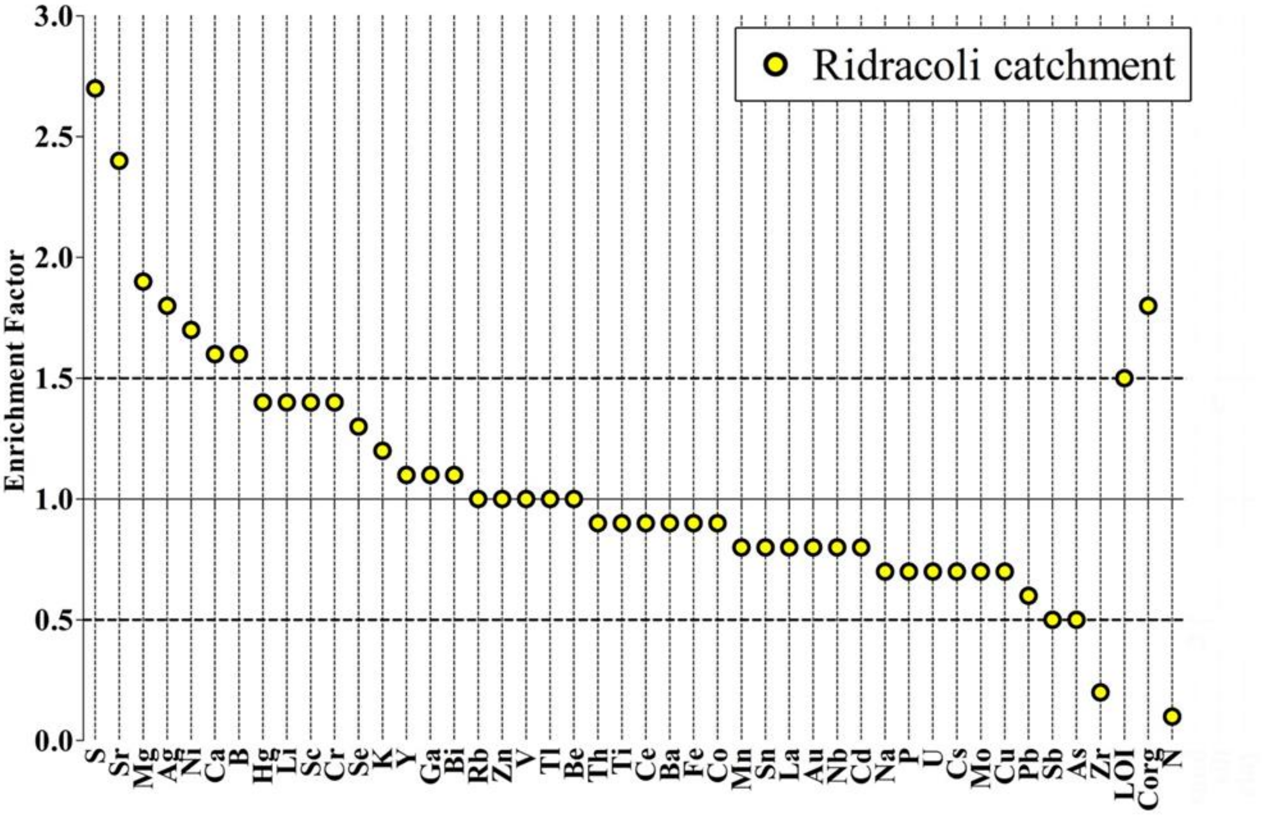

Figure 4.5, Graph reports the enrichment factors in descending order for samples from the Ridracoli reservoir.

Figure 4.5 reports the enrichment factor of S, Sr, Mg, Ag, Ni, Ca, B, Hg, Li, Sc, Cr, Se, K, Y, Ga, Bi, Rb, Zn, V, Tl, Be, Th, Ti, Ce, Ba, Fe, Co, Mn, Sn, La, Au, Nb, Cd, Na, P, U, Cs, Mo, Cu, Pb, Sb, As, and Zr, in a descending order. S and Sr can be classified as moderately enriched, showing the highest values along with Mg, Ag, Ni, Ca, B, LOI, and Corg. These elements reflect the carbonate and organic matter components of the study site, and LOI, and Corg the direct supply of thick vegetation of the Natural Park. Most of the elements present EF values between 0.5 and 1.5, of which greater than 1 are Hg, Li, Sc, Cr, Se, K, Y, Ga, and Bi, equal to 1 are Rb, Zn, V, Tl, and Be, and finally below 1 are Th, Ti, Ce, Ba, Fe, Co, Mn, Sn, La, Au, Nb, Cd, Na, P, U, Cs, Mo, Cu, and Pb. All of them can be considered of no concern about environmental pollutions in the solid phase and derived entirely by the background. Fe and Mn, relevant in the monitoring of the water body of the reservoir, show no enrichments in the sediments, as well as other consistent elements as As, Cd, Co, Cr, Cu, Hg, Mo, Pb, Sb, V and Zn which are metals usually taken into account. Few parameters are below 0.5, Sb, As, Zr, and N, showing depletion respect to values proposed for Italian soils. Elements between 0 and 0.5 as Zr and N, Zr because of a depletion in the MAF. In general, higher values can be found for Ca, Li, Ni, S, and Sr which are soluble elements, mobile cations, and mobile oxyanions, that can be found in the water in contact with the sediment.

Chemistry of waters (Toller et al., 2020) and sediments (Chapter 3) at Ridracoli reservoir is controlled by rock weathering of the catchment, weathering of the outcrop sandstones and marls in the direct catchment area. In addition to Ca^{2+} derived from the weathering of fine-grained lithologies, the turbiditic unit of MAF, there are also sandstone beds enriched in (Gibbs, 1970), which have a higher content of CaO than other turbiditic sandstone units present in the northern Apennines (Dinelli et al., 1999; Lancianese and Dinelli, 2015), and to which are also bounded Mg and Sr.

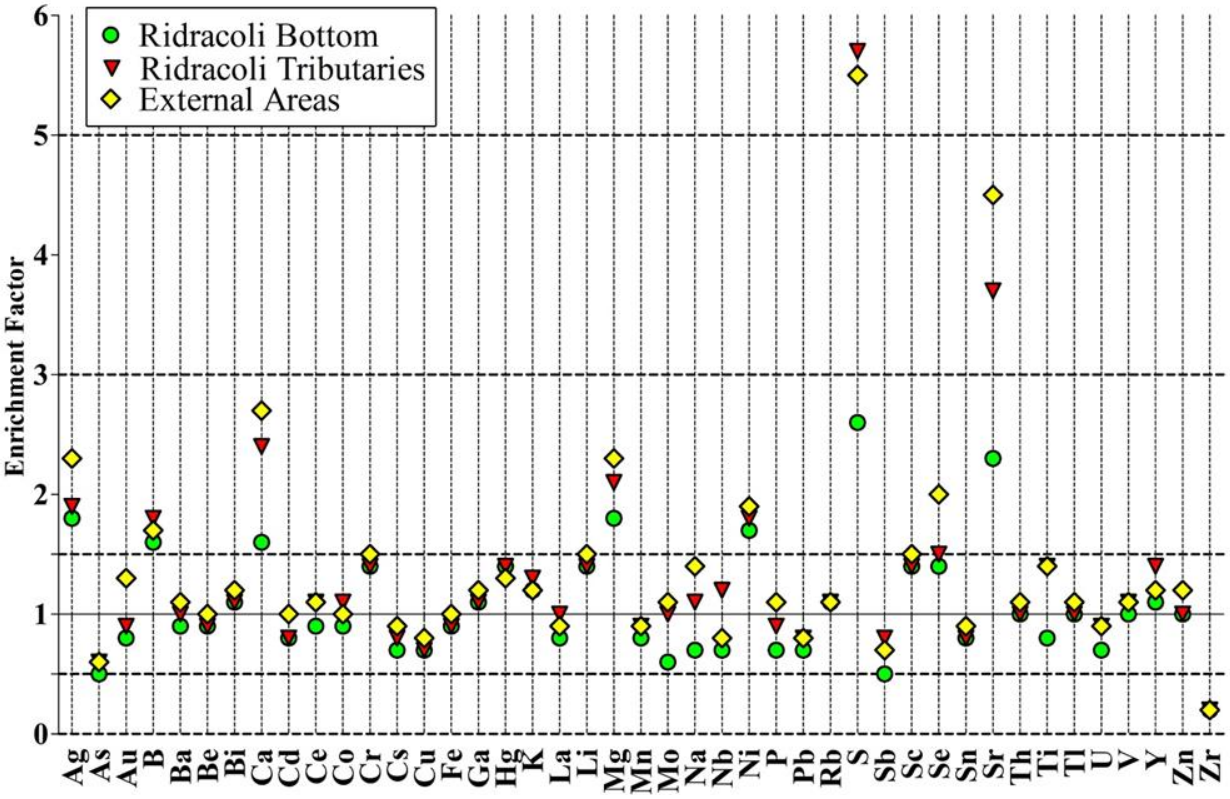

Figure 4.6, Enrichment factors for each group of the considered samples from the bottom of the lake (Ridracoli Bottom, n=20), samples inside Ridracoli catchment but from tributaries (Ridracoli Tributaries, n=7), and sediments samples of rivers of the surrounding area external to Ridracoli catchment (External areas, n=8).

About S and Sr, which display the higher values, samples from tributaries and riverbed sediments from external areas are much more enriched respect to the once from the bottom, which are below EF of 3. Overall, samples from the bottom (Green circles in Figure 4.6) show less enrichment compared to samples from tributaries and external areas, suggesting not a strong accumulation in concentrations at the bottom compared to ones in other sediments. The biggest differences can be found for Ca Mg, and Sr due to the geological background, of Corniolo and Premilcuore Members.

In general, all parameters show a lower Ridracoli Bottom value, but with a very limited range, except for the previously mentioned parameters. These lower values are probably due to the aqua regia digestion which is more effective on extraction on bottom sediments than on the tributary and riverbed once. This is due to the fraction of each element that is not bound to the stable structure of minerals but to the extractable one, highlighting that the sediment at the bottom is more interested in absorption and weaker chemical bonds with solid fraction, which more easily go into solution.

4.4 Conclusions

Obtained results show that sediments are clayey-silt, sand-silt to silty sand in texture with a composition characterize by Al_2O_3 clayey fraction inside the Ridracoli catchment and by CaO and carbonate and coarser size in the outside basin, reflecting both the local geology of an alternation of sandstones and marls (Marnoso Arenaceo Formation (MAF)) and the deposition system ruled by the morphology and transport energy. Overall, collected samples inside the Ridracoli catchment are enriched in organic matter and volatile, while are coarser and more carbonate in the external areas.

The positive correlation with Al_2O_3 and Fe_2O_3, suggest that most of the trace elements are probably bound in the clay mineral and/or on iron oxide crystal lattices, otherwise absorbed on charged surfaces in the finer fraction of sediments. Moreover, organic matter (Corg) and volatiles (LOI) play an important role in sediments dynamics, as suggested by their high concentrations.

PCA analysis indicates an influence of the granulometry on metals behaviour at trace level and on PHEs. Samples with fine size can adsorb elements thanks to the high specific surface area, determining higher concentrations of PHEs respect to samples with coarser grain size, which means that at the bottom of the reservoir, where the finer sediments are deposited, are also present the linked analytes.

The study of the chemical composition of reservoir sediments allowed to assess how it is influenced by the geological substrate and to evaluate the chemical effects due to hydraulic sorting.

The presence of clays and Fe-Mn oxides in sediments explain the behaviour and the mobility of many elements due to adsorption processes. The sampling stations with more iron show also higher concentrations of metals as Cu, Ni, Cr, Co, V, Pb, and Y, demonstrating that changes in environmental conditions, as in pH and Eh, can cause the release of metals into the water column.

The comparison between the pseudo total and total concentrations showed high extractability for selected PHEs (Zn, As, Pb, Cu, Co, Ni), comparable to that of Fe and Mn, attributable to oxy-hydroxides colloidal phases, P, easily extractable because related to organic matter, and S, easily extractable as associated to sulfides.

Enrichment factor values resulted all very low, testifying any enrichment by external sources as anthropogenic activities or agricultural practices. Moreover, enriched elements as Ag, B, Ca, Mg, Ni, S, Sr, LOI, and Corg, mainly for bed sediment samples, showed lower values for all samples from the bottom when compared to the literature.

The similarity of the nearby area with river sediment samples also suggests the absence of anomalies in the reservoir respect to the surrounding areas. EF together with the comparisons with limits by law and literature assessed that no hot spot of any type of contamination is present in the area.

In conclusion, our results show limited variations both for total and pseudo total composition. The PHEs concentrations are in line with what suggested by the regional geochemical survey involving stream sediment analysis and soils of Italy, even if some values are slightly higher due to the effect of trapping of the dam, however below the limits provided by Italian legislation.

This work is helpful to understand the stability of metals and elements of concern at the bottom of the reservoir in comparison to different sources. Sediments have characteristics comply with the purpose of drinkable water storage of Ridracoli reservoir, which, after almost forty years of activity, don’t display any external pollution or anomality, without any apparent effect of concern for the near future.

Chapter 5 – Fluxes of dissolved major and trace elements in a water-sediments interface from the bottom of a drinking water reservoir

Abstract

The development of seasonal stratification and the formation of low dissolved oxygen in sediments can lead to the oxidized and insoluble iron and manganese reduction, as well as other elements. The soluble forms that derived from this process and resulting from oxidation are subsequently released into the water column. As harmful elements deteriorate drinking water quality, the evaluation of metal fluxes at the bottom a reservoir together with the study of those processes that happen in water-sediment interface are of great interest. In this work are investigated some of the biogeochemical cycle processes that occur in bottom sediments of Ridracoli reservoir, paying particular attention to heavy metals and organic matter behaviour. The characterization of core sediments, interstitial pore water, and benthic fluxes allowed to evaluate the environmental conditions to better understand the early diagenesis processes and pollution hazards that take place in the study area. Our results showed organic matter degradation and early diagenesis at the water-sediment interface together with mineral formation. Our observations on nitrification, sulfides behaviour and element mobility into the water column or in sediment influence the release or burial of elements.

Keywords: Geochemistry – Artificial water reservoir – Benthic fluxes – Sediment-water interface – Early diagenesis

5.1 Introduction

The assessment of water quality in multipurpose water bodies has gained great importance in recent years, not only because of its ecological, economic and social role, but also for environmental and sustainability issues (Pott, 2000; Ampadu et al., 2015). Water bodies, rivers, lakes, and reservoirs, which provide fresh water for human consumption and exploited also for other purposes, are of political and environmental concern (WHO, 2008), and increasing in importance due to the demand of good quality waters that increases over time (Boretti, 2019). For human consumption, many elements are considered essential nutrients in drinking water (WHO, 2005), but it is all a matter of concentrations. In any environment, water interacts with rocks and sediments, triggering a series of processes, such as weathering, leaching, and precipitation of new phases thus promoting circulation of chemical elements in the environment.

Alterations in the biogeochemical cycles of elements at the bottom of a reservoir can affect the water column, bottom sediment, and the sediment-water transfer processes at the interface (Yang et al., 2014). The sediment-water interface is a site of intense chemical, physical and biological reactions, which can lead to both the production of new phases and the alteration of existing minerals, as well as changes in the composition of both the water body or the bottom sediments, involving processes of early diagenesis, degradation of organic matter, dissolution, precipitation, and adsorption (Erickson and Auer, 1998; Katsev et al., 2007). In reservoir environments, with new sediment deposited trapped on the reservoir bottom (Ran et al., 2013), early diagenetic processes can be part of the biogeochemical cycles of nutrients or metals (Soares and Mozeto, 2006; Yang et al., 2014); these fluxes can represent an input to the water body comparable to that of external inputs from terrestrial sources from banks or tributaries. At the sediment-water interface a rapid rate of mineralization, early diagenesis, can occur (Froelich et al., 1979; Schultz, 2006), these reactions can modify not only the minerals on which the trace elements are adsorbed, but also the entire speciation of the elements and, therefore, the mobility, bioavailability and toxicity of these chemical species (Beutel et al., 2020; Krueger et al., 2020). Therefore, these diagenetic processes are often considered responsible for the creation, through diffusion, of chemical gradients along the interface between the sediment pore water and the water column. The concentration profiles of several chemical species have shown that the fluxes are bidirectional, which means that the sediment can either be a source or a sink of dissolved elements, nutrients or contaminants (Petersen et al., 1995; Riedel et al., 1999; Mozeto et al., 2001) across this interface (Lyons and Fitzgerald, 1980; Ciceri et al., 1992).

Concentrations of dissolved oxygen have a strong influence on the dynamics of metals and elements, directly or indirectly (Davison, 1993; Koretsky et al., 2006), and seasonal stratification and the cyclical oxic and anoxic environment that occur seasonally at the bottom of this site are a matter of interest (Toller et al, 2020).

In this work we aim to understand the early diagenesis processes in trapped sediments at the bottom and to explain the heavy metal, organic matter, and dissolved nutrient behaviour inside Ridracoli reservoir on Northern Apennines in Italy. In order to better investigate the behaviour of the dissolved substances at the water-sediment interface and their effects on the chemistry of water column of the reservoir, two sampling campaigns were planned in the two extreme environmental conditions: in late summer, with a stratification and an anoxic layer at the bottom, and in spring, when the water column is all oxygenated and mixed. In both sampling campaigns flows were calculated thanks to a benthic chamber and cores, with relative sediment and pore water analysis.

We aim to characterize from a sedimentological and geochemical point of view the deeper waters and sediments from the base of the dam, to study the early diagenesis processes, the direct measurement of the benthic fluxes, and finally identify and quantify the extent of nutrient releases, majors and trace elements, including some metals, with particular attention to Fe and Mn which are of concern in this area. Flow measurements are used to quantify metal loads in the water column or sediment, and metal fluxes under variable oxygen conditions results useful for understanding inputs or outputs into water.

5.2 Material and Methods

5.2.1 Site description and sampling station

The Ridracoli dam, located upstream of the Municipality of S. Sofia (FC), Italy, has been active since 1982, is 103.5 m high and holds a reservoir of 33×10^6 m^3 of water capacity and of 1.035 km^2 of water surface. The site is located in the Casentinesi Forests - Campiglia National Park, between Romagna and Tuscany regions, at 480 m a.s.l. in a mountainous area of the Northern Apennines and is fed by the Bidente River. The reservoir water and sediment supply comes from a total drainage basins of 88 km^2 composed by a direct catchment of about 36.9 km^2 and an indirect one of 51.1 km^2 connected by a gutter gallery. The entire area within the area of the dam and surroundings is characterized by outcropping rocks belonging to the Marnoso Arenacea Formation (MAF) (Ricci Lucchi and Valmori, 1980; Gandolfi et al., 1983).

Ridracoli reservoir is affected by an alternation of water stratification and mixing processes due to seasonal change in water temperature, density, and reservoir volumes. The two extremes are represented by late summer and spring (Chapter 2): in late summer the reservoir water column is at the lower water lever, about 50 m, for the coupling of hydrological conditions and the increase in water demand along the Adriatic coast. In this period a water stratification develops due to the temperature gradient found along the water column, which promotes the creation of an anoxic layer at the bottom because of the consumption of the oxygen. In spring the water inputs bring to the maximum the reservoir water level, about 74 m, and low temperatures allow the layers to mix and oxidizing the entire water column.

The total characterization of the reservoir's water shows a Ca-Mg-HCO_3 (bicarbonate – calcium – magnesium water) composition (Toller et al., 2020). In October 2015, the water column was under stratification and with an anoxic layer at the bottom, where were found high concentrations of Ca^{2+}, TIC, TOC, Cl, Ba, Fe, very high levels of Mn and Zn, and decreased amount of NO_3^- and SO_4^{2-} with the concomitant increase of NO_2^- and NH_4^+. During the homogenized state of April 2016 all the concentrations were diluted, showing a limited variation along the water column for NO_3^-, or an increase of NO_2^- and NH_4^+ (see Chapter 2).

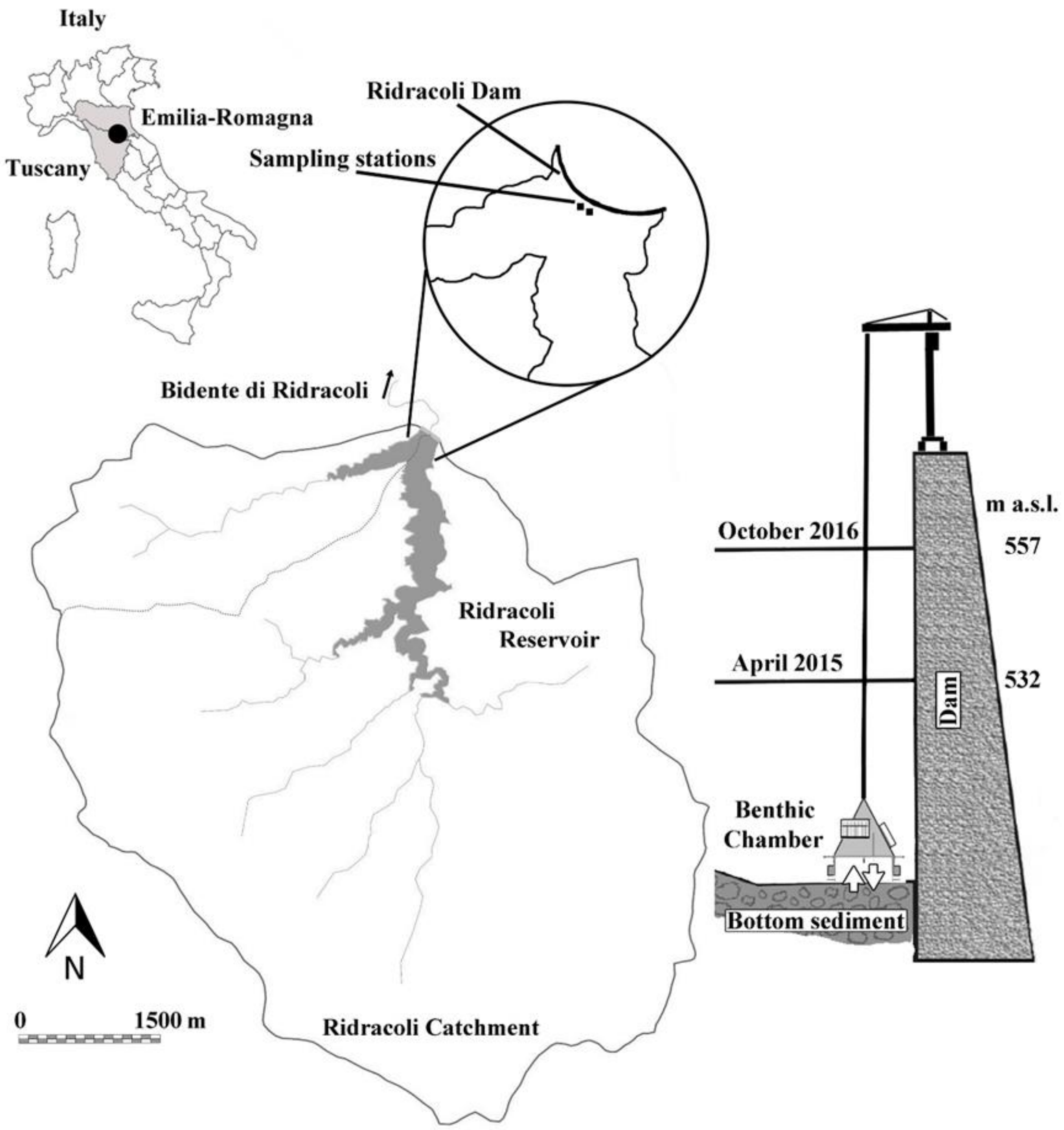

Figure 5.1, Ridracoli reservoir location and topography, sampling sites position, and sampling configuration at the sampling station.

The two sampling campaigns of October 2015 and April 2016 have been conducted in two neighbouring sampling stations located nearby the floating sampling station of ARPA ER (the environmental agency that operates in this region), which is monthly monitored since 2009 for chemical, physical and biological characteristics of the water body. Those sampling stations therefore allows to study a well known spot which is also located in the deepest profile, nearby the structure of the dam (Figure 5.1).

5.2.2 Samples preparation and analytical procedures

5.2.2.1 Cores, sediments and pore waters

On the bottom sediment in the area near the dam were collected two gravity cores, the first in October 2015 and a second one in April 2016, collecting sediments and interstitial waters. Each core was taken from the bottom of the reservoir in the same area as the floating sampling station thanks to a crane to which the SW104 gravity core was connected, and armed with two rings, was able to collect 40 cm of sample. The core was carried in an inert environment, a glove-box under a N_2 flux, to be divided in samples for every layer. A total of 24 samples of sediments and 24 corresponding samples of interstitial waters along each profile were collected to be measured for physico-chemical parameters as temperature, pH and Eh, and described for macroscopic characteristics as colour, texture, lithology, degree of hydration and bioturbation. For interstitial water extraction, each sampled layer was sealed and centrifuged for 15’ at 5000 rpm at +4°C; the supernatant was then 0.45 μm filtered under N_2 flux and aliquoted for several type of analyses.

5.2.2.2 Benthic chamber

The sampler is an Automatic Benthic Chamber (CBA), an instrument used to assess benthic fluxes of dissolved chemical species (Spagnoli et al., 2019) that can carry a variety of instruments to study the water column and the water-sediment interface by measuring environmental parameters and collecting samples. It consists in a Plexiglas cylinder open on the bottom and closed to the top, which volume is known (approximately 100 litres), covering a known sediment area of about 3116 cm^2. With these information the flux can be calculated. Its inner diameter is 63 cm and its height is 30 cm, of which usually 5 cm penetrate into the sediment while standing on the bottom.

The CBA is equipped with a multiparameter probe (Hydrolab MS5, OTT HydroMet, Kempten, Germany) for continuous monitoring of temperature, pH, conductivity, dissolved oxygen, and Eh in the chamber. A collecting system of water samples inside and outside the chamber (Vampire) is present, which consists in an electrical system of syringes working at programmable times. The benthic chamber was settled at the bottom of the reservoir for 24 hours to evaluate exchanges between water and sediment, and every pre-determined period has been activated the automatic system of syringes for the collection of water samples in time, together with the physical parameters. After sampling and recovery, data and samples were collected in order to be stored. The CBA have been designed to measure the release and adsorption of dissolved substances at the sediment-water interface. The assumption of flux measurement with this instrument involves establishing the concentration differences of a solute over time in a known volume, confined over a known area of sediment (Berelson et al., 1990).

The benthic fluxes of dissolved substances inside the benthic chamber (J) are calculated by dividing the concentration of each solute (Ci), as NH_4^+, NO_2^-, NO_3^-, carbonate species (TIC, alkalinity, CO_2), trace elements (including heavy metals), and organic pollutants at the time of the collection or measurement (t), multiplied by the volume of the benthic chamber (V) and divided by its base area (A) (Hammond et al., 2004) ($J = (\delta C_i/\delta t)V/A$ (modified by Munger et al, 2016)). All those parameters contribute to create a regression line which slope best fit the flow of the soluble in time. The obtained unit for the flux is mmol/sqm×d (or µmol/sqm×d), which express the amount of the analyte per surface over time. The benthic fluxes of each solute are consequently computed using a linear regression, and the measured flux is linked to the slope of the line based on the measured data of each sample. A further verification is performed evaluating the amount of a non-reactive solute inserted during the collection and analysed.

5.2.2.3 Sample preparation, instruments and analyses

Samples were analysed at the laboratories of Romagna Acque at Capaccio S. Sofia (FC) and of Ismar-CNR (Istituto di Scienze Marine), Bologna. A temporary laboratory for core extraction and interstitial water separation was organized in the Romagna Acque laboratories at Capaccio. Interstitial water extraction from core samples was performed as described in *5.2.2.1*. For each water sample from CBA and cores TIC (Inorganic Carbon) and TOC (Organic Carbon), anions NO_2, NO_3, PO_4, Cl^-, SO_4 , S and cations NH_4^+, Ca, Mg, Na, K have been analysed by a Dionex ICS 3000 at the Capaccio laboratories of Romagna Acque; Organic matter determination (Ctot, Corg, Ntot) of sediments and TIC and TOC in bottom waters, from the benthic chamber and of interstitial water, have been carried out by wet oxidation SRA OI model AURORA 1030W. Majors and trace elements (Li, Be, B, Al, V, Cr, Fe, Mn, Ni, Co, Cu, Zn, As, Se, Sr, Ag, Cd, Cs, Ba, Tl, Pb, Bi, U) for bottom waters of the Vampire sampler and interstitial were acidified by HNO_3 5% and stored at 4°C before analysis by HPLC and ICP-MS PerkinElmer. pH and conductivity were measured by Mattler Toledo T90 automatic tritator.

Water percentage of cores has been calculated as follows:

$$\%H_2O = 100\times(\text{wet weight} - \text{dry weight}) / (\text{wet weight} - \text{tare weight}).$$

All samples were dried at 60°C for 48h in an oven, and relative weights before and after were measured. The porosity has been calculated as follow:

$$\Phi = ((\%H_2O/100)\times2.5) / ((\%H_2O/100\times2.5)+1.027-(\%H_2O/100\times1.027))$$

Each prepared sample have been afterwards carried in laboratory in order to be analysed.

5.3 Results and Discussion

5.3.1 Cores

5.3.1.1 Sediment cores description

The sediments from the cores are extremely homogeneous from a lithological and textural point of view. They consist mainly of mud, extremely hydrated in the superficial levels. Increasing with depth, the sediment becomes progressively more compact and plastic, due to the progressive expulsion of the water content during the post depositional processes of the sedimentary layers, and with a higher coarse component. The two cores both display a uniform colouring (grey-greenish) along the entire sedimentary succession with streaks and local dots of black wet organic matter.

Porosity and water content are bounded and display similar patterns, showing a strong decrease in the first 4-5 cm and below a regular constant decrease with depth (Figure 5.2), due to the progressive compaction of sediments.

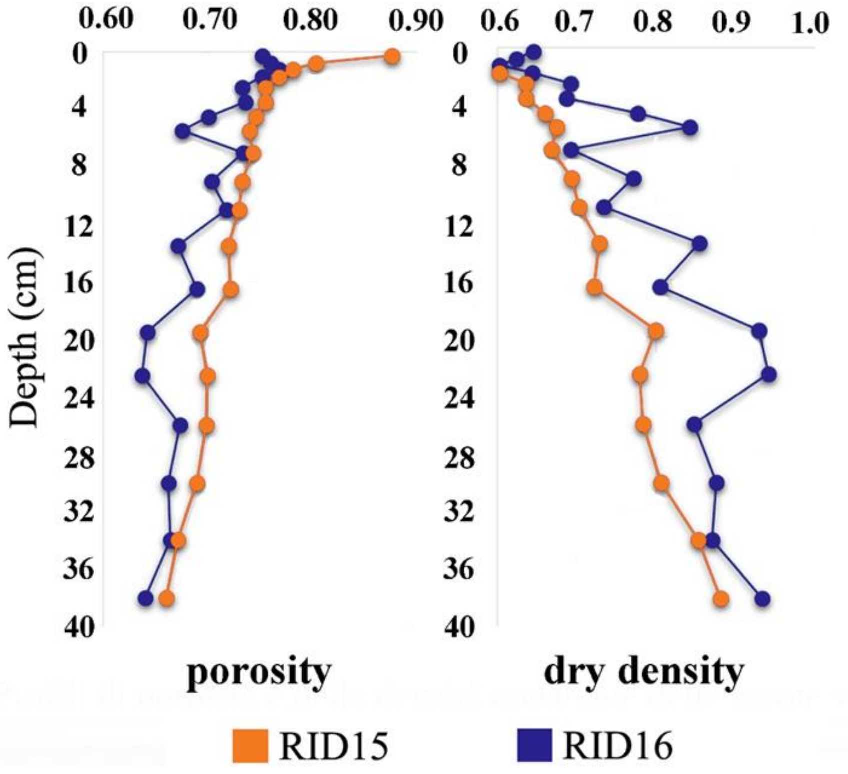

Figure 5.2, Graphs report porosity and dry density in depth for cores sampled in October 2015 (RID15) and in April 2016 (RID16).

The porosity values of the two analysed cores are quite high, with slightly higher values in the October 2015 core compared to the one sampled in April 2016. The porosity profile of RID15 is more uniform with a continuous and constant decrease throughout the sampled thickness, whereas the profile of RID16, is irregular and with several levels characterized by a lower average porosity. Both RID15 and RID16 show an exponentially decreasing trend of porosity, indicating that the compaction that occurs in the sediments is the most important process in the formation of the profile, which is not disturbed by any mixing or disturbance and that the sedimentation rate over the time considered remained constant (Audry et al., 2004).

5.3.1.2 Granulometry

The grain size of the cores is graphically presented in Figure 5.3 and provides an integration to the areal point of view already presented (Chapter 3, 3.3.1.1), although limited to the deepest part of the reservoir near the dam. This sampling station showed a main *silty* composition, a small fraction of *clay*, and almost inconsistent of *sand*, showing among the highest values of the whole area of the reservoir of *silt* for the superficial sediment.

Core sampled sediments are made of a finer fraction that varies from *clay* to *silty clay* in RID15, and from *silty clay* to *clayey silt* in RID16 (Shepard Diagram, Figure 5.3).

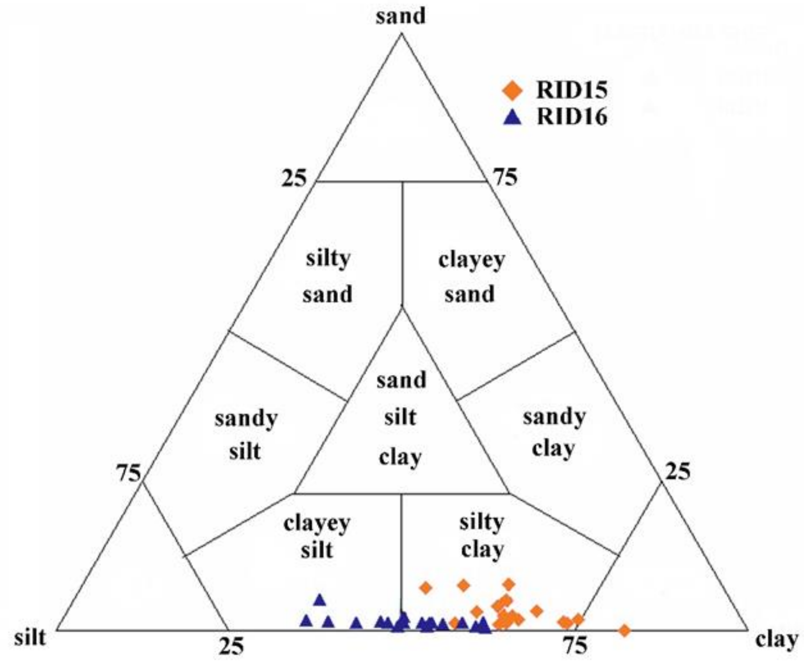

Figure 5.3, Shepard's diagram. Core sediment samples from October 2015 and from April 2016 are shown in orange and in blue respectively.

Profile's analyses show that the dominant grain size is mainly clayey (<0.002 mm), in both cores (Figure. 5.4), clearly more abundant in RID15 (all layers > 65 % clay) than RID16 (all layers >51% clay). The silty (0.002-0.06 mm) fraction is more abundant in RID16 (maximum 48 % silt) than

RID15 (maximum 32% silt). The sandy fraction is marginal in both cores (overall maximum of 7% sand).

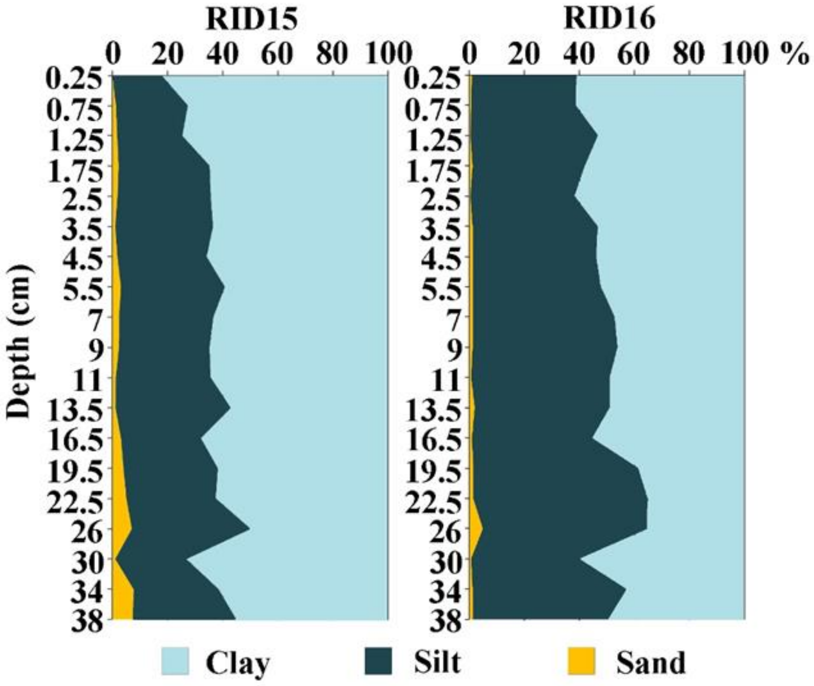

Figure 5.4, cores granulometry expressed in percentage (%); the total composition is divided in clay (light blue), silt (dark blue), and sand (yellow).

The prevalence of fine particles in the sampling station near the dam is consistent with other core sediments found in literature for reservoirs (United States Society on Dams, 2015). However, as already mentioned some differences are appreciable comparing surface sediments granulometry (Chapter 3, 3.3.1.1), displaying a main *Silty* granulometry in the centre of the reservoir and a *Clayey* one in the cores.

Overall major river inputs, reservoir maintenance, landslides or extreme weather events can lead to a supply of coarse material where usually is deposited the fine one, forming alternating layered profiles (Morris and Fan, 1998). In Ridracoli's bottom sediment the presence of coarse fractions limited to the lower parts of the cores could be linked both to a different flow rate of the Bidente river in the past, with a corresponding greater transport of coarser sediments, and to a different depositional regime within the valley. It may be due to the torrential regimes of tributaries which during the wettest winter season crate turbidity currents.

It has to be assumed that a deposit of finer material occurs in the basin over a period of calm. The alternation of silty and clayey levels suggests flood events in which the discharge reaches levels sufficiently significant to transport coarser (silty) sediments near the dam rather than deposit them upstream and in peripheral areas, where the coarser fractions are dominant (Chapter 3, 3.3.1.1; Shin et al., 2020). Furthermore, both RID15 and RID16 show a relative decrease in the porosity profile at the 20 cm layer in depth (Figure 5.2) due to the increase of the coarser (silty) fraction at about the same depth (Figure 5.4). In some levels, the profile trends of porosity are influenced by the granulometric variations, with high porosity average corresponding to a predominantly fine grain size and with lower porosity values to slightly coarser levels.

5.3.1.3 Cores chemical-physical parameters

The Eh values are generally negative with an average of about -308 mV in RID15 and -223 mV in RID16, the redox conditions are therefore reducing, remaining virtually unchanged with depth in both cores (Figure 5.5). It is interesting to note that in RID15 the highly negative Eh are observed also in the overlying water whereas in RID16 the overlying water records positive values, testifying for oxidizing conditions (Figure 5.5). The pH decreases from the water-sediment interface (pH= 7.3-7.4) to the deepest layer (pH=6.7), irregularly in RID15 and more regularly in RID16. Eh swings around values of about -300 and -200 mV. The lowest Eh values in the superficial sediment layer were found in October (RID15), when the lack of an effective hydrodynamic water circulation prevents good oxygenation of the lower part of the water column, thus favouring the decrease of the redox potential values in the interstitial water of the sediment (Miao S. et al., 2006). This behaviour is supported by pH values of RID15 and its irregular profile correspondent to lower Eh values.

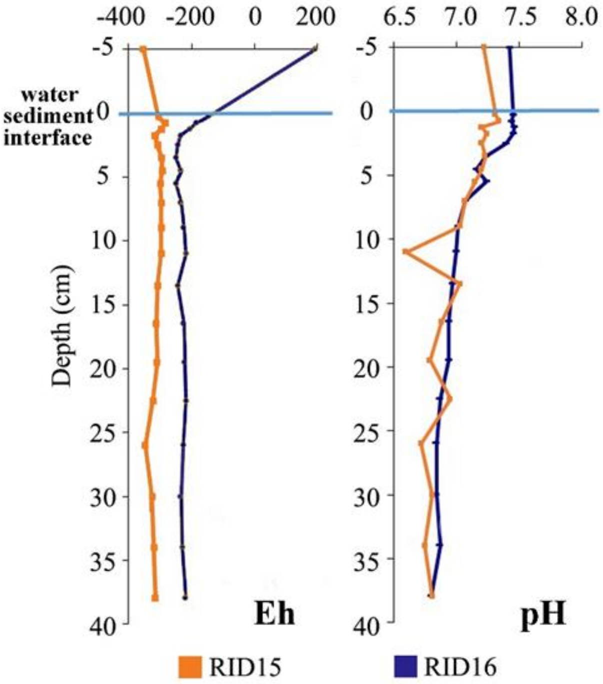

Figure 5.5, Graphs report Eh and pH values of October 2015 (orange) and April 2016 (blue) cores.

As already discussed (Toller et al, 2020), along the water column there is a seasonal variability that determines anoxia conditions at the bottom of the reservoir, common in eutrophic lakes (Beutel and Horne, 1999), and in the core sediments too (Figure 5.5), however without significant variations in depth. The accentuated anoxia measured in RID15, reflects the complete anoxia of waters, and in RID16, where the water column shows a good state of mixing and oxidation even in depth, the lack of stratification and the good state of oxidation of the waters affect the first superficial 2 cm and water-sediment interface (upper part of the blue line in Figure 5.5), but then rapidly decreases in depth.

The pH profiles of both sampled cores show slightly decreasing values in the first 10 cm with initial values greater in late winter (average value 7.2); below this depth tendentially constant pH values slightly lower than 7 are measured (average value 6.8), with a greater irregularity in the profile of the sediments sampled in October (Figure 5.5).

The pH trend and values suggest the presence of metabolization processes of organic matter in a reducing environment with the consequent formation of organic and inorganic acids (Lovley and Phillips, 1986; Forsberg, 1989). The highest values are found in the superficial layers, in contact with the bottom water and its acidity is then buffered by the water itself.

5.3.1.4 Core organic composition

The contents of total nitrogen (Ntot) and organic carbon (Corg) within the sediments sampled in the Ridracoli reservoir are high. Corg contents in both cores are found to range between 2.4 and 4 wt% (Figure 5.6), with a mean of 3 wt%, values slightly higher compared to the surface sediments (overall mean 2.4 wt%, Chapter 3) and to an average literature value for artificial lakes (of about 2%, Mulholland and Elwood. 1982; Ritchie, 1989). The mean concentration of Ntot is 0.26 wt% in sediments along the cores, with a minimum of 0.22 wt% and a maximum of 0.29%. Since the average value observed in superficial sediments within the entire area of the reservoir was about 0.4 wt%, in this station near the dam, is plausible a consumption of Ntot in the solid phase both in superficial and in deeper layers (Kemp and Mudrochova, 1972; Small et al., 2014). Corg and Ntot profiles show that the organic matter content is generally high and constant throughout the sampled sedimentary sequence (Figure 5.6), but the pattern is not uniform and shows in the first 16 cm a mean value of 3% starting from 2.5-2.6 wt% at the water-sediment interface, reactive layer due to organic matter degradation processes.

Corg and Ntot profiles show that the organic matter content is generally high, but some cyclic variations appears, particularly in the Corg profile (Figure 5.6). The high amount of organic matter is the reason for the development of the anoxic conditions (as observed by the Eh profiles, Figure 5.5)

(Sobek et al., 2009; Maerki et al., 2009). In both cores, a relative maximum value of Corg and Ntot is measured in correspondence with an increase in the coarser particle size fractions both at the same layer around 26 cm, probably due to an accumulation of organic matter deposited and quickly buried. This level probably corresponds to an event of great energy, flood or meteoric, in the reservoir system which resulted in a preferential accumulation in this position of coarser sediments and more organic matter.

Also the profiles of the Corg/Ntot ratio (Figure 5.6) show some high C:N values indicate the presence of organic matter of terrestrial or detrital origin whereas the low one could be related to organic matter of algal origin (Meyers, 1994; Kaushal and Binford, 1999). Although it is reported that this ratio could be affected by diagenetic reactions involving preferentially N-species (Fenchel et al. 1998), thus leading to a general increase in C/N ratio with depth (Gälman et al., 2008), in recently deposited sediments these changes could be of limited extent. Thus, the cyclic variations observed could represent the annual deposition, with lower values corresponding to the summer period when the autochtonous deposition prevail and the second with higher C/N corresponding to the winter/spring period with increased supply of organic matter of terrestrial origin, eventually transported by extreme event. These considerations are based on sediments accumulation rate of the reservoir which ranges between 12.5 and 25 cm/year near the dam and calculated on the basis of data of dam design studies, base at 468 m a.s.l. (Oberti et al., 1986) and bathymetrical data carried out in 2014 and 2019 (data not published).

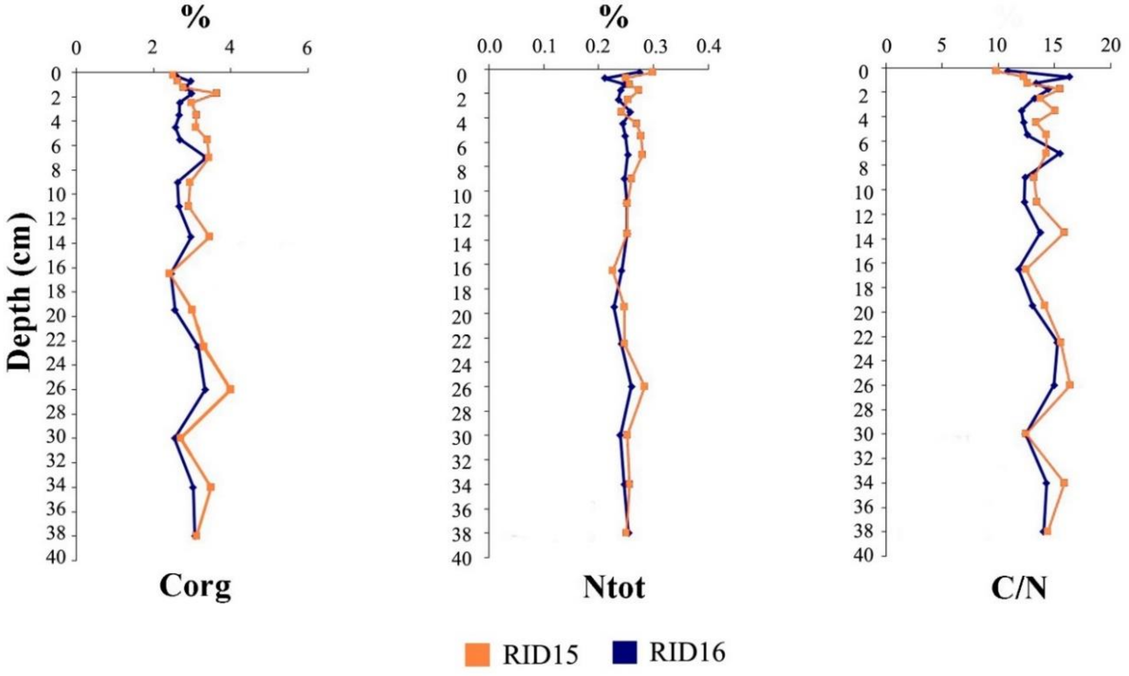

Figure 5.6, Graphs report the percentage of organic matter (Corg), total nitrogen (Ntot) and the ratio C/N of cores in depth.

Data collected above are consistent with the assumption of continuous inputs of terrigenous material that accumulates in the bottom sediments of the reservoir near the dam and which are assumed to increase if flood events occur. Close to the dam, where the sampling point is located, the fast burial processes prevent the organic matter rapid degradation in an oxygenated environment, favouring instead a slower degradation processes in an anoxic environment in depth (Maerki et al., 2009). This is also confirmed by the finding of vegetable remains along the entire sedimentary succession of both cores, even in the deeper layers.

5.3.2 Core chemistry composition

The total composition of sediments is SiO_2, Al_2O_3 and CaO, with an important fraction of a volatile compound (LOI), Fe_2O_3, MnO and Na_2O, in agreement with the chemistry of sediments found within the reservoir (Chapter 3, 3.3.1.2). Si and Al are both linked to the abundance of silicate minerals, and Ca is bound to the lithological background of carbonates. High values of LOI are due to the abundance of organic matter that comes from the surrounding or the reservoir, water present in the lattice of clay minerals, and carbon dioxide in carbonate.

The patterns of major elements SiO_2, Al_2O_3, TiO_2, MgO, Na_2O, and K_2O is similar to each other, all are conservative elements and follow the biogeochemical cycles and maintain a constant concentration along the core profiles, with slightly lower values below the sediment surface and around layers at 7, 17, and 34 cm of depth. CaO shows opposite trends, having higher values at the water-sediment interface and enriched in the upper 4 cm. The Fe_2O_3 pattern shows a similarity with major elements bound to silicate minerals, but with a maximum at the top of the core at the water-sediment interface, and the same behaviour is followed by MnO. It is important to remember that both elements are sensitive to the redox state of the environment, tend to be less mobile under oxidizing conditions (Davison, 1993; Linnik and Zubenko, 2000). P_2O_5 is present at low concentrations, mean of 0.15%, and its distribution is similar to other major elements, as conservative once, except for a peak at 2-3 cm layer, probably due to adsorption processes of iron oxides.

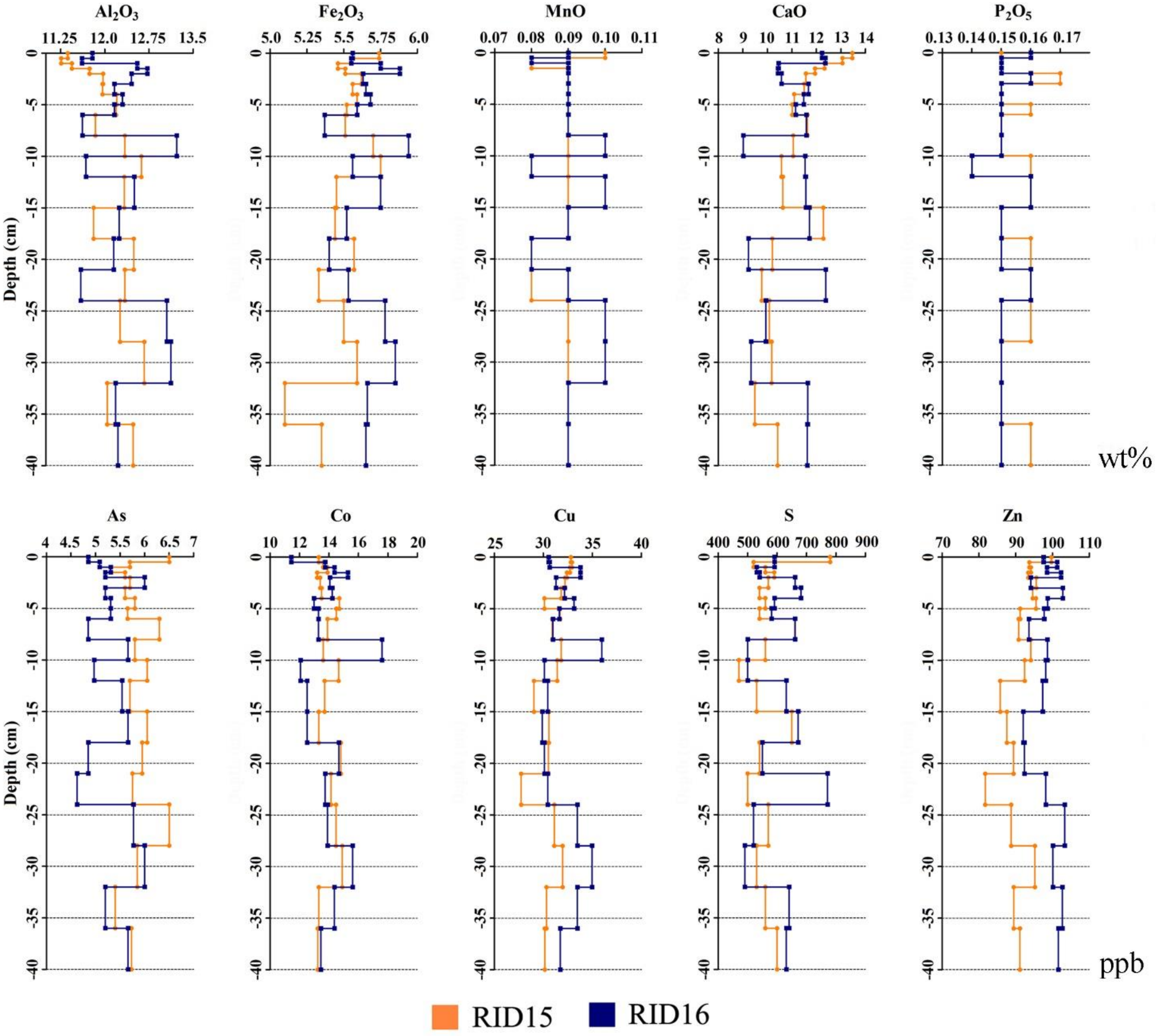

Figure 5.7, Grpahs report major (wt%) and trace (ppb) elements of sediments analysed on 2015 core (orange) and 2016 core (blue).

Overall, trace elements do not show any strong variation along and between the two cores, although small oscillations in bulk concentration are registered, as for Cu and S which both have higher values in the first 0-4 cm layer of RID15. In RID16 Fe_2O_3, Co, Cu, Ni, Pb, Rb show a maximum in the 10 cm layer. Finally, only Zn is found to have higher concentrations along the RID16 core compared to RID15. Among the above elements, Cu and Zn, as well as others like Cd, are weakly linked to the hydroxide, carbonate and organic phases, playing an important role in the explanation of observed water-sediment interface acidification and organic matter degradation (Figures 5.5 and 5.6 respectively), since sediments are subjected to exchanges with the overlying water and to a more marked bioavailability of elements.

5.3.3 Interstitial water chemistry and early diagenesis

Analyses of chemistry composition of pore water is fundamental to trace and understand the water-sediment interactions and the processes occurring within the sediment. Their chemical composition is a particularly sensitive indicator of early diagenetic reactions (Petersen et al., 1995), which shows changes in chemistry also when the solid fraction seems to not be affected (Berner 1980). The concentrations of analytes in the interstitial waters can change ruled by three main processes: (I) removal from the solution due to the precipitation or absorption on the surface of the solid phase; (II) release in solution by dissolution or desorption; and (III) diffusion transport of dissolved substances in interstitial waters through water-sediment interface (Schulz, 2006).

Early diagenesis is the biogeochemical process that takes place in the superficial sediments, activated by the degradation of the organic matter and by micro-organisms. It produces and consumes dissolved chemical species in water, using degradation products of the organic matter and final electron acceptors.

Oxygen provides the great part of energy for all the electron acceptors available (Claypool and Kaplan, 1974; Ciceri et al., 1992), but its effectiveness in depth depends on several factors, including the autotrophic production rate and the rate of fauna use, the O_2 demand from the solid phase and its permeability and porosity at the bottom.

In environments where deposition rates are high, content in organic matter is usually high too, and consumption of oxygen fast enough to be entirely consumed in few millimeters below the water-sediment interface (Jorgensen, 1983; Capone and Kiere, 1988).

Before describing the results, it must be noted that Ag, Be, Bi, Cd, Se, Tl, and U were always below detection limit, and Cr, Pb, and V have only few observations above their limits.

Ca^{2+} and Mg^{2+} increase in a regular way in depth, whereas Na^{+}, Cl^{-}, K^{+}, and SO_4^{2-} show a peak between 21 to 28 cm (Figure 5.8), with higher concentrations at the water-sediment interface.

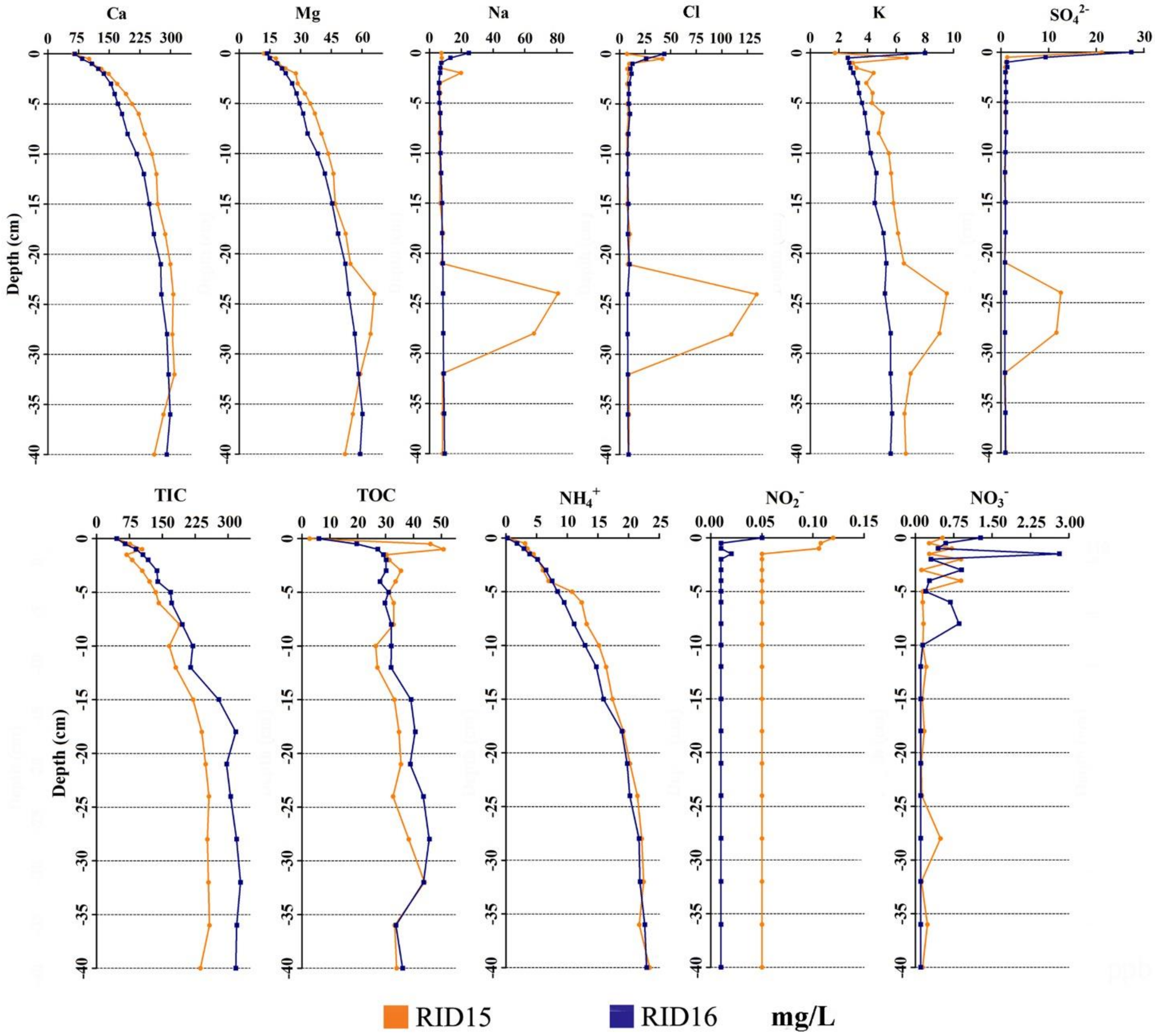

Figure 5.8, Graphs report the amount (mg/L) of the indicated elements of interstitial waters in depth.

The investigation of the first centimeters of sediments allows to identify the ongoing biogeochemical processes as the degradation of the organic matter (TIC, TOC). Among the degradation products in interstitial waters, TIC (Figure 5.8) shows a strong increase in concentration in depth, both in RID15 and RID16, with a low peak at 3–4 cm in late summer, due to the CO_2 produced by the microbial degradation of the reactive organic matter. This increase subsequently leads to TIC entry the water column. The TIC peak present near the interface in late summer indicates the formation of newly organic matter, particularly reactive, at the bottom, as consequence of primary production during the hot season. This deposit of newly organic matter, is, at the same time, confirmed only in RID15 by the TOC peak near the interface (Figure 5.8). TOC increases compared to waters of the reservoir and remains about 30 mg/L along the core. The increase in concentrations of TIC in the deeper layers of the cores in both late winter and late summer, instead, indicates a more gradual degradation process of less reactive organic matter, that results not disturbed.

It has to be noted, however, that the similar increase observed for Ca^{2+} and Mg^{2+} could indicate a contribution from carbonate mineral dissolution, favoured by the degradation of organic matter that in turn determines the formation of mildly acidic conditions (Berner, 1980).

NO_3^- decreases in depth along the water column until zero (Figure 5.8), which represent the base of the nitrate reduction zone. NO_3^- shows low concentrations (about 0.1 mg/L of mean), with a consistent irregular concentration only at the interface. Despite being a favoured electron acceptor (Sorensen et al., 1979; Capone and Kiene, 1988), in this situation nitrates do not appear to be significant of the carbon oxidation, due to their low concentrations along the water column and in interstitial waters (Kemp and Mudrochova, 1972). Nitrites show a peak immediately below the water sediment interface, both in RID15 and RID16, and this peak is greater in the late summer period (Figure 5.8). NO_2^- is present in the interstitial waters in the first 1.5 cm, while in the lower layers is less than the D.L. values, 0.05 mg/L and 0.01 mg/L in RID15 and RID16 respectively. This means that, at the time of sampling, ammonium ion released from sediments was oxidating to nitrite, and then to nitrate, once reached the oxidizing environment above the water column. The peak becomes greater in late summer, probably due to the increased nitrification process during this season.

Concentrations of NH_4^+ in interstitial waters (Figure 5.8) steadily increase in depth, reaching a maximum of 22.9 and 23.4 mg/L at the base of the sampled cores with similar intensity in RID15 and RID16. TIC values also increase in depth, but in this case, concentrations are lower in late summer compared to late winter.

Due to its low concentration, sulfide usually can be found only in the first 10 cm of depth (Molongoski and Klug. 1980; Smith and Klug 1981), corresponding to the most active layer in terms of sulfur reduction (Ingvorsen et al., 1981; Sass et al., 1997). In a reservoir environment the importance of sulfur reduction is linked to the presence of organic matter and to the availability of adequate amount of sulfide (Widdel, 1988; Holmer and Storkholm, 2001). Eutrophic lakes generally have high rates of this process in the upper sediment layer, but sulfur is also rapidly removed and methanogenesis becomes usually the most important process of mineralization in anoxic condition (Holmer and Storkholm, 2001). Sulfide tends to reach values close to zero in interstitial waters since used at the interface, showing concentrations of 21.1 and 27.3 mg/L in the 0-0.5 cm layer, but decreasing immediately below (about 1 mg/L) (Figure 5.8). In late summer sulfides decrease along water column near the bottom sediment due to the anoxic conditions, while in late winter they increase slightly near the water-sediment interface due to rising and oxidation of sulfides produced in the anoxic interstitial waters and the reduction of sulfides in the oxidizing environment of the water column. Dissolved sulfur in interstitial waters is supposed to precipitate together with trace metals and to form secondary minerals as metal sulfides, an intermediate product of early diagenesis. Early diagenesis is of concern as it contributes to the flows of dissolved substances between the water body and the sediment.

As regards trace elements, two main type of patterns (Schultz, 2006) have been observed (Figure 5.9): As, Co, Ba, and Sr show an increase in concentration in depth, while other elements such as Al, Cu, Zn, and Li, are more concentrated in the upper layers, within the first 5 cm, and displays decreased concentrations in depth. This trend can be explained by processes as precipitation, absorption or changes in the oxidation state of this elements, which reduce their concentrations in interstitial waters. This is also the same pattern of dissolved oxygen which has a greater concentration at the water surface and then is rapidly consumed in depth (Motion, 2007).

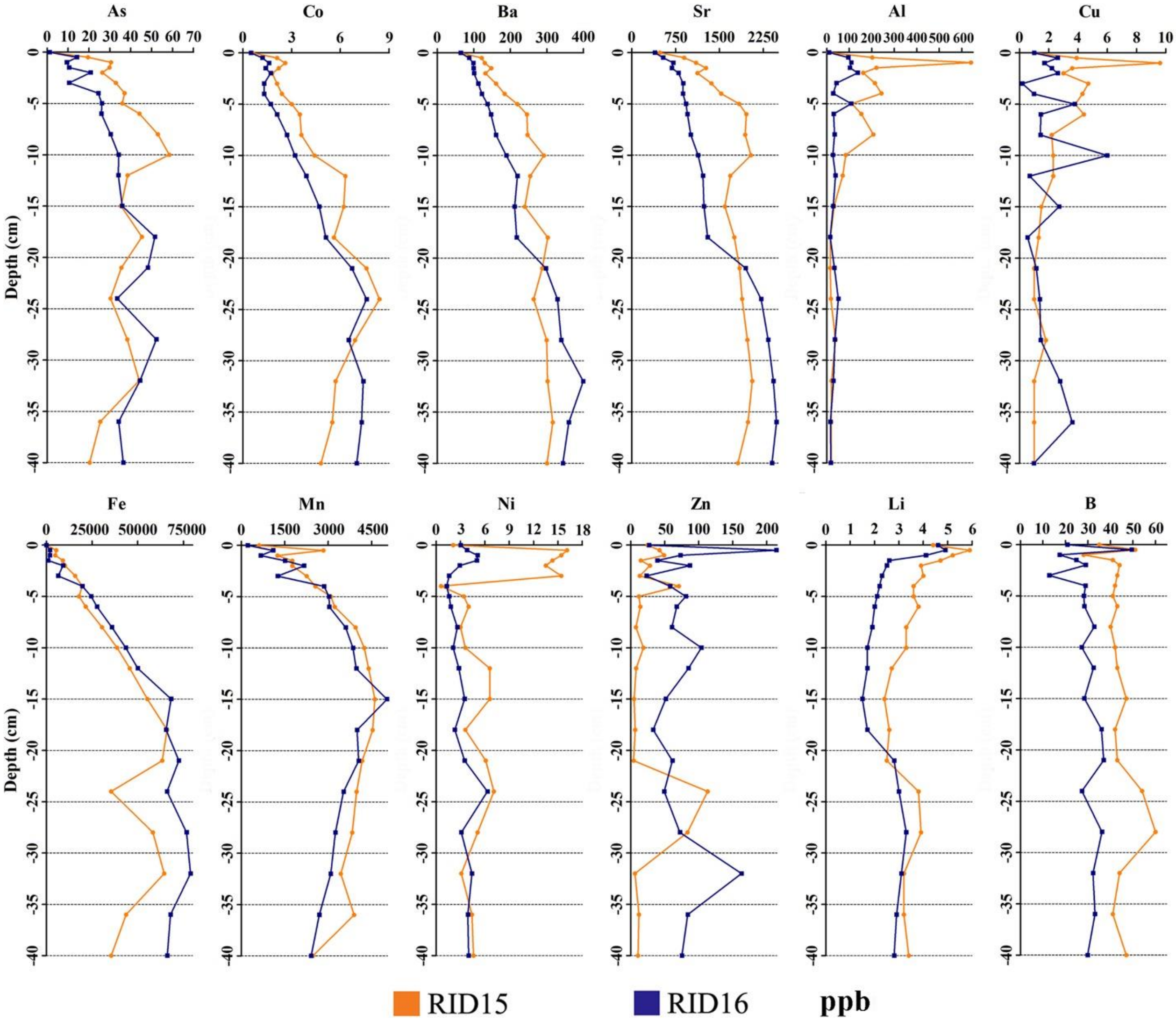

Figure 5.9, Graphs report interstitial waters' concentration (ppb) of trace element in depth.

High concentrations are found for Mn and Fe (supposed to be like Mn(II) and Fe(II) in this kind of environment), which are linked to degradation of organic matter, favouring reduction conditions (Figure 5.9), (Froelich et al., 1979).

Mn reduction is favoured by the higher redox potential than the one of Fe, oxidized in a shorter time respect to Mn (Balistrieri et al., 1992). Both increased in concentration until layers of 15 or 20 cm, similar trend in depth to TIC for Fe (lower values for RID15 then RID16) and to $NH_4^+$and TOC for Mn (approximately same concentration for RID15 and RID16). The absence of NO_3^- and SO_4^{2-} in interstitial water also is a further indicator of organic matter degradation in this environment. The organic matter oxidative reactions are usually mediated by bacteria through several electron acceptors which operate at decreasing redox potentials in depth inside the sediment matrix (Reimers et al. 2001). Under oxic conditions (DO> 2 mg/L), Fe and Mn occur in their oxidized insoluble forms (Fe-Mn oxides and hydroxides) in sediments, and the development of anoxic conditions (DO<0.5 mg/L) during summer, due to thermal stratification, leads to microbial reduction of Fe and Mn in solid fraction, releasing reduced and soluble forms of Fe and Mn, as well as As and Co, into water column (Davison 1993; Munger et al. 2016).

Another pattern of interest is the one of B and Li which show a constant trend in depth. The pattern of Zn, instead, is irregular, with a maximum between 25 and 32 cm, as for other observed analytes.

Most of analysed elements (Li, B, Al, V, Cr, Ni, Cu and Pb and, to a lesser extent, As, Co, Se, Zn, Na, K, F, and Cl) undergoes a first mobilization at the water-sediment interface, as can be confirmed by their positive concentration peak in interstitial waters, present in the first millimeters of the sediment. This elements mobilization is caused by the dissolution of more labile Mn and Fe oxides and hydroxides, due to the anoxic environment under the water-sediment interface and the desorption by clay minerals depending on the prevalence of the elements it the first (As, Cu, Co, Cr, Ni, Se, V, Pb, and Zn), or the other substrates (Al, B, Cl, K, Li, and Na). At greater depths solid continues to release some of mentioned elements, as confirmed by their increase in the interstitial waters, derived from the dissolution of Mn and Fe oxide/hydroxides, such as As and Co, from clay minerals, K and, to a lesser extent, Sr, and from carbonates Ca and Mg.

In the case of the Ridracoli reservoir, oxygen is used and completely consumed in the first millimeters at the sediment-water interface, as can be deduced from the trend of nitrates in interstitial waters which reach values close to zero in the 0-0.5 cm layer. Once the oxygen and nitrates are exhausted, the organic matter starts to mineralize at the expense of Mn and Fe oxides and hydroxides. In the case of Ridracoli reservoir a particular trend is registered, with a first peak of Mn and, to a lesser extent, of Fe dissolved immediately under the interface, due to the consumption of more available hydroxides and oxides, and a second peak, at a depth of 14 cm, for Mn, and of 20-30 cm, for Fe, due to the reduction of the more resistant Fe-Mn hydroxides and oxides, once the availability of sulphates is finished, to mineralize the less reactive organic substance. This second peak is staggered and oxides and hydroxides of Mn are reduced slightly earlier than those of iron, as can be seen from the depth of the maximum peak of Mn which is 14 cm, compared to the peak of Fe between 20 and 30 cm, due to the faster reaction for Mn than Fe.

5.3.4 Benthic chamber fluxes

The benthic chamber was placed for 24 hours in the deepest point of the reservoir near the dam, to measure the dissolved fraction flows at the water-sediment interface in late summer and late winter. Calculated flows of analytes are shown in Figure 5.10. Significant positive flux, meaning a release into the water column, emerge for TIC, Sr, Ba, B, Ca, and to a less extent for Na, K, Mg, Cl, NH_4^+, as well as low positive fluxes for Mn and Fe (Figure 5.9). Parameters with a negative flux include TOC, O_2, NO_3^-, NO_2^-, and in the late summer period also SO_4^{2-} (Figure 5.9), meaning in this case the mobility of analytes from water column to sediments

The positive values of Al, B, Ba, Ca, Cl, K, Li, Mg, Na, Se, and Sr measured at the water-sediment interface together with their increased concentrations in depth, mean a direct flow towards the water column in both seasons. The Zn shows an individual trend both in the interstitial waters and in the benthic chambers and any particular behaviour is difficult to be determined.

The organic matter degradation can be now confirmed by the positive fluxes of TIC and NH_4^+, which are the main chemical species product of the aerobic or anaerobic degradation of the organic matter. These positive flows are higher, for both chemical species, in late summer (RID15), due to the degradation of newly formed organic matter deposited on the bottom sediments, from vegetable remains, leaves, or algal bloom. The little differences in temperature at the bottom of the lake, between summer and winter, however, do not accelerate or increase organic substance degradation.

Our results show that the switch from positive to negative fluxes coincides with changes in oxygen concentrations and redox potential for only few analytes, such as Mn, Fe, SO_4^{2-}, and, in general, less stronger fluxes in RID16 than RID15. Higher metal release under reducing conditions and lower release under oxidizing have been observed in many other studies on metal fluxes (Debroux et al. 2012; Beutel et al. 2020).

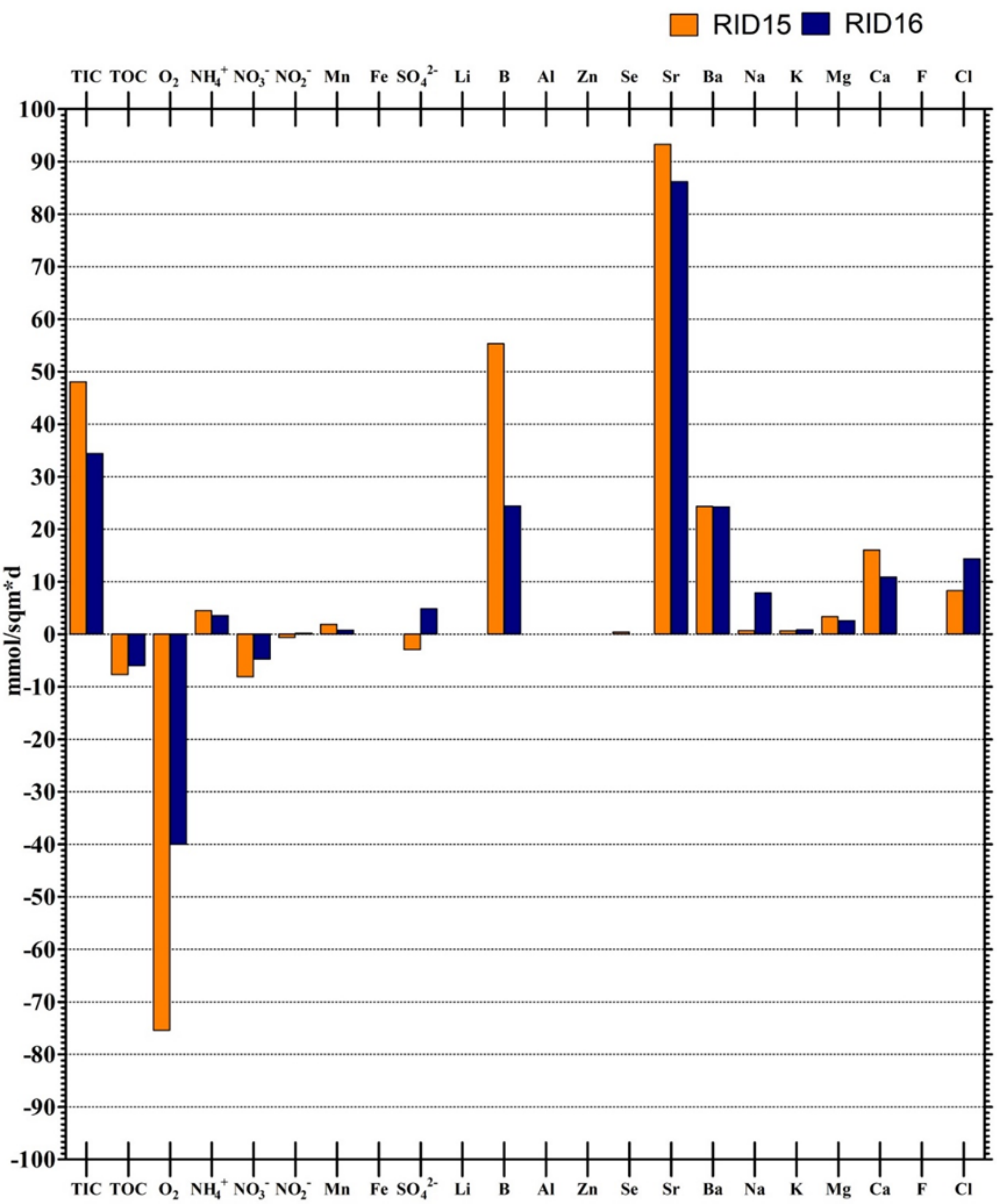

Figure 5.10, Graph showing the positive and negative fluxes at water-sediment interface. Values from October 2015 (RID15) and from April 2016 (RID16) campaigns are represented in orange and blue, respectively.

The concentrations profiles already described for interstitial waters agree with TIC, Ca^{2+}, Fe^{2+}, Mn^{2+}, and NH_4^+ flows, which are characterized by an increased concentration in depth, with a relative diffusion upward. TIC, Ba, Ca, and Sr are bound to the dissolution of calcium carbonate due to the acidification that happens at the bottom of the solutions bound to the organic matter. On the opposite, NO_3^- negative values suggesting its involvement in the nitrification reactions described in interstitial water. The decreased NO_3^- in depth, in fact, is in response to denitrification processes in deeper layers. Consequently NH_4^+ flows are positive and tends to increase in depth in the pore water. Nitrification occurs in the first layer of sediment and is a significant source of NH_4^+, which comes from the decomposition of the organic matter, following a transformation in NO_3^- by nitrification and entering the water column. Nitrites are an intermediate product in the nitrification process, for this reason and also for the inconsistence of their flows, they are not taken into account in the measurements of benthic flows except as indicators of nitrification processes. In the case of the Ridracoli reservoir, the nitrite flows indicate a safe nitrification in late winter (positive flow) and a less intense one in late summer (negative flow).

At water-sediment interface the flows of the final electron acceptors, used by micro-organisms to mineralize the organic substance, are affected by different environmental conditions on the bottom sediments at the time of the measurement. Flows of oxygen (O_2) and nitrate (NO_3^-) are negative since both consumed by microorganisms at the bottom to degrade the organic matter.

The flows of two elements of concern as Mn and Fe are positive, with this latter very low, both enter the solution by reduction of their oxides and hydroxides explaining the concentrations found at the water treatment plant downstream of the collected water of the reservoir (Toller et al., 2020).

Mn behaviour in freshwater differs from the Fe ones because oxidizes more slowly (Davison 1993). Thus, fluxes of reduced Mn into the overlying water column can persist even when the water column is oxic, and also concentrations of Mn double during the 24 hours of the sampling. Other elements that increase in time are Ba, but only of 10 µg/L, and in a more irregular way Fe, Sr and B. Lower values are observed for Al, and swinging ones of Li and Zn.

In the case of SO_4^{2-}, the flows, negative in late summer and positive in late winter, are attributable to the consumption by reduction of sulfates, used in the degradation of the organic substance. In late summer, degradation processes of the newly formed reactive organic matter consume more sulfate than that one produced by oxidation of sulfides, while in late winter the opposite process dominates due to a less marked degradation, caused by the lower neoformation of organic matter at the bottom and by the oxic environment near the interface.

For each species discussed above, the negative or positive flow is more intense in late summer probably due to the increased contribution of more easily degradable organic matter (of algal origin) deposited at the bottom in summer. Furthermore, the slightly higher flow of Mn and Fe in this season compared to late winter is also due to the most extreme dissolution of the oxides and hydroxides of these two elements under anoxic conditions, and the persistence of anoxic water at the bottom (Toller et al., 2020).

5.4 Conclusions

The characterization of sampled waters of this study, interstitial and from the benthic chamber, is in agreement with the ones from the reservoir, showing a Ca-Mg-HCO_3 composition, and only a little pauperization in SO_4. Comparing interstitial and benthic chamber water samples, the first ones seems enriched in dissolved components, with an increase of both inorganic (TIC) and organic carbon (TOC). It also does not display SO_4^{2-} and NO_3^- but NH_4^+ contents. These observations suggest that interstitial waters are in an environment characterized by anaerobic conditions at the bottom of the reservoir caused by the degradation of organic matter and features as a modification factor of the reservoir water chemism. High concentrations of Fe and Mn confirms this behaviour, and redox conditions and the absence of S favours the presence in solution of As, Co, Cu, Ni, Zn.

The concentration profiles reflect the strong influence of the redox status of the sediment-water interface. Ridracoli reservoir is a dynamic water body which volumes change seasonally in equilibrium to its management in withdrawals and electricity production, as well as climatic conditions and water inputs. Profiles provide by the present study shows that some chemical species are strongly concentrated at the water-sediment interface, demonstrating the importance of redox processes in this layer, and promoting nutrient mobilization and/or retention. The diffusion seems to be the main vector of transport of species, not only at the sediment-water interface, but also in depth along the sediment profiles. The observed fluxes, the steady-state conditions of the diffusional processes, and bioturbation events that also occur at the bottom, may also remobilize elements to the water column.

The sediments deposited close to the dam are fine and homogeneous from a granulometric and geochemical point of view, with only some terrigenous organic matter that is deposited in some preferential layers. The sampled sediments are in conditions of anoxia, which become more and more accentuated in depth and stronger in the late summer compared to late winter. The two cores (RID15 and RID16) are characterized by fine sediments generally rich in organic matter only partially degraded or under slow anoxic degradation.

The study of early diagenesis processes has highlighted the presence of an intense degradation process of the organic matter, along the first 40 cm, consumption of dissolved oxygen, near the water-sediment interface, nitrate reduction in the first centimeters, reduction of oxides and hydroxides of Mn and Fe, both on surface and in depth, and even sulfide reduction active in the upper layers. This early diagenesis is stronger at the water-sediment interface in late summer, due to the deposition of newly formed organic matter and to dissolution of Mn and Fe oxides and hydroxides in the anoxic environment.

The early diagenesis, witnessed by the modification of interstitial waters composition, have also generated positive flows towards the water column, greater in late summer and lower in late winter, of TIC, Mn, Fe and of other elements (Al, B, Ba, Ca, Cl, K, Li, Mg, Na, Se, and Sr). The same processes generate a significant flow directed towards the sediment for dissolved oxygen and nitrate, with a greater extent in late summer season. TOC shows negative flows in both the two seasons and it is probably due to the fast mineralization on the superficial sediment and incorporated inside the benthic chamber during the analysis. SO_4^{2-}, which is a little absorbed in late summer, is consumed in anoxic environment and released in late winter due to the new formed oxic environment.

The combination of these processes of release and absorption and oxic and anoxic conditions has created a particularly critical situation for the reservoir water potability and issues for its management. In late summer, the thermal stratification occurs and a consistent release from the sediment of Mn and Fe, and less of PHEs happen, creating an anoxic environment in lower portion of the water column rich in metals and reduced nitrogen. In late winter on the other hand, the presence of an almost complete mixing of the water column, dilution over the entire water column, together with the lower consumption of oxygen and nitrate and lower releases of metals at the water-sediment interface, create an oxic and metal-poor water body with good quality standards for potability. From this context it is to state that there are no water withdrawal problems throughout the year, and only in late summer, when the lake level is at its annual minimum, the withdrawals of water for potable uses should be drawn above the anoxic layer of the water column.

Chapter 6 - Leaching test and sequential extraction on sediments from a Large Dam reservoir on northern Apennines, Italy.

Abstract

The concentration of elements in sediments is an important aspect of the quality of water ecosystems. Sediments from the Ridracoli reservoir on northern Apennines in Italy were studied to evaluate the degree of contamination, elements accumulation and distribution, and the ecological risks related to trace metals by combining a geochemical characterization with the assessment of the bioavailable forms of trace metals. With this purpose of speciation, mobility, and bioavailbility, sediments within the area of the reservoir were studied through leaching test and sequential extraction procedure. We found that sediments are homogeneously distributed through the area of study, with a prevalent composition of clay minerals, carbonates and Fe-Mn secondary minerals. We observed a well define partitioning of elements between the different fractions, peculiar for each sampling station, both regarding the spatial and in-depth distribution. Station near the dam and in the centre part of the reservoir presented more mobile sediment unlike the more deepest and external ones. Leaching test and PHAs extraction also showed a great quality of sediments from an environmental point of view, with concentrations of those elements considered toxic and/or carcinogenic below the limits proposed by the law.

Keywords: Geochemistry – Artificial Reservoir – Reservoir Sediments – Sequential Extraction – Heavy Metals – Sediment Quality Assessment

6.1 Introduction

Sediments are an important and useful matrix to evaluate the status of an aquatic ecosystem with regard to metals and nutrients, playing an important role in elements circulation in water environments (Alpitz, 2012; Palma et al., 2014; Ghaleno et al., 2015). Elements are constantly moving in a reservoir; metals which enter the water body from tributaries in an undissolved form sink to the bottom, accumulating in the sediment (Dabioch et al., 2013) and during the transport they may undergo partial dissolution and enter in the dissolved fraction (Calmano et al., 1993; Linnik and Zubenko, 2000). Balance between water column and bottom sediments is in constant equilibrium, but several processes and events may cause an imbalance. The environmental importance of sediments is that they represent a sink for elements, but can also act as a secondary source of contamination when environmental conditions change (e.g. pH, redox potential), releasing contaminant in the water column.

Trace metals are included in environmental monitoring programs given their bioaccumulation and possible toxic effects on aquatic organisms (Li et al., 2015; Arfaeinia et al., 2016). The release of any substance accumulated into the bottom sediment into water column could interfere with the water body quality, for example releasing nutrients, such as phosphorus and nitrogen, which could affect the trophic state of the lake, or represent a source of potentially harmful elements (Zerbe et al., 1999; Linnik and Zubenko, 2000). Metals can occur in sediments in various forms, in association with different geochemical phases that determine their mobility, bioavailability and potential toxicity (Yu et al., 2001). Therefore, knowing their total content in the sediment alone is not exhaustive to assess their potential ecological risk for aquatic organisms (Baran and Tarnawski, 2015; Botwe et al., 2017). To date, it is widely recognized that distribution, mobility and bioavailability of heavy metals and radionuclide in the environment depend not only on their total concentration but also on the association form in the solid phase to which they are bound. Sediments samples have been found as a carrier of most metals and some elements may be recycled through biological and chemical reactions within the water column.

Environmental studies on soil and sediment are often based on the use of leaching or extraction procedures, single or sequential extraction, which enable to investigate how an element is bound in sediment or evaluate the bioavailable fraction, often required by environmental policies (Sahuquillo et al. 2003; Joksič et al., 2005). These approaches enable the determination of elements distribution within different sediment fractions, their mobility and consequent bioavailability. A variety of methods based on sorption and desorption experiments have been used to determine the potential mobility and changes of interaction over time of pollutants in soils and sediments (Kennedy et al., 1997; Rauret et al., 2000). Metal ions in sediments and soils are partitioned between different phases, as organic matter, oxides or hydroxides of iron, aluminium and manganese, phyllosilicate minerals, carbonates and sulfides. Metal free ions are retained on these solid phases by different mechanisms, such as ion exchange, outer and inner sphere surface complexation (adsorption), precipitation or co- precipitation (Rate et al., 2000). The leaching tests are useful as they allow the evaluation of the normal release and the stability of any type of analyte from a solid phase in contact with a liquid one, represented by the leaching agent (EN 12457-2, 2002; Lécrivain et al., 2019). A further methodology, the sequential extraction, was first designed for the selective removal of trace elements bound to operationally defined sediment fraction, by using different leaching agents (Tessier et al., 1979; Salomons and Förstner, 1980). Although these procedures can provide comparative information on the mobility of trace metals in sediments with changing environmental conditions, such as pH or redox potential, and can help to determine the relative contribution of mixed pollution sources to this mobility- Although not completely specific they provide useful insight about the mode of occurrence of chemical elements in a solid matrix. Sequential extraction provides details about origin, modes of occurrence, biological and physicochemical availability, mobilization, and transport of trace metals, and has been shown to provide a convenient means in determining the metals associated with the major accumulation phases in sedimentary deposits.

Fractionation is usually performed by a sequence of selective chemical extraction techniques, which include the subsequence removal of these phases and their associated metals. The information obtained by the BCR technique (proposed by European Community Bureau of Reference), that allows to investigate metal partitioning and thus identify different fractions of samples (Rauret et al., 1999; Sahuquillo et al., 1999), is operationally dependent, and its application to field samples taken at different steps after a contamination event can also provide valuable data on dynamic processes (Brady et al., 2003).

The aim of this study was to evaluate the bottom sediment quality of the Ridracoli reservoir (Emilia-Romagna, Italy). We determined levels, accumulation and distribution of elements in sediments and understood the contamination and the potential mobility or toxicity of elements within the area of study, as well as any differences in sediments, in depth and in the area of the reservoir, by the geochemical analysis of total and bioavailable metals.

6.2 Material and Methods

6.2.1. Study area and sampling sites

The study area is the Ridracoli reservoir, located on Apennines at 480 m a.s.l. in Italy, built about 40 years ago and storing a volume of 33.06 × 10^6 m^3 of fresh water on a water surface of about 1035 km^2 (Figure 6.1). The Ridracoli catchment covers an area of 37 km^2 and is closed downstream by the dam which since 1982 stores water for drinkable usage and electricity production. The construction of the dam changed the area of study in a short time, filling the valleys with water and modifying the environment downstream and upstream the dam, in particular eroding and transporting sediments, in time collected and deposited inside the basin. The reservoir shows a seasonal water level fluctuation ranging from a maximum of 80 m to a minimum of 50 m close to the dam. The reservoir has an irregular shape, controlled by the morphology of the filled valleys with two main branches: the Bidente di Ridracoli southern, the main ones, and the Rio Celluzze western (Figure 6.2). This minor branch receives waters from an indirect catchment by a gutter gallery that acts as an important water input, helpful to fill the reservoir which usually reaches the conditions of complete filling in March or April with even overflows events on the top of the dam.

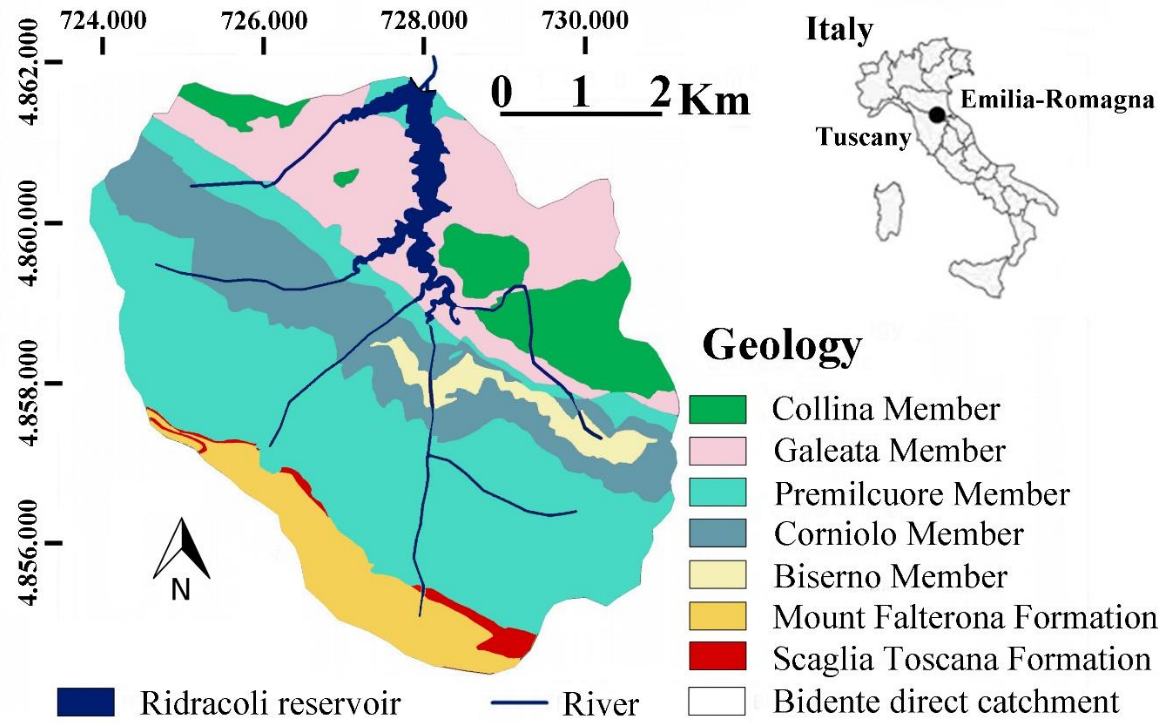

Figure 6.1, Ridracoli reservoir location and catchment morphology and simplified geology (coordinate system WGS84-UTM zone 32 N; geology more details http://ambiente.regione.emilia-romagna.it/en/geologia/temi/geologia/geology?set_language=en).

The reservoir is a fundamental part of the management of drinking water in Romagna, reaching a maximum of one million people and 48 municipalities with drinking water supply during summer. It is managed by the Romagna Acque Società delle Fonti S.p.A. company which own the local water network, including water treatment plants, laboratories for water quality monitoring and control, wells, and other water storage systems to better administer the water supply of the area.

The reservoir catchment is the uppermost sub-catchment of Bidente River, it is part of the Foreste Casentinesi and Mount Falterona National Park and is characterized by a mountainous area with rocky steep slopes and densely wooded forests. Considering bedrock geology, in the entire area of the catchment and surroundings the Successione Romagnola outcrops, in particular the Marnoso Arenacea Formation (MAF), Mount Falterona Formation (FAL) and Scaglia Toscana Formation (STO). STO is made of dark red, brown, grey and greenish clays, and pelagic marl with chipped fracture (Upper Eocene – Lower Miocene), and FAL of principally arenaceous turbidites of the Upper Oligocene, both part of the upper portion of the Successione Toscana (Mutti and Normark, 1987; Martelli et al., 2005). The MAF is a thick turbiditic unit deposited in the Tuscan-Umbrian portion of the Inner Periadriatic basin, formed during the Miocene, and includes 14 different members. Among them, in the catchment area, 5 different members outcrops: Collina, Galeata, Premilcuore, Corniolo, and Biserno, in descending order of age. In the southern part of Ridracoli catchment two other formations are present: Mount Falterona and Scaglia Toscana (Figure 6.1). The contact direction of these two groups of formations is from northwest to southeast, following the elongation of the basin in front of the Apennine orogenic wedge.

6.2.2 Sample collection and chemical analysis

The studied sediments included surface sediments and historic one. Surface sediments were collected at 6 sampling station (Figure 6.2) selected according to the results of previous studies (see Chapters 3 and 4). The first 0-10 cm of sediment was collected by a Van Veen grab mounted on a boat and installed on a winch. Historic samples were selected from those recovered using a gravity core (see Chapter 5) at a sampling station close to the dam (Figure 6.2). The 6 sampling stations are distributed within the area of the reservoir in order to collect sediments from different areas and from the station nearby the dam. From this latter station 3 samples have been collected: at water-sediment interface, at 18-21 cm and at 36-40 cm. Samples were taken from 6 points respectively from south to north: the east branch of the bifurcation of the Bidente di Ridracoli, the west one, in the area of the bifurcation, center of the reservoir, from the north-west area of Rio Celluzze, and in the central area near the dam.

Samples were collected with two different campaigns: in June 2018, for the superficial sediments, and in April 2016, for core sediments.

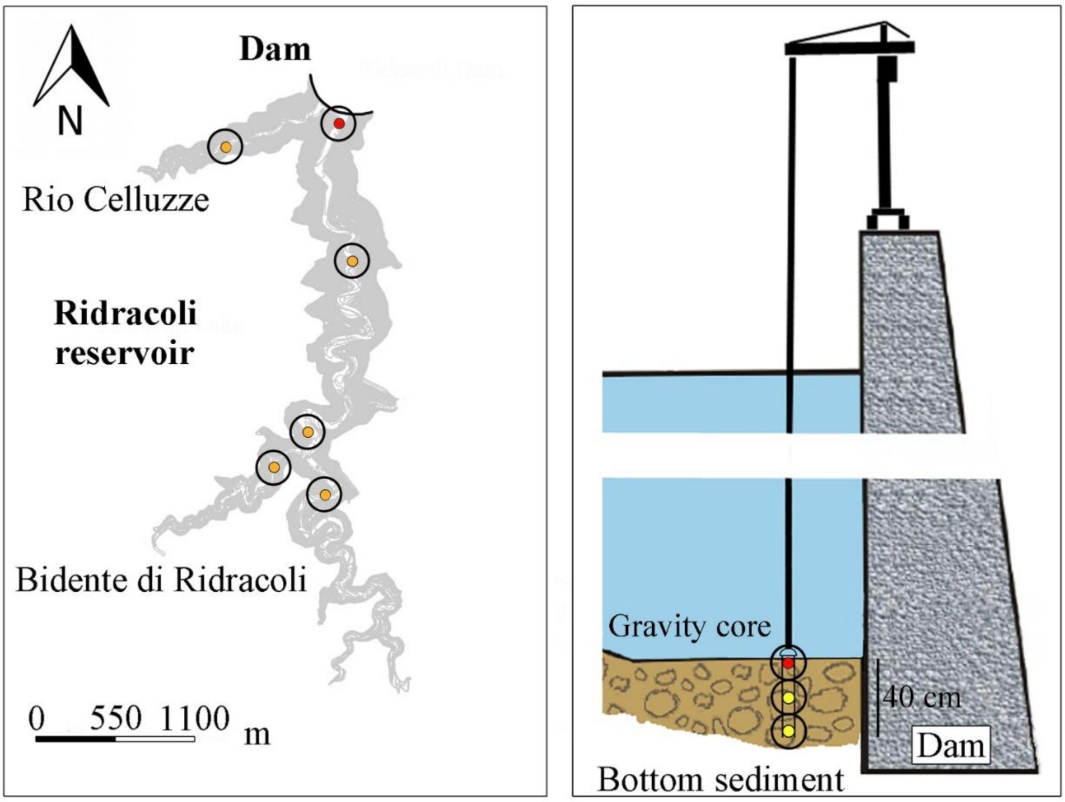

Figure 6.2, Ridracoli reservoir samples station location within the catchment and in depth.

All samples were cleaned from vegetable remains and placed in plastic containers, transported to the laboratory, and stored at +4°C for sample treatment and further analyses. Samples were dried in an oven at 40 or 60°C and sieved or ground in an agate mortar depending on the subsequent analyses. The X-ray fluorescence PANalytical Axios spectrometer with Rh tube was used for the detection of major and trace elements for the total composition of sediments (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pb, Th, S, Br, Mo, Sn) on pressed powder pellets, following the matrix correction methods (Franzini et al., 1972, 1975; Leoni and Saitta, 1976; Leoni et al., 1986). The XRF data were obtained at the Department of Biological, Geological and Environmental Sciences (BiGeA), in Bologna (Italy). In addition, these samples were digested using an aqua regia attack (AR fraction). This component 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 applied 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 of the same sample with several consequential steps in order to identify the different fractions. The summary of the chemical attacks on the samples and methodology plan includes a first step of water, acid soluble, carbonate, and exchangeable fraction, such as those observed and present in carbonates and labile organic compounds (step 1), operationally consisting in adding a 0.11 M acetic acid solution to 1 g of sample and shaking at room temperature for 16 h. This first phase is followed by a second step in which the oxidable fraction, bound to reducible Fe^{3+}- Mn oxides and hydroxides, is isolated by using a 0.5 M of NH_2OHCl solution (adjusted to pH 2 thanks to HNO_3), added to the residue sample from step 1 and shaking at room temperature for 16 h. A third step consists of oxidizable fraction/bound to organic matter and sulfides (step 3), where the residue from previous steps is added with 8.8 M H_2O_2 solution, digested for 1 h at 90°C, and then added with 1 M NH_4OAc. The residual (fraction Res), representing the fraction of the element bound to the sediment-forming minerals, is defined as the difference between the total content of the element (XRF) and the sum of the first three steps (Res = XRF - ∑[step 1 + step 2 + step 3]). Blanks (e.g. reagents without the sediment matrix) were run in parallel with each batch of sediment sequential extraction procedure to check the accuracy and precision of the leaching test and BCR extractions., both performed at the laboratories of Ravenna Environmental Sciences Campus of UniBo (Italy).

For leaching test was used a UNI EN 12457-2 (EN 12457-2, 2002), a test of compliance for the leaching of granular waste and sludge, which in this case has been adapted for bottom sediments assessment. The test is based on a one stage batch at a liquid to solid ratio of 10:1 for materials with particle size below 4 mm, without or with size reduction. Samples have thus remained in deionized water for 24 hours under mechanical oscillation in a controlled environment.

A further extraction has been done on an additional aliquot from two samples for analysis of polycyclic aromatic hydrocarbon (PAHs), hydrocarbons organic compounds containing only carbon and hydrogen found in coal and tar deposits, that are Soxhlet extracted with an acetone/cyclohexane (1:1) solvent mixture and analyzed by GC-MS after silica gel clean-up (Fabbri et al., 2013). Analysis were conducted using a gas chromatograph Agilent 6850 (GC-MS) connected to a 5975 Agilent HP quadrupole mass spectrometer at the laboratories of Ravenna and Rimini Campus of the University of Bologna.

6.3 Results and Discussion

6.3.1 Geochemical characterization of sediments

Table 6.1 reports the geochemical composition of the Ridracoli reservoir sediments for both total and AR concentrations. The range of variation for major and trace elements are limited, suggesting a general homogeneity for the composition of the sediment within the reservoir. Further studies on the characterization of sediment on a larger dataset which provides key information on the composition of sediments have been already seen in Chapter 3 and Chapter 4.

The 8 sediment samples from the 6 stations within the area of the reservoir are composed by a content of 46.1 ± 1.5 wt.%, 13.8 ±0.8, and 9.1 ± 1.8 wt.% of SiO_2, Al_2O_3, CaO respectively (Table 6.1), which form the majority of the sediment, accounting for about 69 % by weight of the sediment. To these is added the volatile fraction (LOI) which represents about 18.3 ± 1 wt.% and is mostly formed by both carbonate and organic matter content. The SiO_2 and Al_2O_3 mostly reflect the clay mineral contribution whereas CaO, not homogeneously distributed within the reservoir, probably reflects the direct geological source inputs of carbonate rocks of the different members that outcrop in the area (Figure 6.1). We focused the discussion on selected elements: Fe, Mn, Cu, Co, Cr, Ni, As, Pb, and Zn; the first relevant elements in the area, and the others as potentially harmful elements (PHEs). As highlighted in Chapter 3 and Chapter 4, no element exceeds the legislative limits, and generally reflect the concentrations of natural sediment influenced by geology.

Table 6.1, Statistical parameters calculated for the analysed elements for Total and Pseudo total composition: median, median absolute deviation (MAD), minimum (min), and maximum (max).

XRF	min	Median	MAD	max	Aqua Regia	min	Median	MAD	max
Major oxides (wt.%)					Elements (%)				
SiO_2	42.3	46.1	1.5	48.6	Al	1.18	1.91	0.11	2.03
TiO_2	0.57	0.62	0.04	0.69	Ca	4	6.2	1.24	9.01
Al_2O_3	12.2	13.8	0.8	14.7	Fe	2.09	3	0.18	3.25
Fe_2O_3	4.9	5.7	0.3	6.3	K	0.2	0.27	0.01	0.3
MnO	0.07	0.09	0.01	0.11	Na	0.008	0.01	0	0.01
MgO	3.2	3.5	0.1	4.0	Ti	0.006	0.011	0.002	0.024
CaO	6.3	9.1	1.8	11.6	S	0.05	0.065	0.01	0.07
Na_2O	0.65	0.84	0.15	1.16	Trace elements (ppm)				
K_2O	2.4	2.6	0.1	2.8	As	3.6	4.6	0.2	5.9
P_2O_5	0.14	0.15	0.00	0.18	B	7	8	1	11
LOI	15.8	18.3	1.0	20.5	Ba	81	121	9	140
Corg	2.0	3.5	0.6	4.9	Bi	0.2	0.4	0.1	0.5
N	0.2	0.2	0.01	0.3	Cd	0.2	0.2	0	0.3
Trace elements (mg/Kg)					Co	10.7	13.5	0.9	14.6
As	4	5.1	0.6	7	Cr	40	58	4	63
Ba	374	406	31	464	Cu	16.7	28.6	2	31.3
Ce	56	60.7	4.2	76	Ga	4	6	0	6
Co	13	17.5	2.4	20	Hg	0.02	0.04	0.01	0.06
Cr	103	119	14	142	La	11	13	1	14
Cu	30	32.8	2.6	39	Mg	1.05	1.33	0.05	1.4
La	25	33.6	2.9	41	Mn	373	626	49	755
Nb	11	14.7	0.5	16	Mo	0.3	0.4	0.1	0.7
Ni	66	82.7	12.3	98	Ni	44.9	63.8	2.2	70.5
Pb	19	22.8	1.3	26	P	0.052	0.061	0.002	0.064
Rb	84	108.8	11.1	133.5	Pb	16.4	19.1	1.1	20.2
S	385	589	57	980	Sb	0.3	0.4	0	0.4
Sn	3	5.0	1.5	12	Sc	3.7	6.3	0.3	7.5
Sr	185	227	26	297	Sr	132	194	31	253
V	80	91.0	8.2	111	Tl	0.1	0.2	0	0.3

Y	20	26.8	1.1	30	V	32	40	3	44
Zn	59	91.4	4.0	102	Th	4.1	5.5	0.6	6.6
Zr	110	129	13	148	Zn	65	85	6	94

The presence of high amounts of clay minerals in this area, as highlighted by the concentrations of Al_2O_3 and SiO_2, might contribute to partially adsorb metals to sediments, acting as a geochemical barrier and thus determining an increase of PHEs concentrations. The presence of Fe-Mn oxide hydroxide at the bottom of the reservoir can affect also other elements dissolved in solution. These secondary minerals, unlike clays, are thought to not be equally distributed within the area of study which shows different environmental condition depending on parameters such as depth, kinetic energy, oxygenation, redox state. Fe_2O_3 and MnO are more concentrated in the station near the dam, in the centre, and at the bifurcation, showing a deposition and an accumulation at the bottom in the deepest and most central areas, where it is supposed to have favourable conditions for sediment deposition in time. In addition, they are involved in early diagenetic reaction within the sediment (see Chapter 5) and are actively recirculated within the sediment. These reactions affect the organic matter, particularly abundant in the reservoir sediment (Corg 3.5 ± 0.6 wt.%), a reactive component of the sediments.

6.3.2 Sequential extraction

Since bioavailability and consequent toxicity of trace metals strongly depend on their chemical binding within sediments, metal content in different fractions of sediments, exchangeable (step 1), reducible (step 2), oxidizable (step 3), and residual (Res) fractions were investigated in order to assess the element mobility (Table 6.2 and Figure 6.3). Table 6.2 reports the percentages of each fraction obtained by the sequential extraction for each element in descending order of total concentration. In the upper part can be found parameters as Al, Ca, Fe, Mg, Mn, Ba, and Sr, part of the major composition of the geological background of clay minerals, carbonates, and Fe-Mn secondary minerals. In the lower part are present instead the PHEs (Cr, Zn, V, Ni, Cu, Pb, Co, and As).

Aluminum, the major component of the sediment occurring in silicate minerals, is strongly bound to the residual fraction (median of 95.2%), suggesting an origin from the geological background and thus a limited mobility. In addition to Al, also V, Cr, Cu present high percentages of residual fraction, predominantly bound to the most immobile part of the sediment with percentages greater than 80%. Below and between 50 and 80% can be found Ba, Fe, Mg, Ni, and Co in descending order. Most of these likely occur in primary and secondary minerals and are the least mobile elements bound to the crystalline structure and the more stable fraction of the solid phase.

Conversely, Ca, the second major component, shows a strong partition in the first step of soluble and exchangeable fraction which includes carbonate, with a 57.8% in this step, and only 36.0% in the residue. Other elements, such as Sr and Mn are actively extracted by Step 1 (Sr 72.3%, Mn 43.3%), both affected by calcium carbonate occurrence or direct formation (e.g. $MnCO_3$).

Step 2, the reducible fraction, as should be expected, includes an important fraction of Fe, but many PHEs are strongly associated to this fraction. Pb is the elements mostly extracted (54.4%), followed by As (39%), Zn (24.9 %) and Co (20%) and minor percentages of Mn, Ni, and Ba. This fraction is linked to oxides and hydroxides and therefore attributable to secondary minerals formed and deposited at the water-sediment interface, including those of Fe, and these results suggest element that could be strongly linked to this sediment fraction. The presence of As and Co in this fraction is in line with their concentration and similar pattern of Fe observed in the interstitial waters (see Chapter 5).

Table 6.2, Percentages of the different fractions of sediments from Ridracoli reservoir, elements are in descending order of concentration.

Element	Step 1 %	Step 2 %	Step 3 %	Res %
Al	0.04	2.5	1.6	95.9
Ca	57.8	5.6	0.5	36.0
Fe	1.2	15.3	3.8	79.7
Mg	12.4	7.3	4.7	75.7
Mn	43.3	13.6	2.8	40.3
Ba	10.7	10.8	1.6	76.9
Sr	72.3	6.9	1.2	19.6
Cr	2.0	3.0	10.1	84.8
Zn	26.2	24.9	14.5	34.3
V	0.4	7.7	5.2	86.6
Ni	7.5	11.9	15.7	64.9
Cu	4.9	5.5	6.9	82.8
Pb	0.4	54.4	3.3	41.8
Co	10.3	20.6	8.6	60.5
As	3.9	39.0	9.8	47.3

Elements mainly bound to the oxidizable phase of the sediment (step 3) are, in descending order, Ni, Zn, Cr, As, Co, and Cu (Table 6.2). However, this fraction is a subordinate one, recording low percentage of association (maximum 15.7%). It is interesting to note that this is the most important fraction for Cr and Ni.

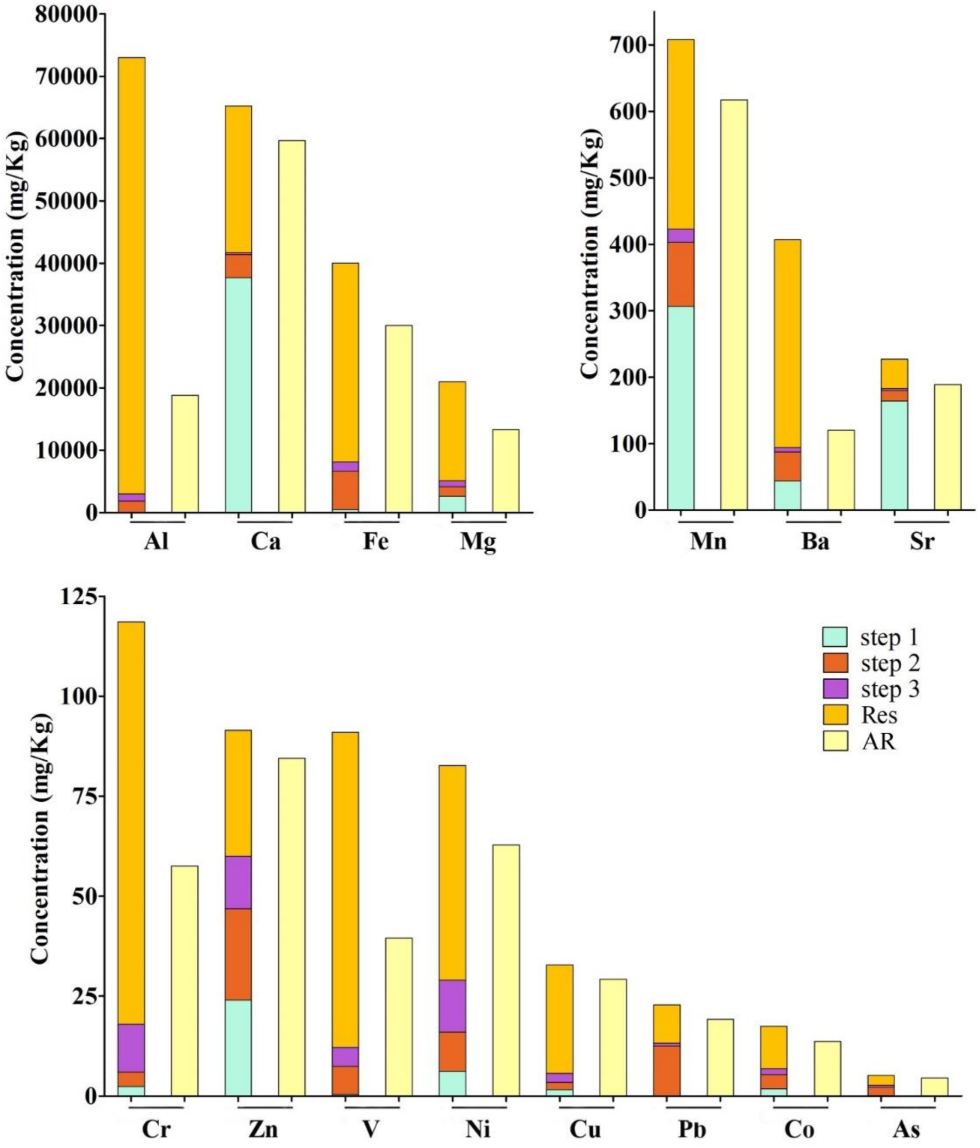

Figure 6.3, Median total concentration (XRF) of samples and relative exchangeable sites and carbonates (step 1), oxides and hydroxides (step 2), organic matter and sulfides (step 3) and residue (Res) from sequential extraction results and relative Aqua Regia values (AR).

In conclusion, considering the sum of step 1, step 2, and step 3 fractions as the total extractable fraction, Sr, Zn, and Ca are the most mobile elements in sediments in descending order (more than 64%). Whereas Mn, Pb, As, and Co are in the middle between mobile and immobile elements, showing a similar partitioning into the mobile and residual phase of the sediment, splitting at 60-40%. Al, V, Cr, Cu, Fe, Ba, Mg, and Ni instead are predominantly bound to the residual fraction of the sediment, suggesting a lithogenic origin, and a low mobility, regardless pH and redox conditions.

The geochemical maps (Figure 6.4) show interesting patterns, resulting in a peculiar metal distribution in the station at the dam, that for all the presented element, the residual fraction has the lowest percentage, suggesting active remobilization processes, and a particular geochemical environment at that site. This is especially evident for Cu, Ni and Pb, each one with its peculiar partitioning.

Also, the sampling station along the main (eastern) branch, nearer to the dam display some difference compared to the other stations, in particular Mn, Cu and Ni still show a residual fraction lower that the southern stations (Figure 6.4). Pb shows a peculiar distribution, with only the station at the dam with a prevalence of the reducible fraction, which is almost paired by the residual fraction in all the other stations. Focusing on iron, its spatial distribution is dominated by the residual and oxides and hydroxides fractions (step 2 and Res), quite homogeneous with the exception of the north-east sampling station near the dam, which shows significant higher values for the step 2 fraction, higher in the station located in deep and less in stations in the branches. The second element of concern is Mn, which unlike Fe, is equally partitioned between the weakly bound and residual fractions of sediments (step 1 and Res), with the highest mobile portion localized in the northern area at the dam as Fe, and indeed in tandem with Fe–Mn oxide/hydroxides. In this case the difference between the stations in the external areas and the two once near the dam, and also in the centre of the reservoir, is even more evident. Residue’s values (Res) are higher at the branches stations and higher is the mobile fraction, in particular for the reducible fraction (step 2) near the dam. Hence, in this site maximum peaks of 13800 mg/Kg of Fe and 570 mg/Kg of Mn could be released if changes in pH or redox state occur (Figure 6.3). Spatial distribution of Mn bound to the reducible phase (step 2) of sediment is similar to that of clay minerals within the reservoir, and higher concentration are found where organic matter and sulfides fraction (step 3) are registered, linking these two components with the change of Mn behaviour, depending on the site.

The percentage of residue Cu is generally high (>80%) but visibly less in the station near the dam. The Cu fraction bound to the reducible and oxidable phases are associated with the Fe-Mn oxides and hydroxides and the organic matter. Cu affinity to those components in the sediments is particularly evident in the station near the dam, less in in the centre of the reservoir and in the west branch. This behaviour is inversely correlated with a lower concentration, detectable from the smaller diameter of the pie charts in Figure 6.4. Cu can be mobilized from sediment by changes in redox conditions at the bottom during the seasonal environmental condition change, and could be released due to organic matter oxidation, or reduction of Fe-Mn oxy/hydroxides but not at concentrations of concern for the environment (Figure 6.3).

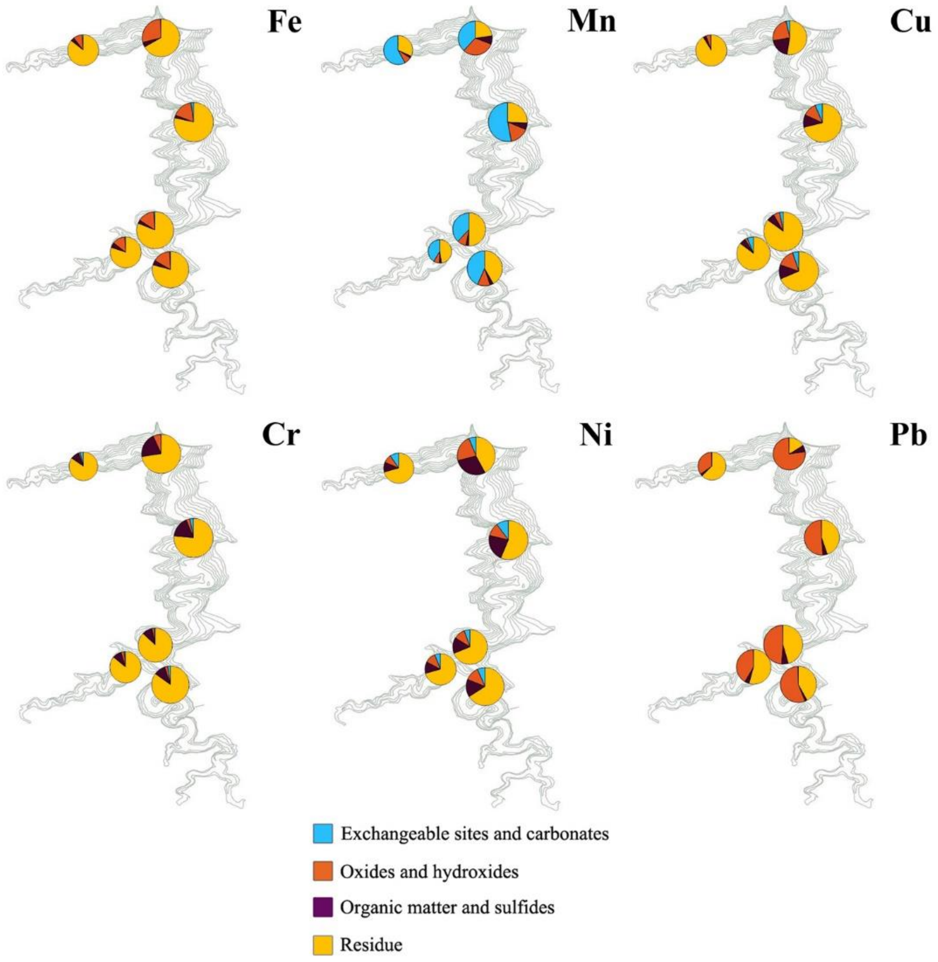

Figure 6.4, distribution maps of percentage of elements in the different fraction obtained by sequential extraction process analysis, the diameters of the pie chart are proportional to the total concentrations.

Ni and Cr are the two elements mainly bound to the oxidable fraction of the sediment, organic matter and sulfides; both appear to be spatially more concentrated for total composition in stations from the deepest part of the reservoir (in the centre and near the dam), and this behaviour is also followed by step 3 fraction. Under oxic conditions in this sampling station, Cr shows high values of 29 mg/Kg compared to a median of 12 mg/Kg, and Ni of 27.5 mg/Kg compared to 13 mg/Kg, and both could be released due to organic matter degradation (Figure 6.3).

Pb, the last element taken into account, shows a great affinity with oxide/hydroxides (reducible fraction), especially in the station near the dam where it accounts more than the 75%, less in the external areas, and with organic matter and sulfide (oxidizable fraction) particularly in this same station.

The residual percentages of almost all the elements are mainly concentrated in the branches, where are supposed to be the more stable elements in the crystalline structure of minerals. The extractable fractions are mainly detectable in the station near the dam and slightly less in the two stations of the centre and of the fork. The stations near the dam and at the centre are located in an area covered by the anoxic layer that forms during late summer (Figure 6.5), that is supposed to affect the composition of sediments in these stations.

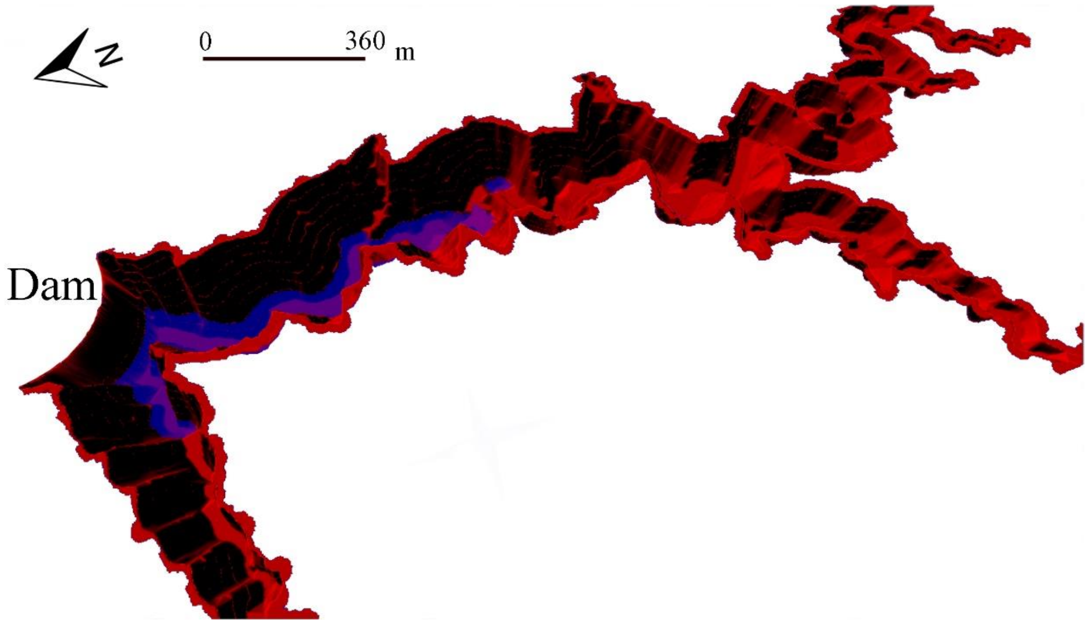

Figure 6.5, 3D representation of the entire Ridracoli reservoir (in red) and relative surface interested by the anoxic layer in late summer (in blue).

As observed by the distribution of elements, the most interesting area is the one in the northern sector of Ridracoli reservoir, of the sampling station near the dam, where have been collected not only the superficial sediment but also layers at 18-21 and 36-40 cm of depth. Sediments transported inside the reservoir by tributaries are in fact deposited in the bottom and in the area near the barrier, where about 12.5 – 25 cm/year of sediment are deposited (see Chapter 5) and where seasonally alternation of oxic and anoxic conditions occur (Toller et al., 2020).

Percentages for the station near the dam (Figure 6.6), apparently more influenced by mobile elements compared to median values (Table 6.3) and other stations (Figure 6.4), show also a more mobile for the superficial sample than the ones in depth, as already described (see Chapter 5) as a particular reactive environment. For all the parameters considered the residue (Res) fraction increases in depth, and, vice versa, the extractable fractions decrease (Figure 6.6), suggesting that the investigated elements are more stable in deeper sediments, with a pattern very similar to those of the southern station among surface sediments.

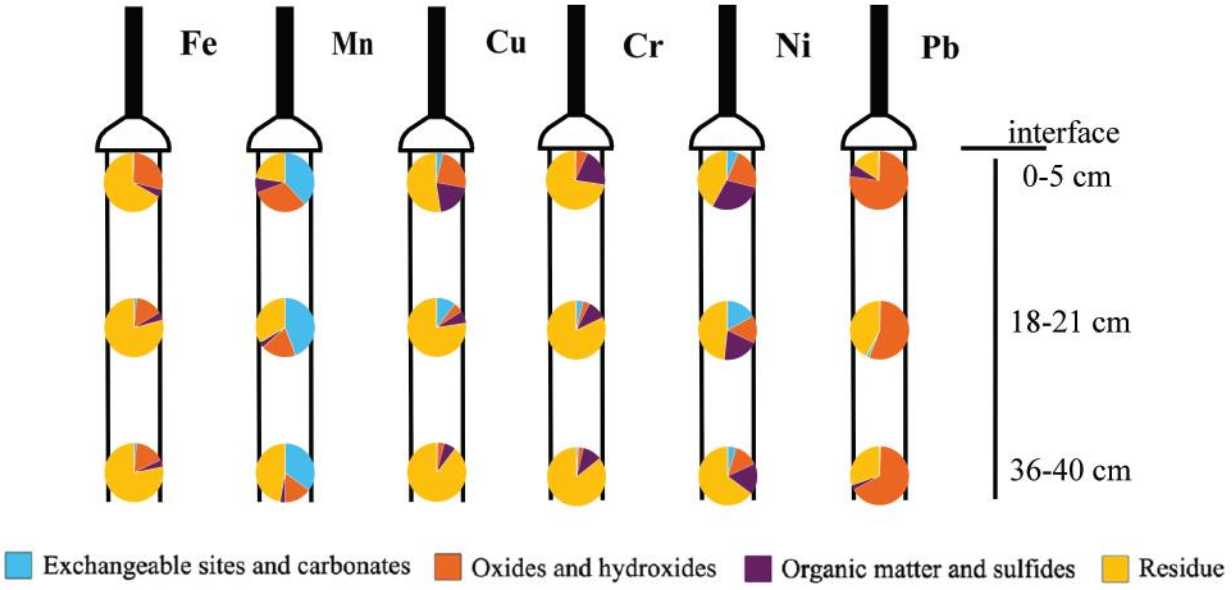

Figure 6.6, sequential extraction step 1, step 2, step 3 and residue pie charts in depth for 40 cm for selected elements at the station nearby the dam.

The exchangeable sites and carbonate related fraction seem not affected by depth at all, and layer at 18-21 generally shows more consistent elements values suggesting that their bound to this fraction is not influenced by the burial but by the sediment composition itself.

The reducible fraction linked to the oxides and hydroxides instead shows a decrease in depth, confirming that in depth is less affected by reduction processes because perhaps already sustained during sediment deposition and bury of overlying layers in the reducing environment that formed at the bottom and which is should have already released part of these elements in solution.

The organic matter and sulfides fraction have the same behaviour, decreasing in percentage in depth, not with a constant lowering, but maintaining higher values in the uppers superficial part and then constant in the underlying ones.

6.3.3 Environmental assessment, leaching test and PHAs

Leaching test used liquid/solid ratio of 10:1 which simulate open landfill conditions, provides information about the end life stage for sediment, evaluating the most easily leachable fraction for the elements. In the leachates were analysed F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Ca, Mg, K, Na, Al, Fe, Sr, Mn, Ba, Zn, Cu, Ni, Ti, Mo, Pb, As, Cd, Se, V, Li, Co, and Cr concentrations against the threshold limitations stated by the Italian and European regulations. The leachates were analysed to determine the concentrations of metals and anions considered in the Italian Decree (D. Lgs, n. 22, 1998), about non-hazardous waste, and the EU Waste Landfill Directive (Council Decision n. 2003/33/CE, 2003), about acceptable leaching values at landfills for inert waste, and compared with these limits.

Table 6.3, statistical description of leaching test results and leaching limits values from the D. Lgs, n. 22, 1998 and the 2003/33/EC.

	µg/L				mg/Kg			
	Min	**Median**	**Max**	**D. Lgs, n.22, 1998**	**Min**	**Median**	**Max**	**2003/33/EC**
F^-	101	171	260	1500				
Cl^-	569	1440	3448	100000				
NO_2^-	18	29	32					
Br^-	49	167	277					
NO_3^-	356	609	1258	50000				
PO_4^{3-}	227	257	287					
SO_4^{2-}	12659	21788.5	58528	250000				
Ca	16000	30950	45200		160	310	452	
Mg	4350	7645	10800		44	76	108	
K	2450	3130	3510		25	31	35	
Na	787	1770	2570		8	18	26	
Al	134	310	1440		1	3	14	
Fe	294	370.5	817		3	4	8	
Sr	198	361	560		2	4	6	
Mn	139	291.5	734		1	3	7	
Ba	50	87	153	1000	0.50	0.87	1.53	20
Zn	24	39	69	3000	0.24	0.39	0.69	4
Cu	7	18	29	50	0.07	0.18	0.29	2
Ni	5	8	16	10	0.05	0.08	0.16	0.4
Ti	3	7	21		0.03	0.07	0.21	
Mo	4	8	13		0.04	0.08	0.13	0.5
Pb	1.8	4.5	6.9	50	0.02	0.04	0.07	0.5
As	2.2	3.5	6.5	50	0.02	0.03	0.06	0.5
Cd	0.5	2.1	6.3	5	0.00	0.02	0.06	0.04
Se	1.5	2.7	5.2	10	0.01	0.03	0.05	0.1
V	1.6	3.2	5.2	250	0.02	0.03	0.05	
Li	1.2	1.7	2.8		0.01	0.02	0.03	
Co	0.7	1.3	2.9	250	0.007	0.013	0.029	

Cr	0.5	1.1	2.5	50	0.005	0.011	0.025	0.5
Be	0.007	0.035	0.07	10	0.0001	0.0003	0.0007	

As can be observed in Table 6.3, all median values calculated on the solid/liquid ratio are below the limits proposed by the Italian Legislation and the European Union for non-hazardous waste and waste acceptable at landfills for inert waste respectively. In Table 6.3 elements are listed in descending order of median concentration. The most leached are Ca, Mg, K, and Na in the range of 310 - 17.7 mg/Kg, and the second group, the one of Al, Fe, Sr, and Mn, in the range of 3.7 - 2.9 mg/Kg. Ca, Mg, Sr, and Al are parameters to consider from a lithogenic origin, carbonates and clays, K and Na are ions easily weathered and are favoured to enter the solution, and in the end Fe and Mn are the two elements that are quite interested in the processes that happen at the water-sediment interface, in particular in the stations near the dam and in centre of the reservoir, and their release have been studied deeply in Chapter 5. The remaining elements are below 0.87 mg/Kg, and in particular Ba, Zn and Cu are above 0.1 but Ni, Ti, Mo, Pb, As, Cd, Se, V, Li, Co, Cr, and Be are all below. All the parameters considered of environmental concern from European and Italian limits are in this group and no one show consistent concentrations. Overall, data collected do not suggest any significant differences between the sampling stations, with the exception of the once near the dam, where Cu, Li, Mn and Zn show slightly higher leaching values respect to the median calculated within the entire area.

Another important environmental parameter to consider is the concentration of polycyclic aromatic hydrocarbons (PAH) listed by the Environmental Protection Agency (EPA) (US EPA, 2002). PHAs are well known carcinogenic and persistent pollutants that are ubiquitous in the environment (concentrations are expressed as ng g^{-1} on the total weight of the sample (median and standard deviation for each component are shown in Table 6.4)). Based on their occurrence and carcinogenicity, 16 PAHs have been identified as priority hazardous substances by 367/03 Italian Decree (D.M., 2003) and can give more information on the health of the reservoir in a different way.

Table 6.4, mean concentration of PAHs of Ridracoli reservoir samples (two replicates) collected near the dam (A) and in the centre of the reservoir (B). * sum is calculated on Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(ghi)perylene, and Idenopyrene.

Sample	A		B		DM 367/03
PAH	ng g^{-1} ± SD				
Naphthalene	73.0	5.7	71.1	0.8	35
Acenaphtylene	2.91	0.08	3.35	0.24	
Acenaphthene	2.36	0.12	2.38	0.09	
Fluorene	9.1	0.5	10.6	1.4	
Phenanthrene	71.1	5.0	82.4	2.4	
Anthracene	2.83	0.05	2.76	0.04	45
Fluoranthene	16.3	1.2	14.3	0.5	110
Pyrene	17.7	2.5	15.0	0.4	
Chrysene	9.0	0.3	6.6	0.3	
Benzo[a]anthracene	28.1	1.6	28.0	1.4	
Benzo[b]fluoranthene	16.1	2.2	12.4	0.3	40
Benzo[k]fluoranthene	10.0	0.5	11.0	0.7	20
Benzo[a]pyrene	12.1	0.4	6.8	0.2	30
Indeno[1.2.3-cd]pyrene	10.4	0.4	10.6	0.7	70
Debenzo[a.h]anthracene	4.8	0.4	5.0	0.5	
Benzo[ghi]perylene	18.7	0.2	16.4	1.6	55
Total	305	5.2	299	8.2	200*

The values found for the Ridracoli reservoir site are very low in comparison to values found in literature for bottom sediment of reservoirs and quality guidelines (Hiller et al., 2009; Baran et al, 2017; McGrath et al., 2019).

6.4 Conclusions

The geochemical characterization of the Ridracoli reservoir sediments, that interested their spatial and in-depth distribution, was performed analysing environmental parameters and extractions and leaching test data. This allowed to identify different patterns of sediment partition of exchangeable, reducible, oxidizable and residual fractions, with branches characterized by the presence of more stable residual fraction and the sampling station near the dam and in the centre of the reservoir with a composition more affected by extraction processes. In particular, higher percentages of Al, V, Cr, Cu have been observed in the residual fraction, occurring in silicate minerals, while Ca, Sr and Mn, associated to carbonate, were prevalently constituent of the exchangeable once. In the reducible fraction, instead, were found Fe, Pb, As, Co and Zn, linked to secondary minerals oxides and hydroxides, while low extraction percentages were detected for the oxidizable fraction. The change in composition of sediments along the reservoir is attributable to the different environmental conditions, prevalently oxy at the branches while the once near the dam and the centre interested by seasonal formation of an anoxic layer. The deepest part of the reservoir, near the dam, presents a peculiar repartition of metals within the sediment, responsible of the greater mobility of metals in this station respect to the rest of the area. Although, no change in metals total concentrations has been observed. From an environmental point of view, this study revealed great quality of sediments in Ridracoli reservoir, with concentrations of putative toxic and/or carcinogenic elements below the limits proposed by the law, confirming and expanding data obtained in Chapter 4.

Chapter 7 – General Conclusions

In this PhD thesis the seasonal changes in water and sediment chemistry of the Ridracoli reservoir, the main water supply of the Emilia-Romagna region (Italy), was investigated through the analysis of an extended and integrated database collected with a series of sampling campaigns carried out during the period from 2015 to 2019. 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.

Water analysis showed a Ca-Mg-HCO_3 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 Arenaceo 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, our 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 sulfide 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 sulfides 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.

Overall, our 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.

In conclusion, our 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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Co-author declaration

This declaration states the independent research contribution of the PhD candidate for each paper compiled in the thesis.

<table>
<tr><th>Paper No.</th><th colspan="3">Title and full bibliographic reference</th></tr>
<tr><td>Paper I</td><td colspan="3">“Assessment of seasonal changes in water chemistry of the Ridracoli reservoir (Italy): implications for water management.” Toller, S., Giambastiani, B.M.S., Greggio, N., Antonellini, M., Vasumini, I., Dinelli E., 2020, Water 12, 581.</td></tr>
<tr><th>Role of PhD candidate</th><th>Type of contribution</th><th>Overall contribution (%)</th><th>Signature of PhD candidate and tutor</th></tr>
<tr><td>[First author]</td><td>[Data curation, Investigation, Methodology, Writing-original draft, Formal analysis]</td><td>[40-60%]</td><td>Simone Toller
Enrico Dinelli</td></tr>
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<tr><th>Paper No.</th><th colspan="3">Title and full bibliographic reference</th></tr>
<tr><td>Paper II</td><td colspan="3">“Geochemical characterization of surface sediments from the Ridracoli reservoir area and surroundings. Details on bulk composition and grain size.” Toller, S., Funari, V., Vasumini, I., Dinelli, E., submittet at Journal of Geochemical Exploration on 25 November 2020, accepted with revisions.</td></tr>
<tr><th>Role of PhD candidate</th><th>Type of contribution</th><th>Overall contribution (%)</th><th>Signature of PhD candidate and tutor</th></tr>
<tr><td>[First author; Corresponding author]</td><td>[Data curation, Investigation, Methodology, Writing-original draft, Formal analysis, visualization, editing]</td><td>[>75%]</td><td>Simone Toller
Enrico Dinelli</td></tr>
</table>

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