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**GEOCHEMICAL SEDIMENT ANALYSES:  
A CASE OF THE FIFTH LAKE IN JULIAN ALPS**

MASTER'S THESIS

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Nova Gorica, 2014

**STATEMENT**

I declare that the thesis is a result of my own research work. Results generated in the context of collaborative research with other researchers or contributed by other researchers (experts) are explicitly shown or mentioned (cited) in the thesis.

Tina Ravnikar

## **ACKNOWLEDGEMENTS**

I would like to express my gratitude to my mentor, Assist. Prof. Gregor Muri, PhD, for his support, assistance and guidance in the learning process of this master thesis. I deeply appreciate his professionalism and knowledge that he shared with me. He taught me so much that I can't thank him enough for his tremendous support and help. Furthermore, I would also like to thank Polona Vreča, PhD, from the Jožef Stefan Institute, Department of Environmental Sciences, for the measurements of  $\delta^{13}\text{C}$  and all the helpful discussion, to Assist. Prof. Branko Čermelj, PhD, from the National Institute of Biology, Marine Biology Station Piran, for his help with the measurements of organic carbon and total nitrogen, and to the colleagues from the Slovenian Environment Agency, Chemical Analytical Laboratory, for their assistance by performing analyses of forms of phosphorus. Last but not least, I would like to thank Prof. Marko Bohanec, PhD, from the Jožef Stefan Institute, Department of Knowledge Technologies, for his effort in guiding me through the process of developing multi-attribute decision model.

I am especially thankful to **MY MOTHER** for all the help, care, encouraging and faith in my success.

## **SUMMARY**

The Fifth Triglav Lake is a remote mountain lake in the Julian Alps. The area of the Julian Alps where the lake is situated is protected by law and lies within the Triglav National Park (TNP). The distribution of different forms of phosphorus, the composition of organic matter (organic carbon and total nitrogen concentrations), as well as stable carbon isotopic composition were determined in the surface sediments of the Fifth Triglav Lake, in order to study the impact of anthropogenic activity on the lake and natural lake characteristics. C/N ratios and stable isotopes in the surface sediments were employed to assess sources of organic matter in the sediments. Surface sediment atomic C/N ratios ranged from 13.3 to 15.6, suggesting that both autochthonous and allochthonous sources contribute organic matter to this lake constituting approximately 49-63 % and 37-51 %, respectively of the total organic matter.  $\delta^{13}\text{C}$  values varied from -22.4 to -26.4 ‰ which could also indicate contribution of both autochthonous and allochthonous sources. Total phosphorus concentrations ranged from 802 to 1704  $\mu\text{g/g}$  dry weight sediment. Most of phosphorus compounds are in organic form, followed by calcium-bound, iron-bound, aluminum-bound and loosely bound phosphorus compounds. Phosphorus compounds are unevenly distributed across the lake. Correlations among all geochemical parameters were also calculated. Finally, multi-attribute decision model was developed with DEXi software. In order to understand the dimension of the ecological effects on the lake, four main parameters were chosen, i.e. the trophic state, lake characteristics, environmental parameters and anthropogenic stressors. Dependence of environmental impact on various external factors beyond our control, such as temperature, precipitation, retention time, and factors on which we have influence, such as the amount of wastewater and the presence of fish in the lake was also evaluated. According to the model results, fish seem to be the most important factor affecting the state of the lake.

Key words: mountain lakes, the Fifth Triglav Lake, sediment, eutrophication, organic matter, phosphorous, stable isotopes, DEXi, multi-attribute model, decision support

## POVZETEK

Peto jezero je odmaknjeno visokogorsko jezero v Julijskih Alpah. Območje v Julijskih Alpah, kjer jezero leži, se nahaja v Triglavskem narodnem parku (TNP), ki spada med zavarovana območja Slovenije. Določila sem porazdelitev različnih oblik fosforja, sestavo organske snovi (koncentracijo organskega ogljika in celotnega dušika), kot tudi kakšna je izotopska sestava ogljika v površinskem sedimentu Petega jezera, z namenom preučevanja vpliva antropogenih dejavnikov na jezero in njegove naravne značilnosti. Za oceno izvora organske snovi sem uporabila C/N atomska razmerja in stabilne izotope v sedimentih. C/N atomsko razmerje površinskega sedimenta znaša med 13,3 in 15,6, kar nakazuje, da predstavlja glavni izvor organske snovi tako vodna (avtohtona) kot kopenska (alohtona) organska snov in predstavljata približno 49-63 % oziroma 37-51 % celotne organske snovi. Vrednosti  $\delta^{13}\text{C}$  znašajo med -22,4 in -26,4 ‰, kar prav tako nakazuje prispevek obeh, avtohtone in alohtone, organske snovi. Koncentracija celotnega fosforja znaša med 802 do 1704  $\mu\text{g/g}$  suhe snovi. Večina fosforja je v obliki organskega fosforja, ki mu sledijo fosfor vezan na kalcij, fosfor vezan na železo, fosfor vezan na aluminij in adsorbiran fosfor. Fosfor je neenakomerno porazdeljen po jezeru. Med vsemi geokemijskimi parametri sem izračunala tudi korelacije. Na koncu sem izdelala tudi večparametrski model s pomočjo programske opreme DEXi. Da bi spoznala in razumela, kakšne so ekološke posledice na jezero, sem izbrala štiri glavne parametre t.j. trofičnost jezera, naravne okoliščine, v katerih se jezero nahaja, antropogene dejavnike in nekatere značilnosti jezera. Ugotoviti sem želela tudi, kako na ekološke posledice vplivajo razni zunanji dejavniki, na katere nimamo vpliva, kot so temperatura, količina padavin, zadrževalni čas vode v jezeru, itd. ter dejavniki, na katere

imamo vpliv, kot so količina odplak in prisotnost rib v jezeru. Iz dobljenih rezultatov lahko povzamem, da ima prisotnost rib največji vpliv na stanje, v katerem se nahaja jezero.

Ključne besede: visokogorska jezera, Peto jezero, sediment, eutrofikacija, organska snov, fosfor, stabilni izotopi, DEXi, večparametrski model, podpora odločanju

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## LIST OF ABBREVIATIONS

C	Carbon
C/N ratio	Organic Carbon to Total Nitrogen ratio
Ca	Calcium
$\delta^{13}\text{C}$	Stable carbon isotopic composition
N	Nitrogen
OC	Organic Carbon
OM	Organic Matter
P	Phosphorous
RSD	Relative Standard Deviation
TC	Total Carbon
TN	Total Nitrogen
TNP	Triglav National Park
TP	Total Phosphorous

## 1. INTRODUCTION

Lakes represent very sensitive ecosystems and interesting sedimentation environments. The biggest concern related to lakes is induced eutrophication caused by anthropogenic activities (Smith et al., 2006). Also, acidification of freshwater environments is of a big concern since acid rain is the primary result of burning fossil fuels by mankind causing subsequent acidification of lakes (ICP Waters, 2003). Acidification may contaminate or alter sediments and create experimental artifacts affecting the validity of resulting H/C, C/N and O/C ratios (Ryba, Burgess, 2002). In addition, a number of other factors can influence the state of freshwater ecosystems, including the presence of livestock in the catchment area and the use of nitrogen fertilizers. It is now well known that anthropogenic nutrient loading of aquatic ecosystems from both point and nonpoint sources typically results in a rapid increase in the rate of biological production and a significant reduction in water column transparency, and can create a wide range of undesirable water quality changes in freshwater ecosystems (Smith et al., 2006). Despite 20th century advances in understanding eutrophication, it remains one of the foremost problems in protecting freshwater ecosystems (Schindler, 2006). As a result, lake sediments contain an archive of past environmental conditions and biogeochemical processes in and around the water body and lake sediments can be used to document ecosystem changes through time (Torres et al., 2012). A variety of elemental, isotopic and molecular indicators can be used in paleoenvironmental reconstruction studies. Elemental composition (the ratio of organic carbon to total nitrogen – the C/N ratio) is a relatively reliable proxy used to reflect changes in sources of organic matter (OM; autochthonous vs. allochthonous), driven either by natural development of the lake ecosystem or human activity (Meyers, 2003; Gälman et al., 2009). Both, OM as well as inorganic particles in lake sediments contain information that helps to reconstruct past environmental conditions, evaluate histories of climate change, and assess impacts of humans on local ecosystems. In particular, the elemental, isotopic, and molecular compositions of OM buried in sediment provide evidence of the biota that have lived in a lake and its catchment area, and they serve as proxies of OM delivery and accumulation, that can be used to reconstruct paleoenvironments of lakes and their surrounding land areas (Meyers, 2003).

Despite the remoteness of alpine lakes, previous investigations showed that these environments are also exposed to enhanced environmental changes. Although eutrophication is also a natural process in the ontogenetic development of lakes, human activities can significantly accelerate this process. The response to a disturbed natural equilibrium and higher input of nutrients from surrounding watershed into water is increased bioproduction and the process of eutrophication. OM produced photosynthetically in the surface water is assumed to be the principal control of C and N cycling, but in eutrophic systems the development of anoxic conditions in the water column and sediments may create conditions favourable for expansion of microbially mediated C and N cycling processes, which can distinctly influence the water chemistry and the isotopic signatures of sinking or sedimented OM (Furrer, Wehrli, 1996; Hollander, Smith, 2001; Lehmann et al., 2002). Eutrophication of the lakes and earthquakes accelerate the process. Various pollutants can be found in these sediments which can be used as indicators of environmental changes that have occurred in the past. Their main source in alpine areas is long distance atmospheric pollution (Brancelj, 2002). Among the biogenic elements in the natural aquatic environment, phosphorus is the least abundant. Phosphorus content in the water along with other environmental factors is thus regulating biological productivity of the ecosystem. Also in lakes and reservoirs in Slovenia, phosphorus compounds are the most important factor that usually limits or accelerates biological production. Average annual total content of phosphorus in the water column is one indicator of the trophic status of lakes. Eutrophication or excessive accumulation of nutrients, especially phosphorus compounds in the water, is the main problem of most lakes in the temperate climatic zone, also in Slovenia. Inappropriate discharge of sewage and the leaching of phosphorus compounds from intensive arable land are the biggest and most common source of this element in lakes and reservoirs (Standardized Database for Water Quality Monitoring,

2009). Nutrient enrichment causes an intensification of all biological activities and typically leads to dramatic changes in the composition and structure of aquatic food webs. Two of the most consistent eutrophication effects are a shift in algal species composition and an increase in the frequency and intensity of nuisance algal blooms, which in eutrophic freshwater lakes are typically dominated by harmful cyanobacteria. One of the most important recent advances in our understanding of freshwater eutrophication is the discovery that the biological responses of producer organisms to nutrient availability can be strongly modified by consumer communities (Smith et al., 2006).

The main purpose of the present study was to investigate the composition and distribution of OM in the surface sediments of the Fifth Triglav Lake. Fish were introduced into the lake in 1991. Additionally, a mountain hut is located on the shore of the lake and could represent a threat with its effluents. Organic carbon (OC) and total nitrogen (TN) concentrations, stable carbon isotopic composition, as well as concentrations of different forms of phosphorus were determined in the surface sediment samples that were collected all across the lake, in order to 1) study the impact of anthropogenic activity on the condition of the lake to gain a better understanding about the dimensions of ecological effects on the lake and 2) assess the natural lake characteristics. Finally, multi-attribute model was developed. Input data for the model were partly obtained from this study and partly from existing, previously published studies. The aim of the model was to find out how to reduce the anthropogenic impact on the lake or how to improve the existing condition of the lake, or even what can worsen the current situation. Outputs of the model could serve as a tool for a better future management of these vulnerable ecosystems.

## 2. THEORETICAL PART

Mountain lakes in Slovenia were considered for a long time as pristine, unpolluted lakes, as opposed to most of low-land lakes. Analyses in the last decade revealed considerable human impact even in such remote places. Lakes are threatened by tourism, long-distance transport of pollutants and fish introduction (Brancelj, 1999 a; Brancelj et al., 2000; Brancelj, 2002; Muri et al., 2004; Muri et al., 2006; Vreča, Muri, 2010; Muri et al., 2013).

In general, mountain lakes are small and sensitive ecosystems with rapid flushing rates. These lakes respond rapidly and strongly to any direct anthropogenic influence and/or change in the lakes themselves or their catchment areas. As a consequence, they can be used as reliable sensors of environmental change (Battarbee et al., 2009). Effects of such environmental changes are potentially recorded in lake sediments that can be used to reconstruct past conditions in the lakes over long time scales (Vreča, Muri, 2006; Muri et al., 2013). Remote mountain and arctic lakes have been influenced by human activities for several decades. In some cases, the influence has been direct, i.e., waste input (Revinga et al., 2012), fish stocking (Brancelj et al., 2000; Pister 2001), deforestation of catchment areas (Schmidt et al., 2002; Zhang et al., 2010). However, most of these lakes were also impacted by regional and global factors such as climate change (Battarbee et al., 2002) and the deposition of pollution from the atmosphere (Muri et al., 2006), mainly products of the combustion of fossil fuels (Gąsiorowski, Sienkiewicz, 2013). The deposition of nitrogen and sulfur oxides, which leads to the acidification of lakes, has been described in several mountainous regions of the Arctic, America, and Europe (Brett 1989; Paterson 1994; Sienkiewicz et al., 2006). However, in many studies, the link between fossil fuel combustion and the acidification of lakes was based only on the time coincidence of both processes. Conversely, many lakes located in regions with significant deposition of nitrates and/or sulfur oxides showed only traces of acidification (Gąsiorowski, Sienkiewicz, 2013; Muri, 2013). The C/N ratio,  $\delta^{13}\text{C}$ , and  $\delta^{15}\text{N}$  of OM in sediments all reflect several complex processes, including biosynthesis in the photic zone, OM degradation and bacterial growth in the water column and in the sediment, and the input from allochthonous sources (Meyers, 2003). A natural mixture of signals from terrestrial organic parts transported into the lake and OM due to the primary production inside the lake can be modified by extra inputs of carbon (C) and nitrogen (N). Urban and farmland waste waters, acidic precipitation, and modifications in the trophic web structure were identified as the most important sources of OM with specific isotopic signatures (Gąsiorowski, Sienkiewicz, 2013). Some of the OM that enters a lake from the watershed (allochthonous) or is produced within the lake itself (autochthonous) is ultimately deposited on the lake bottom and becomes incorporated permanently into the lake sediments. Sediments thus function as sinks for OM and associated macro-elements such as C, N, and P (Torres et al., 2012).

### 2.1 Sediments

Lake sediments provide a historical record of the conditions of the environments that surrounds them. Nutrient cycling throughout lakes is directly linked to processes operating within the lake and surrounding environs. As a result, lacustrine nutrient conditions reflect both the natural processes and human activity and their effects on the lake. Most notably, increases in nutrient loading in a lake can lead to eutrophication and a general decrease in water quality. Lake eutrophication is among the most widespread environmental concerns. Major nutrients (C, N, P) have numerous sources, sinks, and chemical forms in natural waters (Nesbeda, 2004). Lake sediment is a deposit of insoluble material and is primarily derived from rock, as well as organic debris and chemical precipitates. Sediment constituents are transported to lakes by rivers, streams, surface run-off and winds, where they accumulate on the bottom of the lake, layer by layer. Each layer represents the condition of the lake and the lake catchment at the time, when that layer was deposited. In addition, many biogenic

and pollutant compounds are adsorbed on particles and are subsequently deposited into sediment, so that sediment represents a temporary or sometimes a long-term reservoir of compounds. A sediment accumulation rate in the lakes in Julian Alps differs from lake to lake, generally ranging from 1 to 3 mm per year (Brancelj, 2002). So, lake sediments represent a natural record of its history because most substances entering the lake eventually find their way to the sediments. This is true not only for particles that sink directly to the bottom but also for substances dissolved in the water. With time, dissolved substances can be retained in the sediments by various processes, including adsorption to particles and chemical precipitation. Many synthetic organic chemicals, the so-called “hydrophobic compounds”, are virtually insoluble and have especially strong tendencies to accumulate in the sediments. Chemical compounds that reach the sediments do not necessarily remain there permanently. Sediments can function as a reservoir, or temporary resting place, for certain elements, which can be released back into the water column (resolubilized) with changing environmental conditions. For example, resolubilization can be triggered by changes in dissolved oxygen, pH, or temperature (Elder et al., 2000). Substances associated with the sediments can also be released by biological activity (such as burrowing of worms or aquatic insect larvae, algal productivity near the sediment surface, or microbial activity that causes biodegradation of certain complex compounds). Phosphorus is a good example of an element that can move in both directions between water and sediments. A critical nutrient for algal growth, phosphorus exists in various chemical forms in both water and sediments, but it tends to move toward the sediments when it is incorporated into various kinds of particulate matter. However, most of this particle-associated phosphorus compounds are relatively unstable (Elder et al., 2000). Depletion of dissolved oxygen in the overlying water, which typically occurs in the deep zones of lakes, produces conditions that may reduce  $\text{Fe}^{3+}$  (insoluble and often chemically bonded to phosphates) to  $\text{Fe}^{2+}$  (soluble). This resolubilization of iron compounds releases the associated phosphates back into the water. Remobilization from the bottom sediments is termed “internal loading” and can be a major source of nutrients to the lake. Because of the tendency for materials to be deposited in bottom sediments, a great deal of information about relatively recent chemical and particulate inputs and cycles in a lake can be extracted from examination of samples of the surface sediments. Also, because substances can be mobilized from the sediments to overlying water, sediment analysis can show what nutrients and contaminants may be readily available to the water through internal loading (Elder et al., 2000). Human activities can affect the quality of water and sediments in high-mountain lakes. The impacts can be direct or indirect and can be divided into three groups: inputs of harmful and poisonous substances (e.g. resulting from the maintenance and restoration of alpine huts), inputs of nutrients (from tourist facilities, and because of alpine pasturing), and direct interventions that affect the species composition of lakes (e.g. inputs of fish) (Brancelj, 2002; Muri et al., 2004; Vreča, Muri, 2006; Muri et al., 2013). Poisonous or harmful materials, including radioactive outfall, are transported into the lakes by winds and rain, often from long distance atmospheric deposition that is a major pathway for the loading of contaminants to mountain lake sediments (Fernandez et al., 2003; Muri et al., 2006). Wind direction and quantity of precipitation are the main factors on quality and quantity of input (Muri, 2013). Very rare are direct inputs, like spills, into the lakes (Brancelj, 1999 a).

## **2.2 Organic matter**

The OM in lake sediments participates in a variety of biochemical and geochemical processes. Lakes are relatively small and closed systems compared to the ocean, making them ideal sites for studying geochemical cycling. Furthermore, nutrient cycling in lakes has direct implications for the water quality, considering the widespread problem of lake eutrophication. Improvements in the understanding of these systems will enhance our ability to predict their reactions to changes in the environment. Additionally to their advantage of being relatively closed systems, lake sediments differ from most marine sediments in some other important aspects; land plants potentially have a larger influence on the OM in lake sediments than they have in the marine system. This material contains

more complex organic molecules than planktonic tissue (Capone, Kiene, 1988). The OM accumulated in lake sediments constitutes minor but important fraction that provides crucial information in studies of the lacustrine paleoenvironment, the history of climate change, and the effects of man on local and regional ecosystems. It is introduced to lakes by multiple pathways (Meyers, 2003). In aquatic systems, OM is produced in the surface water by primary production of phytoplankton, and subsequently passed along the food chain. From the surface, a fraction is transported to deeper water in the form of sinking dead organisms or fecal pellets of consumers on the first trophic level. Bacteria starts to decompose this sinking organic material in the water column, but the majority of OM reaches the sediment, where degradation continues (Rullkötter, 2000). In the course of degradation, intermediate products like proteins, amino acids, sugars, fatty acids and many others are released to the environment (Jorgensen, 2000). These can serve either as substrate or as energy source for various organisms. Incorporation into bacterial biomass results in 'recycling' of the molecules, which is often referred to as the 'microbial loop'. Thereby, the bacterial biomass becomes an important component of OM itself (Fenchel et al., 1998). So far, not all steps of the process are fully understood and open questions remain. Organic tissue is composed of a variety of organic molecules with very different properties, causing the reactions during degradation to be highly diverse. The compound classes show different reactivities and thus degradation rates during mineralization (Kristensen, 2000; Wakeham et al., 1997; Muri et al., 2004). Although OM content of lake sediments is usually low, its paleolimnological importance is always great. OM in most sediments is a mixture of components from many sources, such as complex mixtures of lipids, carbohydrates, proteins, and other biochemical components produced by the various organisms that have lived in and around the lake and with variable degrees of preservation. A variety of processes act to alter the character of OM in the relatively short time between its origin and its burial in a lake bottom. Foremost among these processes is its degradation during sinking (Meyers, Ishiwatari, 1993). During sinking and incorporation into bottom sediments, over 90 % of the material initially contributed from the source organisms is typically mineralized (Eadie et al., 1984). Some OM components are more susceptible to mineralization than others, and some components undergo partial alteration. The consequence is that the composition of sedimented OM is modified from its starting composition shortly after its formation. Once in the lake bottom, mineralization and alterations continue, but generally at slower rates. Despite these very early diagenetic changes, sedimentary OM retains important paleoenvironmental information about its origins and about how it was delivered and deposited. The two most important types of proxy information provided by sedimentary OM are the origin of the OM and the abundance of the various biota that produced it (Meyers, 2003). Terrigenous (allochthonous) OM, originating mostly from the catchment area via tributaries, consists mainly of degraded remains of leaves and grass and soil OM, as well as material that falls directly into the lake from the riparian zones. Additional contributions from more distant sources are delivered by precipitation and wind. On the other hand, biota (animals, plants, and bacteria) within the water column and the sediments contribute aquatic (autochthonous) OM. The different types of biota populating a lake and its watershed produce OM having a distinctive biochemical composition. Changes in the community structure of this biota create variations in the amounts and types of OM deposited at different times in the history of a lake (Meyers, 2003). The dominant source of OM to lake sediments is the various plants that have lived in and near the lake. Plants can be divided into two geochemically significant groups on the basis of their bulk biochemical compositions: (1) non-vascular plants that contain little or no cellulose and lignin and that have relatively large proportions of nitrogen-rich proteinaceous material (typical representative is phytoplankton), and (2) vascular plants that contain large proportions of lignin and cellulose and that can be relatively rich in waxy hydrocarbons (typical representatives are grasses, shrubs, and trees on land and emergent macrophytes in lakes). The CHNO elemental compositions of the OM derived from these two broad groups of plants retain these general source distinctions. Microbes in the water and sediment of lakes and the soil of the lake watershed are the principal agents of mineralization. They rework and degrade aquatic and land-derived OM and diminish their amounts. While doing this, they create new forms of OM and thereby add to the mixture of different OM

components in sediments. In general, components from aquatic sources are more susceptible to microbial reworking than are materials from land plants. OM in lacustrine sediments consequently often includes a large and relatively durable fraction of land-derived organic residues. As an accumulation of “geochemical fossils”, OM components in lake sediments provide information that can be used to reconstruct natural and human-induced changes in local and regional environmental systems (Meyers, 2003).

The accumulation of sedimentary OM preserves a record of in-lake biological productivity and terrestrial inputs, but the signal can be confounded by post-depositional diagenesis, especially oxidation of OM in oxic pore waters in the upper few centimeters of the sediment. Therefore, preservation of OM in sediments is largely dependent on the burial rate and the supply of electron acceptors, especially oxygen, in the overlying water and pore waters. Many questions concerning the preservation of primary signals in sediments still remain unanswered (Muri, Wakeham, 2006). Nevertheless, the elemental and stable isotope compositions of OM in lake sediments have proved to be useful paleolimnological variables related to changes in (1) the primary productivity and past trophic state of lakes, and (2) their catchments, driven either by natural development of the lake ecosystem or human activities (Meyers, 2003). The C/N ratio is frequently used as a variable to determine the source of OM. Changes in C/N ratio are usually interpreted to result from changes in the relative contributions of terrigenous (allochthonous) and aquatic (autochthonous) OM. C/N ratios of terrigenous sources typically have atomic ratios  $>20$ , whereas aquatic OM (i.e. plankton) is characterized by C/N ratios  $<10$  because plankton, in comparison to terrestrial vascular plants, contains lower amounts of cellulose and lignin, but is rich in protein (Meyers, 2003). Elevated C/N ratios in sediments are often interpreted as periods of enhanced terrigenous input. However, human impacts on lake sedimentation, through land use (e.g. deforestation and accelerated soil erosion), may have various effects on the C/N ratio of lake sediments (Enters et al., 2006).

### **2.3 Stable isotopes**

Stable isotope ecology is a branch of chemical ecology, a tool-based or measurement-based approach that uses chemical tracers to follow ecological dynamics. Ecologists make many types of measurements to understand ecological systems, measurements such as length, timing, or pH. Isotope measurements allow detailed nuanced views of element cycling in all systems that interest ecologists. Isotopes trace ecological connections at many levels, from individual microbes to whole landscapes. Isotopes mix when source materials combine, and in a cyclic process that ecologists can appreciate, the process of isotope fractionation takes the mixed material and regenerates the sources by splitting or fractionating the mixtures. But mixing also occurs during the overall isotope circulation. When larger molecules are simply brought together without changes in bonds, mixing is the process on which to focus. For example, plant carbon from various sources mixes in soils, predators mix various types of prey OM in their diets, and microbes use a mixture of substrates, and so on. Most ecologists use isotopes to study mixing, and only consider fractionation as a background process of secondary interest. As elements circulate in the biosphere, mixtures arise when two or more sources contribute materials. Isotopes are excellent tracers for mixing processes and indicate which sources dominate the mixtures. Isotopes of the same element differ in atomic mass, due to differences in the number of neutrons contained in the atoms' nuclei. Elements and isotopes circulate in the biosphere, and fractionation and mixing combine to produce regular, characteristic isotope distributions on this planet. The amounts of elements and isotopes involved in the circulation are important, with large pools providing points of stability and poise in the overall isotope circulation. Several of these large stable pools are in the ocean, including ocean water itself for hydrogen and oxygen isotopes, the inorganic carbon pool in the ocean for carbon isotopes, and sulfate in the sea for sulfur isotopes. The atmospheric reservoir of  $N_2$  provides an important large pool for the N cycle. All these biosphere pools are part of even larger geochemical reservoirs circulating through the planet on geological time scales (Fry, 2006).

Isotopic methods are complementary to hydrochemical investigations and tracer experiments, because they open new perspectives for the interpretation of hydrogeological conditions (Brancelj, 2002). Stable isotope techniques allow the investigation of these questions quantitatively and non-intrusively (without the environmental hazards of radioisotopes), and thus offer considerable advantages over other techniques. Indeed, many of these questions can only be addressed by using stable isotopes. Many of these techniques also rely on natural differences in the ways that 'heavy' and 'light' isotopes are processed differently in the environment through chemical, biological, and physical transformations. These are referred to as natural abundance isotope techniques. For example, plants preferentially take up carbon dioxide containing the lighter carbon isotope ( $^{12}\text{C}$ - $\text{CO}_2$ ) in photosynthesis, but the degree of preference depends on water availability and on the photosynthetic pathway, which is a major distinguishing characteristic of plants from hot, dry environments versus more moisture rich, wet environments. Thus, the  $^{13}\text{C}$  composition of plants provides a time-integrated measure of the efficiency with which plants use water. It is also possible to tell how much a plant depends on surface water sources compared to deep water sources by measuring the  $^2\text{H}$  and  $^{18}\text{O}$  isotopic composition of water in a plant's stem. "Heavier" water will evaporate at the soil surface more slowly than "lighter" water, causing surface soil water to be isotopically enriched compared to deeper water, such as groundwater. Rain and snow that fall during winter (precipitation that contributes to deeper water sources in the soil) will be isotopically "lighter" than summer precipitation. Other stable isotope techniques rely on adding trace amounts of compounds that are artificially enriched in the rare (heavy) isotope of the element of interest. These are referred to as isotope tracer techniques (<http://www4.nau.edu/cpsil/isotopes.htm>).

Isotope values have their own special notation, the  $\delta$  notation that signifies difference. The  $\delta$  values denote a difference measurement made relative to standards during the actual analysis. The  $\delta$  definition involves a final multiplication by 1000, and this multiplication amplifies very small differences measured between samples and standards. Mass spectrometers currently make most isotope measurements, comparing samples to standards for a difference measurement, or  $\delta$  value (Fry, 2006).

Stable carbon isotopic compositions ( $\delta^{13}\text{C}$ ) of lake sediments, in combination with other sediment proxies (e.g. OC, TN, C/N ratio), derive information on C sources and pathways. Changes in sediment  $\delta^{13}\text{C}$  values can be used as indicators of productivity in lakes. Allochthonous and autochthonous OM have different carbon isotopic compositions. Lake-derived OM from phytoplankton that uses dissolved  $\text{CO}_2$  in equilibrium with the atmosphere is usually isotopically indistinguishable from OM produced by  $\text{C}_3$  plants in the surrounding watershed ( $\delta^{13}\text{C}$ : -33 to -22 ‰). Algal OM, nonetheless, usually has a carbon isotopic composition distinct from material produced by  $\text{C}_4$  plants growing either on the land or in the lakes ( $\delta^{13}\text{C}$ : -15 to -10 ‰). However, this generalization is invalidated when the availability of dissolved atmospheric  $\text{CO}_2$  is limited and algae begin to use dissolved  $\text{HCO}_3^-$  for photosynthesis.  $\text{HCO}_3^-$  becomes important during periods of high photosynthetic uptake and in waters where the  $\text{HCO}_3^-/\text{CO}_2$  ratio is high because of elevated pH. In such cases, the carbon isotopic composition of algae can increase to reach as high as -9 ‰ (Meyers, Teranes, 2001). Increases or decreases in productivity consequently yield increases or decreases, respectively, in the isotopic composition of OM produced in the lake. Therefore, changes in sediment  $\delta^{13}\text{C}$  values are used as indicators of productivity in lakes (Hodel, Schelske, 1998; Meyers, Teranes, 2001). Application of  $\delta^{15}\text{N}$  values to identify OM sources is founded on the difference between the  $^{15}\text{N}/^{14}\text{N}$  ratios of the inorganic nitrogen reservoirs available to plants in water and those on land. The  $\delta^{15}\text{N}$  value of dissolved  $\text{NO}_3^-$ , which is the most common form of dissolved inorganic nitrogen (DIN) used by algae, is typically 7–10 ‰ greater than that of the atmosphere-derived  $\text{N}_2$  that is made available to land plants by nitrogen fixers in soil. The isotopic difference between these two sources of nitrogen is roughly preserved in the  $^{15}\text{N}$  values of OM from algae (+8.5 ‰) and from  $\text{C}_3$  land plants (+0.5 ‰). However, additional factors complicate interpretations of the nitrogen isotopic composition of OM in lake sediments. An increase in  $^{15}\text{N}$  values might record deliveries of isotopically heavy nitrate ( $^{15}\text{N}$ = 10–25 ‰) from farm runoff and human sewage, or it might indicate denitrification of DIN in anoxic



bottom water. Shifts in phytoplankton or heterotroph assemblages will influence the  $^{15}\text{N}$  of sedimented OM (Meyers, 2003).

## 2.4 Phosphorus

Primary producers, organisms able to photosynthesize, are able to absorb and use nutrients dissolved in water. Thus, primary producers serve as the basis for aquatic food chains. Because phosphorus and nitrogen compounds often limit the amount of growth by primary producers, these nutrients are sometimes referred to as “limiting nutrients.” Likewise, phosphorus and nitrogen compounds are also considered to be “causal variables” because in excessive amounts, they may cause proliferation of primary producers (Walker et al., 2007).

Particularly phosphorus compounds are important among the many nutrients that apart from carbon contribute to plant primary production and, thus form the basis for the other components of the food chain. Another significant nutrient, nitrogen compounds, typically occurs in concentrations much higher than those of phosphorus compounds and despite that the demand by primary producers for nitrogen is higher than for phosphorus there will often be a nitrogen surplus (Søndergaard, 2007). Nitrogen in lakes and reservoirs may come from natural sources, such as the decomposition of plants and animals, waste products from aquatic life within the water, urine and feces of wildlife in the catchment, or (in generally small amounts) mineral dissolution of rocks. Nitrogen that enters lakes and reservoirs is often of direct human origin (such as discharges from sewage treatment plants or leachate from septic systems) or is related to human activities (such as wastes from poultry and livestock facilities, runoff of fertilizers, or nitrous oxides from fuel combustion). Nitrogen can be transported to lakes and reservoirs through atmospheric deposition (precipitation on the lake surface), runoff, or groundwater. Nitrogen exists in fresh water in a number of different forms. Most algae and other primary producers are able to utilize inorganic forms of nitrogen: nitrates ( $\text{NO}_3^-$ ), nitrites ( $\text{NO}_2^-$ ), ammonia ( $\text{NH}_3$ ), and ammonium ions ( $\text{NH}_4^+$ ) (Walker et al., 2007).

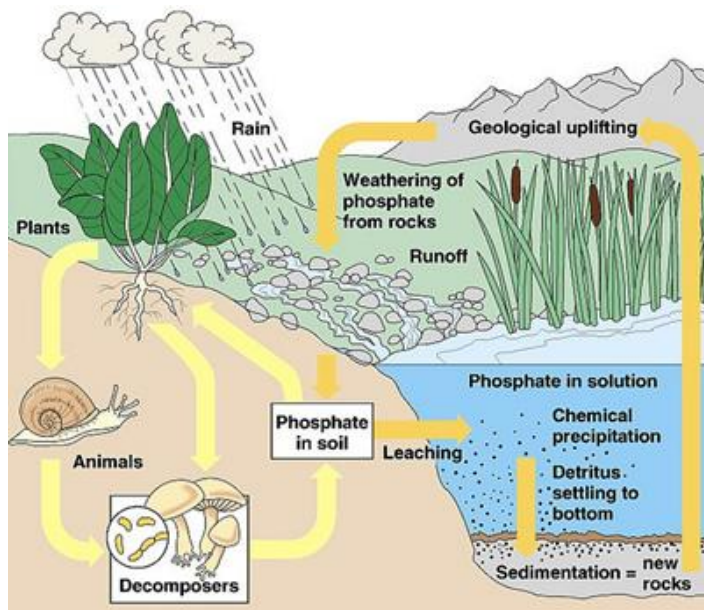
The phosphorus content in water is highly dependent on human population density, municipal infrastructure and land use intensity in lake's watershed. Human-induced eutrophication of freshwaters, also called anthropogenic eutrophication, is largely a result of increased phosphorus inputs from sources such as agricultural fertilizers or partially treated sewage (Standardized Database for Water Quality Monitoring, 2009). Transparency, which is measured with Secchi disc and expressed as Secchi depth, is used as an auxiliary indicator of the status and productivity of lakes. Reduced transparency affects the appearance of the lake and restricts swimming and other sports activities in and around it. If phosphorus loading is excessive, phytoplankton is proliferated and this has significant negative implications for the overall water quality and biodiversity of the lake: the water becomes turbid and levels of light reduce, levels of oxygen decrease, toxic algae may develop, submerged macrophytes disappear, fish stocks change toward less desirable species, and top-down control by zooplankton on phytoplankton decreases; all of these ultimately have negative consequences for organisms that live in the lake (Standardized Database for Water Quality Monitoring, 2009). Oxygen is required for most life forms on this planet, with the exception of some bacteria. For this reason, oxygen depletion is considered to be a serious ecological problem often associated with eutrophication. Eutrophication causes an increased OM production, so more material is sedimented down into the profound waters, consuming oxygen. Since it is impossible for most organisms to function efficiently unless the oxygen concentration in the water is near saturation, such organisms are often absent from eutrophic environments. This problem can preclude fish or other biota from inhabiting deep-water regions of anoxic lakes. (Smith et al., 2006). Phosphorus normally occurs in nature as part of a phosphate ion ( $\text{PO}_4^{3-}$ ), the most abundant form is orthophosphate. Most phosphates are found as salts in ocean sediments or in rocks. Over time, geologic processes can bring ocean sediments to land, and weathering will carry these phosphates to terrestrial habitats. Plants absorb phosphorus compounds from the soil, and then bind it into organic

compounds. Plants may then be consumed by herbivores who in turn may be consumed by carnivores. After death, the animal or plant decays, and phosphorus compounds are returned to the soil. Runoff may carry it back to the ocean or it may be reincorporated into rock (Peltzer et al. 2010). Phosphorus forms parts of obligate life-sustaining molecules that are present in the biosphere. It does not enter the atmosphere, remaining in rock, soil and water as a phosphate. Majority (up to 80 %) of the mined phosphorus is used for fertilizers. Phosphates may be effective in such ways but also cause pollution issues in lakes and streams (Søndergaard et al., 2001). Enrichment of phosphorus compounds can lead to eutrophication of fresh and inshore marine waters, leading to algal bloom because of the excess of nutrients (Peltzer et al., 2010). Respiration of bacteria usually uses all the oxygen in the water, causing many fish to die. Phosphorus compounds enter the lake in either a particulate form, which can be directly deposited in the sediment, or as dissolved phosphorus compounds, which can be incorporated in OM by primary producers that eventually sink to the bottom in an organic form. Sedimentation may also occur via co-precipitation with calcium carbonate or the formation of and adsorption by iron hydroxides. Having reached the sediment, phosphorus compounds become a constituent part of numerous chemically and biologically mediated processes and is ultimately permanently deposited in the sediment or released and returned to the water column via the pore water. Between these two terminal stages, phosphorus compounds may be transformed several times and incorporated into different organic and inorganic phosphorus compounds (Søndergaard et al., 2001). Due to inadequate knowledge of the mechanisms behind internal loading in shallow lakes, it has been difficult to establish general relationships between lake or sediment characteristics, including different sediment phosphorus forms and the intensity and duration of internal loading. Such knowledge may provide information on the overall and long-term conditions for phosphorus sorption expected to prevail in the sediment, whereas knowledge of static phosphorus binding gives only limited insight into the changes of phosphorus forms released under dynamic conditions (Jensen et al., 1998).

#### 2.4.1 Phosphorus cycle

The constant exchange of an element between organisms and the physical environment is called a biogeochemical cycle. Along with the carbon cycle and the nitrogen cycle, one of the most important biogeochemical cycles is that of phosphorus. The phosphorus cycle involves the distribution of phosphorus as it circulates through the living and non-living portions of the biosphere (Turner et al., 2003), i.e. through the lithosphere, hydrosphere, and biosphere (*Figure 1*). Unlike many other biogeochemical cycles, the atmosphere does not play a significant role in the distribution of phosphorus, because phosphorus and phosphorus-based compounds are usually solids at the typical ranges of temperature and pressure found on Earth. The production of phosphine gas occurs only in specialized, local conditions. Phosphorus compounds availability is considered as the most important factor for determining the water quality of lakes. Numerous studies have shown that high loading of phosphorus compounds leads to high phytoplankton biomass, turbid water and often undesired biological changes. Because of their strong impact on lake water concentrations, it is clear that knowledge of sediment–water interactions and the processes behind retention and release of phosphorus compounds is fundamental for understanding the function of shallow lakes (Søndergaard et al., 2003).

Low phosphorus compounds availability slows down microbial growth in soils. Soil microorganisms act as sinks and sources of available phosphorus compounds in the biogeochemical cycle. Locally, transformations of phosphorus compounds are microbially driven; however, the major transfers in the global cycle of phosphorus are not driven by microbial reactions, but by tectonic movements in geologic time. Further studies need to be performed for integrating different processes and factors related to gross phosphorus mineralization and microbial phosphorus turnover in general (Turner et al., 2003).



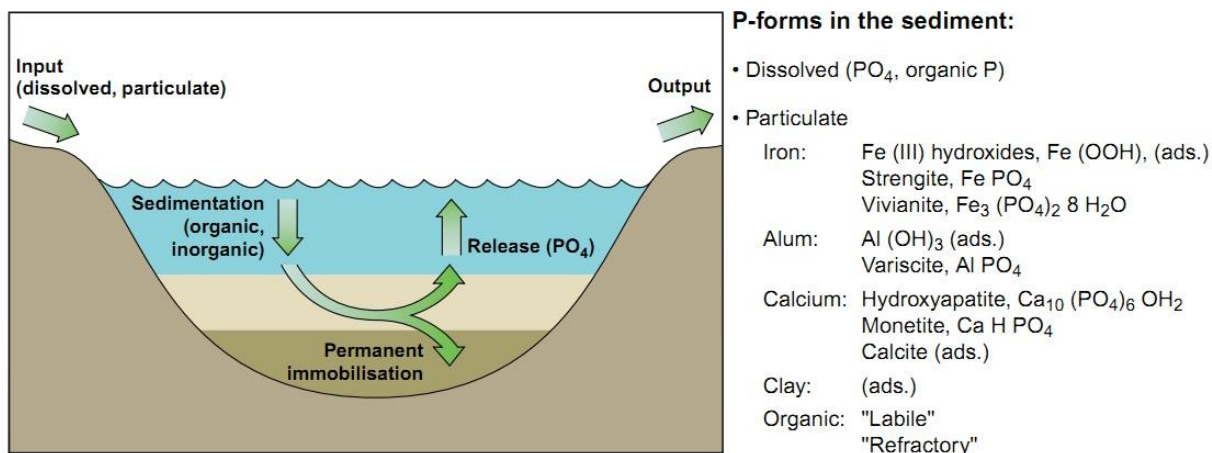
**Figure 1. Phosphorus cycle** (<http://lifeofplant.blogspot.com/2011/03/phosphorus-cycle.html>)

### 2.4.2 Forms of phosphorus in water and sediment

Phosphorus compounds in water exist in two main forms: dissolved (soluble) and particulate (attached to or a component of particulate matter). Ortho phosphate ( $\text{PO}_4^{3-}$ ) is the primary dissolved form of phosphorus and is readily available to algae and aquatic plants.

Fixation of phosphorus compounds in the sediment depends on the transport of soluble phosphorus compounds between solid components through adsorption-desorption mechanisms, chemisorption, and biological assimilation. Chemisorption is the chemical fixation of soluble compounds that are subsequently unaffected by changes in solute concentrations, whereas adsorption is a physical fixation of soluble compounds on surfaces in constant equilibrium with solute concentrations. Adsorption and chemo-sorption processes often depend on both pH and the redox potential and are therefore influenced by the bacterial metabolism (Søndergaard et al., 2001).

Particulate phosphorus compounds can change from particulate to dissolved form (called cycling) in response to a variety of environmental conditions (Figure 2). A portion of particulate phosphorus compounds is contained in OM such as algae, plant and animal tissue, waste solids, or other OM. Microbial decomposition of organic compounds can convert organic particulate phosphorus compounds to dissolved phosphorus compounds. Some of the phosphorus compounds in soil mineral particles can also be converted to dissolved phosphorus compounds both in the water column and during chemical and physical changes in sediments. Only the most strongly bound forms of particulate phosphorus such as aluminum-bound and calcium-bound phosphorus compounds are not generally available for algal growth. Because phosphorus changes forms, most scientists measure total phosphorus (TP) rather than any single form to determine the amount of nutrient that can feed the growth of aquatic plants such as algae (Table 1) (Minnesota Pollution Control Agency, 2007). But we need to be aware that all forms of phosphorus are not available to organisms. TP is a measure of all the forms of phosphorus (dissolved and particulate) found in samples. Therefore, TP does not tell us everything.



**Figure 2. Conceptual diagram showing input/output of phosphorus and some of the most important pathways and phosphorus compounds in the sediment and water in shallow lakes (Søndergaard et al., 2001).**

Variable	Extractant	Biological Availability and Susceptibility to Recycling Pathways
Loosely bound P	1 M ammonium chloride	Biologically labile; available for uptake and can be recycled via eH and pH reactions and equilibrium processes.
Iron-bound P	0.11 M sodium bicarbonate-dithionate	Biologically labile; available for uptake and can be recycled via eH and pH reactions and equilibrium processes.
Aluminum-bound P	0.1 M sodium hydroxide	Biologically refractory; generally unavailable for biological use and subject to burial.
Calcium-bound P	0.5 M hydrochloric acid	Biologically refractory; generally unavailable for biological use and subject to burial.
Refractory organic P	Calcination of remaining particulate P	Biologically refractory; generally unavailable for biological use and subject to burial.

**Table 1. The biological significance of the various phosphorus fractions (James et al., 2004)**

### 2.4.3 Sources of phosphorus

There are many sources of phosphorus compounds in aquatic systems. These sources can be natural such as animal waste, atmospheric deposition, weathering of geologic phosphate material, and plant decomposition or they can be human induced such as fertilizer, urban runoff, industrial and domestic sewage (Figure 3) (Wang et al., 2004).

Phosphorus compounds mobilization as well as phosphorus compounds fixation are affected by a number of environmental factors of which temperature, pH and redox potential are the most important. Microbial processes in surface sediments have a direct influence on phosphorus compounds mobilization through the various biochemical processes. Biological processes also modify

the chemical environment, thereby affecting the physical and chemical mobilization processes as well as transport mechanisms. Microbial activity increases the oxygen consumption and decreases redox potential. With lowered redox potentials alternative electron acceptors are used for the mineralization of organic matter, resulting in the production of reduced products affecting phosphorus cycling in lakes in various ways (Boström et al., 1988).

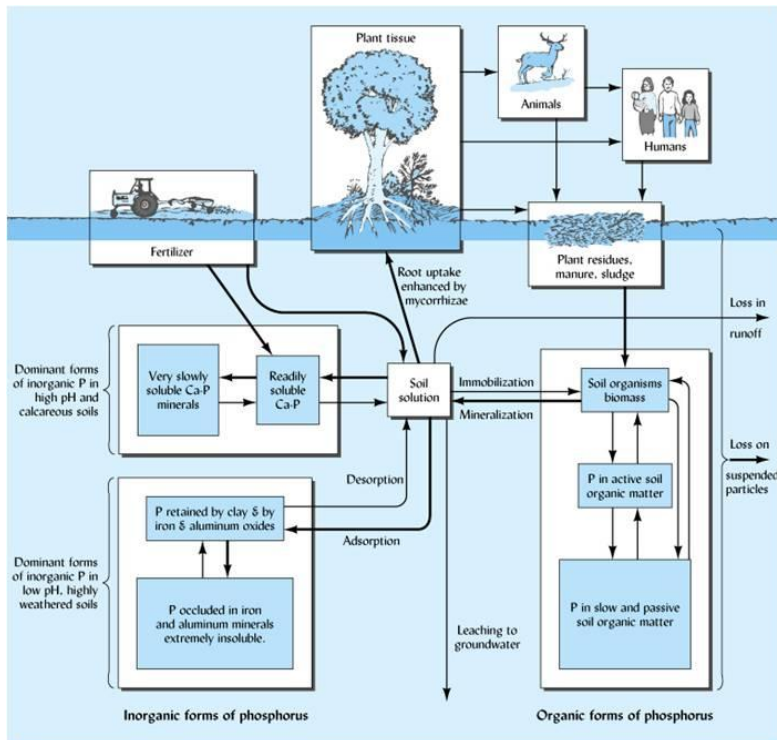
Two different mechanisms have to occur simultaneously or within a short period of time. Firstly, phosphorus compounds bound to particles or aggregates in the sediment must be mobilized by being transferred to the pool of dissolved phosphorus compounds (primarily phosphate) in the pore water. Secondly, processes which transport the dissolved phosphorus compounds to the lake water must function (Table 2). Important mobilization processes are desorption, dissolution, ligand exchange mechanisms, and enzymatic hydrolysis. These processes are affected by a number of environmental factors, of which redox potential, pH and temperature are the most important. Essential transport mechanisms are diffusion, wind-induced turbulence, bioturbation, and gas convection. Redox-controlled dissolution and diffusion are considered as the dominant mechanisms for phosphorus compounds release from stagnant hypolimnetic bottom areas. All the mobilization and transport processes can theoretically contribute to the overall phosphorus compounds release from sediments in shallow lakes. At high temperatures, microanaerobic zones are formed very rapidly, and redox-controlled liberation of phosphate can occur to well-aerated water. Wind-induced turbulences often have a dominating role among the transport processes (Boström et al., 1982).

Environmental parameter	Effect on phosphorus compounds mobilization
Redox potential	Fe-bound phosphorus compounds are released at potentials below 200 mV when Fe(III) is reduced to Fe(II)
pH	An increase in pH decreases the P-binding capacity of Fe and Al compounds, primarily due to ligand exchange reactions where hydroxide ions replace phosphate. Calcite and apatite formation at higher pH-values increase the phosphorus - binding capacity of calcium
Temperature	An increase in temperature gives primarily indirect effects due to increased bacterial activity, which increases oxygen consumption and decreases the redox potential and pH-value. The production of phosphate-mobilizing enzymes and chelating agents might increase accordingly
Equilibrium criteria	Affects adsorption-desorption and dissociation of precipitates
Chelating agents	Replace phosphate from salts with calcium, iron and aluminium. Chelating agents can be produced by bacteria and algae or occur as a pollutant

**Table 2. Effects of important environmental factors on phosphorus compounds (Boström et al., 1982)**

The dual effect of nitrate on phosphorus compounds exchange between sediments and water illustrates the complexity of interactions between abiotic and biotic processes. Nitrate may prevent phosphorus compounds mobilization by maintaining a high redox potential, by competitive inhibition of phosphorus compounds mobilizing bacteria, or by inhibition of iron reduction. On the other hand, nitrate may enhance phosphorus compounds mobilization by stimulating bacteria capable of producing iron reductases. The net effect of nitrate on phosphorus compounds mobility may differ

among sediments and at different times (Boström et al., 1988). Nitrogen retention in lakes does not only occur as incorporation in sedimented OM, but also, and largely so, via denitrification, where nitrate is exploited for the bacterial turnover of OM (Wetzel, 2001). Thereby nitrate converts to ammonium or to free nitrogen ( $N_2$ ) that may diffuse into the water phase and the atmosphere, and thus is lost from the system (Søndergaard, 2007). Phosphates have a strong affinity to iron, aluminium and manganese oxides. Reduction and oxidation (redox) of these metals regulate the dynamics of phosphorus compounds in sediments. The mechanisms of phosphorus compounds mobilization are explained by the reductions of insoluble metal oxides such as  $Fe^{3+}$  to soluble  $Fe^{2+}$  in sediments or water whereby phosphorus compounds bound to  $Fe^{3+}$  or adsorbed to iron complexes is returned to solution when system redox potentials change from aerobic to anaerobic conditions (Wang et al., 2004). Adsorption and desorption of phosphorous and nitrogen compounds are influenced by many factors, such as temperature, pH, the concentration of OM in sediments, the exterior disturbance, and so on. The decomposition of OM affects much the cycle of  $NH_4-N$ ,  $NO_3-N$ , and  $PO_4^{3-}$  in aerobic conditions, but this effect is smaller under anaerobic conditions (Wang et al., 2008). Heterotrophic microorganisms that reduce oxidized compounds using OM as an energy source are directly or indirectly responsible for most of the redox reactions in sediments. Phosphorus compounds dissolved in pore water originate mainly from both  $Fe^{3+}$  oxides and OM, which constitute the main mobile phosphorus-binding pools in sediments. The bulk of the phosphorus, however, is thought to be released from sediment from  $Fe^{3+}$  oxides undergoing reduction. There are two main processes that can reduce  $Fe^{3+}$  oxides in sediments: first, enzymatic microbial dissimilatory reduction and, second, nonenzymatic reduction by the sulphide formed in microbial dissimilatory  $SO_4^{2-}$  reduction (Lovely, 1991). Insoluble  $Fe^{3+}$  oxides are reduced to soluble  $Fe^{2+}$  ions, after which the P bound to  $Fe^{3+}$  oxides is released into pore water. When reduced soluble  $Fe^{2+}$  is diffused to an oxic environment (sediment surface or near-bottom water) it is oxidized to  $Fe^{3+}$  oxides having a high capacity to sorb P. Hence, sediments overlain by aerobic waters often have an  $Fe^{3+}$  oxide-rich surface layer. The precipitated  $Fe^{3+}$  oxides present in the surface layer are considered to effectively prevent P from entering the euphotic surface of water. Adsorption of P onto  $Fe^{3+}$  oxides may occur rapidly, because  $Fe^{2+}$  is oxidized within minutes or hours in the presence of  $O_2$ . As well as chemically,  $Fe^{2+}$  is oxidized by lithotrophic  $Fe^{2+}$  oxidizing bacteria in surficial sediments (Sobolev, 2001). Dissimilatory microbial  $Fe^{3+}$  reduction leads to the simultaneous accumulation of  $Fe^{2+}$  and phosphorus compounds in anoxic pore water (Andersen, 1982). Where suitable conditions develop at the water sediment interface (i.e. anoxic conditions), substances contained in the sediments, including nutrients, are released into the water column.



**Figure 3. Roles of phosphorus forms**

([http://faculty.yc.edu/ycfaculty/ags105/week12/biogeochemical\\_cycles\\_information/biogeochemical\\_cycles3.html](http://faculty.yc.edu/ycfaculty/ags105/week12/biogeochemical_cycles_information/biogeochemical_cycles3.html))

## 2.5 Ecological modeling

The basic question from the viewpoint of computer science and information technology viewpoint is: what can the computer offer to decision-makers and how it can support their work? Therefore, the main issue is to provide support to people who make complex decisions. Decision analysis approaches a decision problem systematically by structuring and breaking it down into smaller and possibly more manageable sub-problems. In doing that, it explicitly considers the possible decision alternatives, available information, uncertainties involved, and relevant preferences of the decision-maker. It also attempts to formally represent these components and combine them in a form of decision models, which are used to assess, evaluate and analyze alternatives (Bohanec, 2009). Computer models are very useful when attempting to understand the geochemical processes in the sediment, particularly when the aim is to predict responses of a system to changes in the future or to interpret indicators of past changes. Probably the most frequently argued thesis in environmental evaluation is that public perceptions have no place in environmental policy decisions because laymen do not have the knowledge to evaluate accurately what may be the changes and consequences in the environment due to a certain (development) action, or what is best for society. Thus, the resultant judgments on alternatives and their acceptability will be subject to noise or bias. Analyses performed by experts should be free from such errors (Kontić et al., 2006). On the other hand, it is well known that environmental evaluation is not just a matter of science, it is also, if not primarily, a matter of relations in society. Therefore, in order to be comprehensive in a multi-attribute environmental analysis, one has to be inclusive, in spite of the issue of different and very often opposing interests and value systems among the participants. Several authors suggest that this issue should be thoroughly considered and subsequently developed into some form of practical mechanism, but unfortunately they give no specific recommendation in that regard (Ferrarini et al., 2001; Ramanathan, 2001; Getzner, 2002). A fact which undoubtedly supports openness and transparency

in environmental decision-making is the uncertainty of predictions of impacts. The response of science to uncertainty is routinely framed in the language of probability theory, but such probabilities are rarely 'pure'. The risk analyst typically needs to invoke a variety of assumptions and hypotheses in order to estimate the impacts and their corresponding probabilities. Also, situations where one has to apply value judgments, preferences and expert opinion as inevitable components of the evaluation process are not exceptional (Cooke, 1991). This is especially the case if the final result of the evaluation is prioritization of (policy) options (Kontić et al., 2006). Ecological models are important tools for planning ecosystem restoration and management activities. Models help to organize thinking, conceptualize understanding of complex systems, and forecast environmental benefits that may result from proposed restoration and management actions. Quantitative modeling is shown to be a dynamic process that is best served using an iterative approach. In practice, individual parts of a conceptual model are quantified and evaluated in a stepwise fashion until the entire model is captured quantitatively. Over the last several decades, models have become an important tool in environmental decision-making; most modern environmental projects require models. Although quantitative models are often required for projects, there is still considerable apprehension when applying models to environmental problems. Ecosystems are inherently complex, and for any given environmental system, the number of interacting factors is large (e.g., weather, species, hydrology, geomorphology, anthropogenic factors, etc.). Each factor operates at different spatial and temporal scales. Therefore, it is rare to have a complete dataset that encompasses all the different permutations of environmental conditions, yet planning activities must often determine how a system will respond under extreme conditions – i.e., outside the range of available field data.

Modeling is an excellent tool for analyzing environmental systems because it helps to fill data gaps and provides a mechanism to systematically compare scenarios across a broad range of conditions that would not be possible in the field. The process of modeling helps researchers to organize their thoughts and research direction, facilitates communication, and creates a level of transparency that can dispel the myth that models are "black-box" endeavors. However, models do have limitations and should not be viewed as all-inclusive or as a resolution for environmental decision-making. Since environmental models are simplified representations of complex systems, they are often built using assumptions regarding the unknown components in the model. The usefulness of a model hinges on understanding whether the data and assumptions used to develop the model are sufficient enough to inform decisions. It is also important to understand that models should inform, not dictate, decision-making processes. Modeling does not provide all the answers, rather good models should inform management/planning decisions and their results should be incorporated with results from field studies and professional judgment (by subject matter experts) before final decisions are made. Many issues must be considered in selecting an appropriate model. One of them is that the project team should align model selection criteria/process with the problems and opportunities to be addressed and associated information demands of the study/project. That means the team should thoroughly discuss project scope, scale and objectives, ecosystem characteristics, availability of data, and project duration with subject matter experts, stakeholders, and staff/leadership of involved agencies. During these discussions, it is common for people to have or form expectations that may or may not be realistic, seek complexity that may or may not be necessary, and be familiar with a particular type or "brand" of model and request that it be used. However, it is important to recognize that many different types of models can be used to address environmental problems and familiarity with a particular type of model does not indicate its usefulness for a specific project (Swannack et al., 2012).

Decision-making is usually defined as a mental process, which involves judging multiple options or alternatives, in order to select one, so as to best fulfill the aims or goals of the decision-maker. Therefore, there are two main components involved in decision-making: the set of alternatives, judged by the decision-maker, and the goals to be satisfied with the choice of one alternative. In the case of missing information and other difficulties, decision analysis tries to provide decisions which are not optimal but "satisfactory" or "sufficiently good". The output of this process can be an action



or an opinion of choice. Decision-making is a process. This means that in general it takes some time and effort until the choice is made, involving several activities, such as:

- identification of the decision problem;
- collecting and verifying relevant information;
- identifying decision alternatives;
- problem decomposition and modeling;
- anticipating the consequences of decisions;
- evaluation and analysis of alternatives;
- selection of the best alternative;
- making the decision;
- informing concerned people and public of the decision and rationale;
- implementing the selected alternative;
- evaluating the consequences of the decision.

If necessary, the stages can be intermixed or repeated. The most distinctive stages of decision analysis are the third stage, in which a decision model is developed, and the fourth stage, in which the model is used to evaluate and analyze alternatives (Bohanec, 2009). The key step of this process is making the decision itself, that is, choosing the most preferred alternative using judgment based on available information. With the decision, we give precedence to the selected alternative, assuming (and hoping) that this alternative will provide the best (i.e., the easiest, most efficient, cheapest, safest, etc.) solution to our decision problem. The decision is considered a conscious and deliberate act, what makes the decision-maker responsible for its consequences. The implementation of the decision often consumes resources, such as time, energy, money and willpower, and is therefore irrevocable. The consequences of a decision cannot be taken back; if necessary, they can only be affected by new decisions (Bohanec, 2009). Decision support systems (DSS) are interactive computer-based systems intended to help decision-makers utilize data and models to identify and solve problems and make decisions. The purpose of developed models is threefold: (1) to capture and represent expert knowledge in the form of hierarchically structured variables and decision rules that can be reviewed, discussed, published, disputed and communicated between decision analysts, field experts, stakeholders, users and other interested groups; (2) to actively assess and evaluate decision alternatives; and (3) to analyze these alternatives using decision-analysis tools, for instance, to identify the advantages and disadvantages of alternatives and analyze the effects of changes by 'what-if' and sensitivity analysis. Decision support models have a wide variety of uses in problematic terrestrial and marine protected areas, including selecting the optimal location for protected areas, modeling the carrying capacity of national parks, managing wilderness recreational activity of park visitors and providing management approaches to balancing ecological, social and economical aspects of protected areas (Štubelj Ars, Bohanec, 2010). Much of the relevance of palaeolimnology to studies of recent environmental change has derived from its ability to reconstruct water-chemistry variables via microfossil transfer functions (e.g. pH, salinity, TP). Predictions of future lake water quality following lake restoration methods tend to be made from dynamic mathematical models (Wright, Cosby, 2003), but they are also used for hindcasting. A problem with using dynamic models is that they are often site-specific and require calibration for a given lake. The use of dynamic models to provide historical reconstructions of chemical variables and/or ecosystem trajectories has become more common in a number of areas of environmental research (climate, acidification, and eutrophication). There have, however, been relatively few attempts to validate these long-term hindcasts (Anderson, 1995). Models have also been used to understand the basic eutrophication processes and thereby assist restoration measures. (Reynolds, 1987).

### 3. MATERIALS AND METHODS

#### 3.1 Site description and sampling

##### 3.1.1 Site description

The Fifth (in slov. Peto jezero) and the Sixth (in slov. Šesto jezero) Triglav Lake form together the lake called Double Lake (in slov. Dvojno jezero). At high water level, the two lakes form a single body of water, but at low waters (in summer and autumn) there are two separate lakes. The lake catchments are composed of Triassic and Jurassic shallow-water carbonate rocks with patches of Cretaceous carbonate-clastic rocks and Pleistocene sediments (Rman, Brenčič, 2008; Šmuc, Rožič, 2009). To the east and south of the lakes there is a moraine, partly covered by screes which actually preserve both lakes from being in-filled. The ridge separating the lakes as well as the northern shore is of glacial origin. The western shore of the Fifth Triglav Lake with its characteristic hook-shaped bay is marked by precipitous rock faces. The surrounding area is characterized by reddish clay. The depth of the lake decreases gradually towards the bottom. Except for some large boulders, which can also be found along the shore, the morphology of the lake bottom is not very diverse. Water level may fluctuate between 2 to 3 meters (Brancelj, 2002).

The Fifth Triglav Lake has no permanent surface tributaries. Periodically, at high water level, it is fed by the water from Močivec, about 150 m north of the lake, and some water flows from the holes in the swamp area near its northern shore. The only permanent yet weak underwater inlet flows from below a large boulder on the eastern side of the lake. There are no surface outlets. The lake, however, has an active underwater outlet through a sinkhole at the beginning of a hook-shaped bay, just below the precipitous rock face. From a depth of 5 m, the lake bottom is covered with thick layer of fine dark brown silt. The surface sediment in the Fifth Triglav Lake contains 92 % water and more than a half (54 %) of solid matter is organic material. The transparency of the lake water has been reduced following stocking with fish so that now sunlight reaches only to a depth of 6 to 7 meters (Brancelj, 2002).



**Figure 4. The Fifth Triglav Lake from the Northern side (Photo by Matej Fister)**



**Figure 5. The Fifth Triglav Lake from the Southern side with the hut (photo by Matej Fister)**

The Fifth Triglav Lake was included in regular lake water monitoring activities at the National Institute of Biology aimed at following changes in the biological and chemical condition of Slovenian mountain lakes (Muri, Brancelj 2003; Muri 2004). A study of the water chemistry of all 14 mountain lakes in Slovenia during the period 2000-2002 revealed that the condition of the Fifth Triglav Lake and the Sixth Triglav Lake did not differ greatly between each other and also from those of other less

productive lakes in the Julian Alps (Muri, 2004). Briefly, the observed lake catchment bedrock characteristics included rather high alkalinity and calcium in the water column (*Table 3*), slightly basic pH (~8) and conductivity exceeding 140  $\mu\text{S cm}^{-1}$ . Hydrogen carbonate and calcium were the most abundant ions, comprising up to 95 % and 85 % of total anion and total cation concentrations, respectively. Regarding nutrients, nitrate concentrations ranged from 1.3 to 1.9  $\text{mg L}^{-1}$ ; total nitrogen concentrations were rather high, but this is characteristic of the entire Julian Alps region (Camarero et al., 2009). Total phosphorus concentrations were in the range usually observed in mesotrophic lakes, and so were chlorophyll *a* concentrations. Simčič and Brancelj (2002) also rated the lake as mesotrophic in a study investigating the intensity of mineralization processes in Slovenian mountain lakes. A comparison of water chemistry data obtained during 2000-2002 with that for the period 1991-1998 (Brancelj, 1999 b) revealed an increase in nitrate and total phosphorous concentrations, and a decrease in oxygen concentration in the water column after 1994 as a consequence of fish introduction. Nevertheless, it is important to mention that water samples from the lakes were collected only once per year in late August/early September. The samples thus represent only a 'snapshot' of limnological conditions (Muri, 2004).

	5J
Surface area (ha)	1.00
Max. depth (m)	11
Alkalinity ( $\text{mmol L}^{-1}$ )	1.6 – 1.9
Ca ( $\text{mg L}^{-1}$ )	19 – 30
Chlorophyll <i>a</i> ( $\mu\text{g L}^{-1}$ )	1 – 7
$\text{NO}_3^-$ ( $\text{mg L}^{-1}$ )	1.3 – 1.9
TN ( $\text{mg L}^{-1}$ )	1.6 – 3.2
TP ( $\mu\text{g L}^{-1}$ )	8 – 23

**Table 3. Basic morphometric and epilimnetic limnological characteristics of the Fifth (5J) Triglav Lake for the period 2000 – 2007 (data from Brancelj, 2002; Muri, 2004; Jerebic, 2008).**

The lake is located close to the local tree line and is partly surrounded by larch forest and/or dwarf pine, and partly by grasses (*Figure 4*). The height above sea level is 1669 m. Maximum depth of the Fifth Triglav Lake is 11 m and median area 1.002 ha. Catchment area of the lake is approximately 90 ha. The area of the Julian Alps where the lake is situated is protected by law and lies within the Triglav National Park (TNP) (Brancelj, 2002). One of the most popular activities in the area is mountain tourism, with the first mountain hut on the shore of the Fifth Triglav Lake built in 1880 and enlarged in 1955 (*Figure 5*). Due to increasing visitor numbers, the hut was modernized again in 1986-1988 when a cesspit for sewage was constructed. In 1990, an additional log cabin was built next

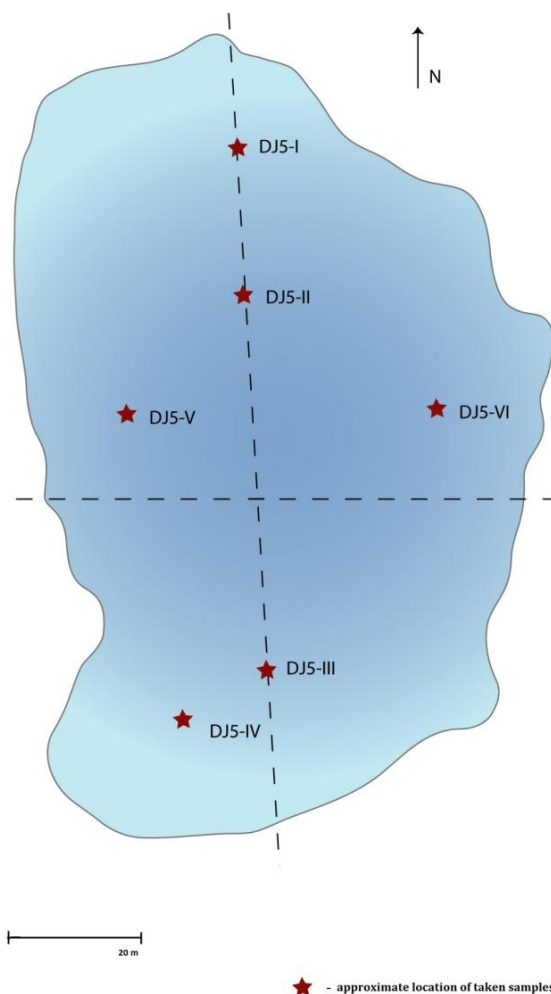
to the mountain hut (Erhartič, 2004). In 2010, a wastewater treatment plant for sewage was constructed. The mountain hut operates only in the summer months, providing accommodation and basic food supply for mountaineers. Despite operating only in summer, the mountain hut at the Fifth Triglav Lake is one of the most frequently visited in the entire Julian Alps, with up to 10,000 daily visitors per month and up to 3,500 overnight stays per month registered in peak summer months (Jerebic, 2008). The main threat to the lakes posed by the hut is the wastewater which was collected in the cesspit but treated no further. Nevertheless, Muri et al. (2013) concluded that the mountain hut has seemingly not had a significant enough impact on the lake to be recorded in the sediments. On the other hand, a study of total and faecal coliform bacteria in seven mountain lakes in Triglav National Park was conducted in 2007 (Odar, Brancelj, 2009). In the Fifth Triglav Lake, faecal coliform bacteria were found only during the season in which the mountain hut at the Fifth Triglav Lake was open, and thus can be attributed to latter's associated wastewater. In contrast, no such bacteria were found in lakes situated in the same valley but at higher altitudes. However, changes in the Fifth Triglav Lake were too rapid to be attributed to natural processes alone, and were instead shown to be related to fish introduction (Brancelj, 1999 b). In 1991, arctic char were introduced into both lakes, with first spawning observed in autumn 1994. Within less than ten years after the introduction of the fish, macrozooplankton disappeared, the population of benthic invertebrates declined, the lakes transformed from oligotrophic to mesotrophic, and filamentous green algae and picoplankton became abundant in the littoral zones of both lakes down to a depth of 4 m (Brancelj, 1999 b; Brancelj, 2002). As a result, high primary production and frequent algal blooms were observed in this lake, reflected in the relatively lower C/N ratio (Muri et al., 2013). After 1998, filamentous green algae expanded deeper into the lakes, eventually reaching the bottom. The fish population in the lake increased considerably between 1994 and 1999 (Brancelj, 1999 b; Leskošek, 2007). Two attempts to remove the fish took place in 1999 and 2000, but both were unsuccessful (Brancelj, 2002).

### 3.1.2 Sampling

Six sediment cores at depths from two to five meters were collected in October 2011 all across the Fifth Triglav Lake (*Figure 6*) using a gravity corer equipped with a 9-cm-diameter plexiglass tube. Only the uppermost centimetre of the sediment was collected. Surface sediment samples were stored in polyethylene containers and kept frozen. Subsequently, frozen wet sediment samples were dried in a lyophilizator.

#### *Preparation of dry sample:*

In dry sediment samples, any residual OM (leaves, twigs) was removed as well as husks or shells of snails, which can be removed with tweezers. The rest of the samples was crushed in mortar, sieved through a sieve with a pore size of 200 micrometers, and homogenized.



**Figure 6. Location of the sampling sites in the Fifth Triglav Lake (Figure provided by Popit, University of Ljubljana)**

## 3.2 Geochemical analyses

### 3.2.1 Determination of organic carbon (OC) and total nitrogen (TN) concentrations

#### Analysis of OC

Sediment sample was weighed into silver capsule 5 x 9 mm (5-15 mg, depending on the content of expected OC). Sample was gradually acidified with HCl (from 0.1 to 6 M). HCl was added until effervescence ceased, indicating complete removal of inorganic carbon (Hedges, Stern, 1984). The capsules were then dried in the oven, closed and analyzed in the CHNS analyzer Elementar (vario MICRO cube) in accordance with the manufacturer's instructions. The analyzer was equipped with a temperature programmed desorption column for efficient separation of gaseous components formed during sample combustion. The chromatographic responses were calibrated against reference materials and the C and N elemental contents were reported in percent (w/w). Blank samples and reference materials of known elemental composition (sulfanilamide) were used for quality control. The precision of the method was up to 3 %.

## Analysis of TN

Sediment sample was weighed into a tin capsule 5 x 9 mm (5-15 mg, depending on the content of expected OC). The capsules were sealed and analyzed in CHNS analyzer. Blank samples and standard samples with known elemental composition, i.e. sulphanilamide, were used for quality control. The precision of the method was up to 5 %.

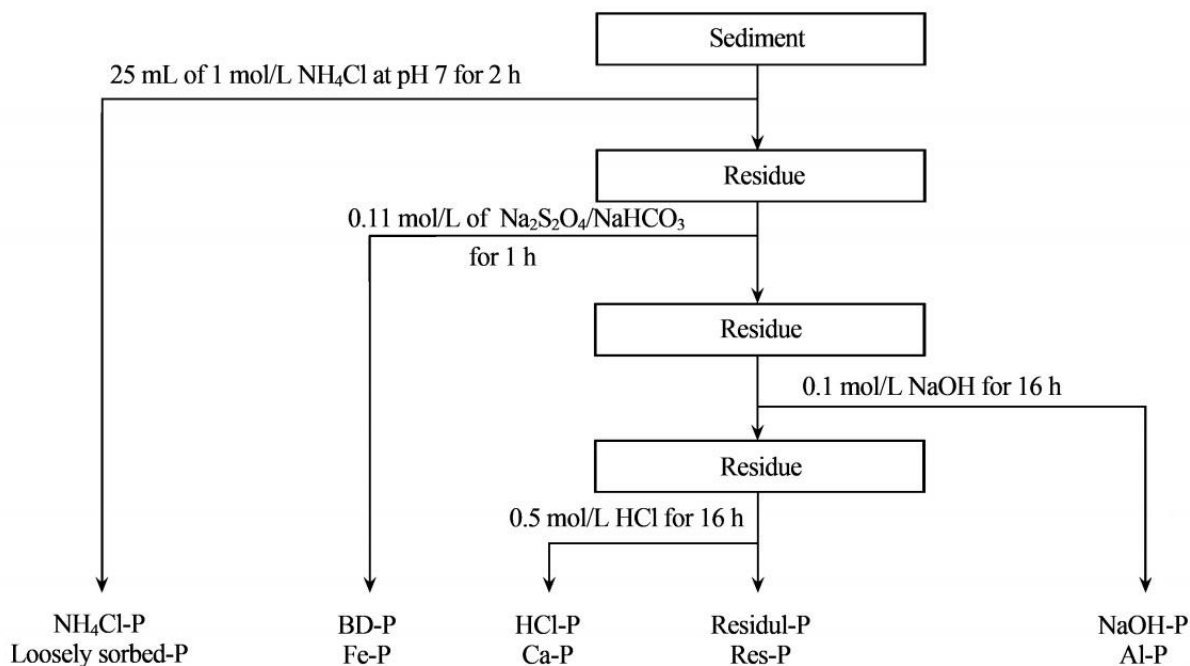
### 3.2.2 Determination of $\delta^{13}\text{C}$ isotopic composition

Dry sediment samples were soaked in 1 M HCl overnight to remove carbonates, and then filtered on quartz-fiber filters (Whatman GF/F), rinsed with deionized water, and redried. Subsamples of 3–4 mg were placed in tin capsules and the stable isotopic composition of organic carbon was determined on a continuous-flow Europa 20-20 isotope ratio mass spectrometer (IRMS) coupled with an ANCA-SL preparation module. All sub-samples were analysed in duplicate. Carbon isotopic ratios are expressed in standard delta notation ( $\delta^{13}\text{C}$ ), which is the per mil (‰) deviation from the V-PDB standard. Analytical reproducibility was  $\pm 0.2$  ‰, as determined by the repeated analysis of reference materials (IAEA-CH-6 and USGS40). The precision of carbon isotope measurements was  $\pm 0.2$  ‰ (Vreča, Muri, 2010).

### 3.2.3 Sequential extraction of phosphorous

Phosphorus compounds in the sediment were analysed by sequential extraction (Jensen et al., 1998). The extraction procedure (*Figure 7*) enables us to fractionate sedimentary phosphorus compounds into loosely adsorbed phosphorus compounds ( $\text{NH}_4\text{Cl-P}$ ), iron bound (reductant) phosphorus compounds (BD-P), metal oxide (aluminium) bound phosphorus compounds ( $\text{NaOH-P}$ ), calcium bound phosphorus compounds ( $\text{HCl-P}$ ) and refractory organic phosphorus compounds (Org-P). These forms of phosphorus were extracted from the same sediment sample and converted into ortho phosphate that was finally determined by the molybdenum blue (Ammonium molybdate) /ascorbic acid) method using a spectrophotometer in accordance with the EN ISO 6878 (2004).

The analytical method was validated in a previous study (Šega, 2013). Shortly, the trueness and recovery of sequential extraction were determined using a certified reference material (BCR 684). The trueness was confirmed by the Student's t-test. Recoveries ranged from 85 to 102 %. The study of repeatability showed that the analytical method is also precise. Relative standard deviations ranged from 1.9 to 8.1 %.



**Figure 7. Sequential extraction method (Jensen et al., 1998; Shujuan et al., 2009)**

*1. Fraction 1: NH<sub>4</sub>Cl-extractable phosphorus compounds - Loosely bound P*

Approximately 250 mg of sediment sample was weighed into Erlenmeyer flask. 25 ml of 1 M NH<sub>4</sub>Cl was added and the flask was shaken for 2h. Suspension was filtered through a 0.45 μm glass filter. The extract was of light yellow color. It was transferred to a 50 ml flask and diluted to mark. The concentration of ortho phosphate ion was subsequently measured using an UV-VIS spectrophotometer.

*2. Fraction 2: Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>/NaHCO<sub>3</sub> extractable phosphorus compounds - Iron-bound P*

Filter with insoluble residue from the previous fraction was put in the same Erlenmeyer flask and a reagent was added (0.11 M dithionite - Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) so that filter didn't dry. The Erlenmeyer flask was put into an ultrasonic bath that the sediment dissolved into solution. The flask was shaken for 1h. Filtration through a 0.45 μm glass filter was quick, extract was of yellow color. 4 ml of 2 M H<sub>2</sub>SO<sub>4</sub> was added (to make the extract acid) and the extract was blown through with synthetic air for 30 minutes to remove excess dithionite. For the determination of phosphorus, it was necessary to dilute the extract (4-10x). Finally, the concentration of ortho phosphate ion was measured using an UV-VIS spectrophotometer.

*3. Fraction 3: NaOH-extractable phosphorus compounds - Aluminum-bound P*

Filter with insoluble residue from the previous fraction was put in the same Erlenmeyer flask and into an ultrasonic bath. 0.1 M NaOH was then added and the sample was left in dark during the night. On the next day, it was shaken for 2h. Filtration through a 0.45 μm glass filter was very slow. Extract was of intensively brown color. 1.5 ml of 2 M H<sub>2</sub>SO<sub>4</sub> was added. A precipitation was formed, and therefore the sample was centrifuged. A 10-20x dilution was necessary to measure the concentration of ortho phosphate ion using an UV-VIS spectrophotometer.



#### 4. *Fraction 4: HCl-extractable phosphorus compounds - Calcium-bound P*

Filter with insoluble residue from the previous fraction was again put in the same Erlenmeyer flask and into an ultrasonic bath. 0.5 M HCl was added and the sample was left in dark during the night. On the next day, it was shaken for 1h. Suspension was filtered through a 0.45 µm glass filter. Filtration was quite quick, the extract was of light yellow color. For the UV-VIS spectrophotometric determination of ortho phosphate ion concentration, a dilution was necessary (20-40x).

#### 5. *Fraction 5: Organic phosphorus compounds*

Filter with insoluble residue from the previous fraction was put in a crucible and dried for 2h at 105 °C. It was cooled down and quantitatively transferred to a crucible and ignited for 2h at 520 °C. The sample was put in desiccator to cool down. Ignited sample was transferred from crucible to Erlenmeyer flask and 25 ml of 1 M HCl was added. The sample was boiled for 10 minutes and filtered when it cooled down. The extract was of a light color. The ortho phosphorus ion concentration was determined after a 20x dilution using an UV-VIS spectrophotometer.

#### 6. *Fraction 6: Total phosphorus*

The total phosphorus concentration was not determined chemically. To obtain its concentration, all fractions of phosphorus (1-5) were summed; no significant mistake was made in this regard as Šega (2013) who studied relations of the sum of all fractions of phosphorus (1-5) with the chemical determination of the total phosphorus found out that the sum of all fractions of phosphorus fitted well with the total phosphorus concentration (yields were from 84 to 93 %).

### 3.3 Model description

DEXi is a software that implements the DEX methodology and offers a user-friendly construction of attributes and their structure, definition of decision rules, evaluation and analysis of alternatives, as well as graphical output (Bohanec, 2013). DEXi offers the possibility of simultaneous graphical comparison of up to six attributes between four alternatives (Štubelj Ars, Bohanec, 2010). In theory, model development proceeds smoothly from conceptual model development through model application; however, this rarely occurs in practice and quantifying models of environmental systems can seem overwhelming.

Regarding the data used in this model, they were collected from several sources. These sources include the data obtained in this study (for sediment characteristics such as nutrients in sediments and C/N ratio), while the data for other basic attributes (i.e., terminal nodes of the tree) were obtained from papers and a book on Slovenian alpine lakes that have already been published (Brancelj, 2002; Simčič, Brancelj, 2002; Muri, 2004; Muri et al., 2013).

The implementation of all these steps did not go only one way, but during the procedure I had to return to the previous step several times, for example, in determining the decision rules back to the determination of the scales. It is also important to state that the model is developed on the basis of the current knowledge and understanding of the problem.

### 3.3.1 Model structure

For this purpose multi-attribute decision model was developed for decision-making support in the evaluation of ecological effects and for the computer support a software tool DEXi was chosen.

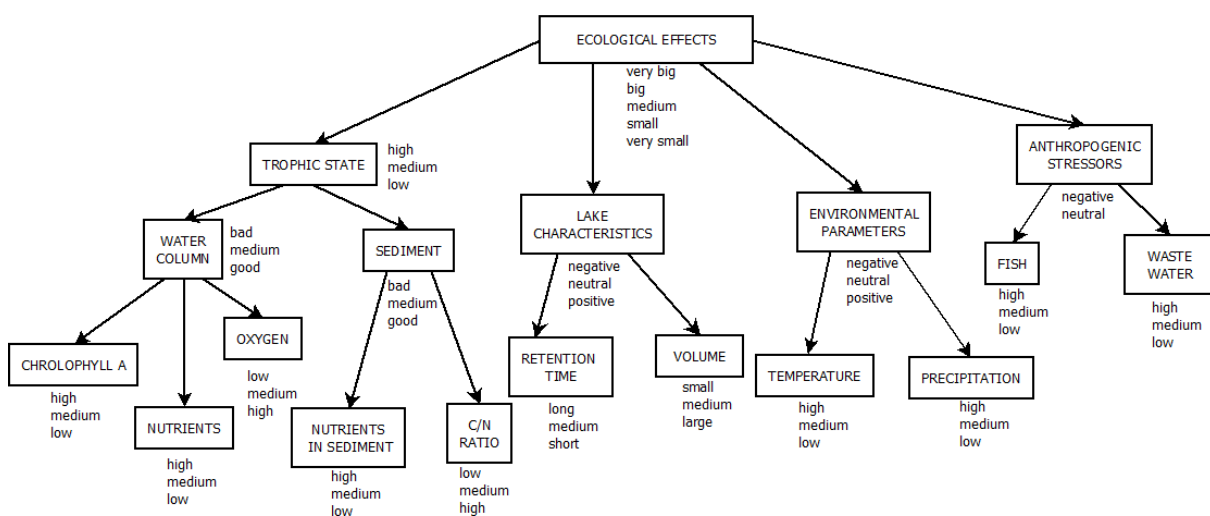
Multi-attribute models represent a class of models used in decision analysis that evaluate options according to several, possibly conflicting, goals or objectives. In principle, a multi-attribute model represents a decomposition of a decision problem into smaller and less complex sub-problems. A model consists of:

- attributes
- utility functions

Attributes are organized hierarchically into a tree of attributes. Each attribute takes values from the corresponding scale. Multi-attribute models are used for option evaluation and analysis. Multi-attribute models used in DEXi are qualitative (Bohanec, 2013). Usually, DEX models are developed in collaboration between decision analysts and experts in the given field. Typically, experts suggest attributes and aggregation rules, while decision analysts conduct the process and define components of the model. The model is gradually 'handcrafted' by following and/or iterating the four steps: (1) identifying attributes, (2) structuring attributes, (3) defining attribute scales, and (4) defining aggregation rules (Bohanec et. al, 2008).

The multi-attribute model designed to evaluate the ecological effects on the Fifth Triglav Lake consists of 18 hierarchically structured attributes (*Figure 8*). There are four main attributes in the model (*Figure 8*):

1. the trophic state (estimation of biological condition of the lake)
2. the environmental parameters
3. anthropogenic stressors (anthropogenic activities in the lake or its watershed and their impacts on the lake)
4. lake characteristics (morphological and hydrological characteristics of the lake)



**Figure 8. Graphical display of the problem – the tree of parameters**

The four main attributes have further attributes:

- The effect of the *trophic state* on the ecological effects is estimated according to the sediment quality (which depends on the nutrients in the sediment and C/N ratio), and water quality (which depends on the nutrients in water column, the concentration of chlorophyll a and the concentration of oxygen dissolved in the water column).
- The impact of *the environmental parameters* on the ecological effects is assessed according to the temperature and precipitation (the annual amount of precipitation).
- The effect of *anthropogenic stressors* is estimated according to the presence of fish in the lake that have been artificially introduced into the lake and is changing during a certain period of time and the amount of wastewater inflow from the nearby hut.
- The effect of *lake characteristics* is determined by the volume of the lake and its retention time (mean time that water spends in the lake).

The description of all attributes is presented in *Table 4*.

No.	Parameter	Description
1.	Ecological effects	Importance of ecological effects on the lake
2.	Trophic state	Estimation of biological condition of the lake
3.	Water column	Physico-chemical parameters for water quality
4.	Nutrients	Phosphorous and nitrogen compounds concentration in water column
5.	Oxygen	Dissolved oxygen concentration in water column
6.	Chlorophyll a	Chlorophyll a concentration in water column
7.	Sediment	Parameters for sediment quality
8.	Nutrients in sediment	Concentration of different forms of phosphorous and nitrogen in sediment
9.	C/N ratio	Source apportionment of OM by the organic carbon to total nitrogen ratio
10.	Environmental parameters	Environmental conditions affecting physical and chemical characteristic of water column
11.	Temperature	Annual air temperature
12.	Precipitation	Annual amount of precipitation
13.	Anthropogenic stressors	Anthropogenic activities in the lake or its watershed and their impacts on the lake
14.	Fish	Presence of fish in the lake
15.	Wastewater	Wastewater inflow from the nearby hut
16.	Lake characteristics	Morphological and hydrological characteristics of the lake
17.	Retention time	Mean time that water spends in the lake
18.	Volume	Volume of the lake

**Table 4. Description of the parameters**

### 3.3.2 Value scales

All together, 11 basic attributes are presented in the model as the terminal leaves of the tree. These attributes are aggregated into higher tree level by the decision rules. Every attribute in the model is described by discrete descriptive values which are represented by words and are also called value scales. Three- or five-grade value scales were used in the model (*Figure 9*). Three-grade value scales (such as bad, medium, good or negative, neutral, positive or low, medium, high or long, medium, short or small, medium, large) were used for basic attributes. For the attribute “Ecological effects” that represents the main evaluation results, a five-grade value scale was employed (i.e., very big, big, medium, small, very small). In total, six different value scales were used in the model. The scales presented on *Figure 9* are ordered preferentially, from bad (negative) values on the left-hand side to good (positive) values on the right-hand side.

#### Scales

Attribute	Scale
<b>Ecological effects</b>	<b>very big</b> ; <b>big</b> ; medium; <b>small</b> ; <b>very small</b>
<b>Trophic state</b>	<b>high</b> ; medium; <b>low</b>
<b>Water column</b>	<b>bad</b> ; medium; <b>good</b>
Chlorophyll a	<b>high</b> ; medium; <b>low</b>
Nutrients	<b>high</b> ; medium; <b>low</b>
Oxygen	<b>low</b> ; medium; <b>high</b>
<b>Sediment</b>	<b>bad</b> ; medium; <b>good</b>
C/N ratio	<b>low</b> ; medium; <b>high</b>
Nutrients in sediment	<b>high</b> ; medium; <b>low</b>
<b>Environmental parameters</b>	<b>negative</b> ; neutral; <b>positive</b>
Temperature	<b>high</b> ; medium; <b>low</b>
Precipitation	<b>high</b> ; medium; <b>low</b>
<b>Anthropogenic stressors</b>	<b>negative</b> ; neutral
Fish	<b>high</b> ; medium; <b>low</b>
Wastewater	<b>high</b> ; medium; <b>low</b>
<b>Lake characteristics</b>	<b>negative</b> ; neutral; <b>positive</b>
Retention time	<b>long</b> ; medium; <b>short</b>
Volume	<b>small</b> ; medium; <b>large</b>

**Figure 9.** The list of parameters and their values from DEXi software

### 3.3.3 Decision rules

In a DEXi model, decision rules define the aggregation of values in the direction from basic attributes (terminal nodes) towards the outputs (aggregate attributes and, particularly, the root node). For each attribute that aggregates two or more other attributes in the model, the decision-maker defines a table that specifies the value of the former attribute for all combinations of values of the latter attributes (Štubelj Ars, Bohanec, 2010).

Tables

	Trophic state	Environmental parameters	Anthropogenic stressors	Lake characteristics	Ecological effects
	20%	20%	39%	20%	
1	<b>high</b>	<b>negative</b>	<b>negative</b>	<=neutral	<b>very big</b>
2	<b>high</b>	<=neutral	<b>negative</b>	<b>negative</b>	<b>very big</b>
3	<=medium	<b>negative</b>	<b>negative</b>	<b>negative</b>	<b>very big</b>
4	<b>high</b>	<b>negative</b>	<b>negative</b>	<b>positive</b>	<b>big</b>
5	<b>high</b>	<b>negative</b>	neutral	<b>negative</b>	<b>big</b>
6	<b>high</b>	neutral	<b>negative</b>	neutral	<b>big</b>
7	<b>high</b>	<b>positive</b>	<b>negative</b>	<b>negative</b>	<b>big</b>
8	medium	<b>negative</b>	<b>negative</b>	neutral	<b>big</b>
9	medium	neutral	<b>negative</b>	<b>negative</b>	<b>big</b>
10	<b>low</b>	<b>negative</b>	<b>negative</b>	<b>negative</b>	<b>big</b>
11	<b>high</b>	<=neutral	neutral	>=neutral	medium
12	<b>high</b>	*	neutral	neutral	medium
13	<=medium	<b>negative</b>	neutral	>=neutral	medium
14	<=medium	<=neutral	neutral	neutral	medium
15	*	<b>negative</b>	neutral	neutral	medium
16	<b>high</b>	neutral	*	<b>positive</b>	medium
17	<=medium	>=neutral	<b>negative</b>	<b>positive</b>	medium
18	*	neutral	<b>negative</b>	<b>positive</b>	medium
19	<b>high</b>	neutral	neutral	*	medium
20	<b>high</b>	>=neutral	neutral	<=neutral	medium
21	<=medium	neutral	neutral	<=neutral	medium
22	<=medium	>=neutral	neutral	<b>negative</b>	medium
23	*	neutral	neutral	<b>negative</b>	medium
24	<b>high</b>	<b>positive</b>	*	neutral	medium
25	<=medium	<b>positive</b>	<b>negative</b>	>=neutral	medium
26	*	<b>positive</b>	<b>negative</b>	neutral	medium
27	medium	<b>negative</b>	*	<b>positive</b>	medium
28	medium	*	<b>negative</b>	<b>positive</b>	medium
29	>=medium	<=neutral	<b>negative</b>	<b>positive</b>	medium
30	medium	<b>negative</b>	neutral	*	medium
31	medium	<=neutral	neutral	<=neutral	medium
32	medium	*	neutral	<b>negative</b>	medium
33	>=medium	<b>negative</b>	neutral	<=neutral	medium
34	>=medium	<=neutral	neutral	<b>negative</b>	medium
35	medium	neutral	*	neutral	medium
36	medium	>=neutral	<b>negative</b>	>=neutral	medium
37	>=medium	neutral	<b>negative</b>	>=neutral	medium
38	>=medium	>=neutral	<b>negative</b>	neutral	medium
39	medium	<b>positive</b>	<b>negative</b>	*	medium
40	medium	<b>positive</b>	*	<b>negative</b>	medium
41	>=medium	<b>positive</b>	<b>negative</b>	<=neutral	medium
42	<b>low</b>	<b>negative</b>	*	neutral	medium
43	<b>low</b>	<=neutral	<b>negative</b>	>=neutral	medium
44	<b>low</b>	*	<b>negative</b>	neutral	medium
45	<b>low</b>	neutral	<b>negative</b>	*	medium
46	<b>low</b>	neutral	*	<b>negative</b>	medium
47	<b>low</b>	>=neutral	<b>negative</b>	<=neutral	medium
48	<b>high</b>	<b>positive</b>	neutral	<b>positive</b>	<b>small</b>
49	medium	neutral	neutral	<b>positive</b>	<b>small</b>
50	medium	<b>positive</b>	neutral	neutral	<b>small</b>
51	<b>low</b>	<b>negative</b>	neutral	<b>positive</b>	<b>small</b>
52	<b>low</b>	neutral	neutral	neutral	<b>small</b>
53	<b>low</b>	<b>positive</b>	<b>negative</b>	<b>positive</b>	<b>small</b>
54	<b>low</b>	<b>positive</b>	neutral	<b>negative</b>	<b>small</b>
55	>=medium	<b>positive</b>	neutral	<b>positive</b>	<b>very small</b>
56	<b>low</b>	>=neutral	neutral	<b>positive</b>	<b>very small</b>
57	<b>low</b>	<b>positive</b>	neutral	>=neutral	<b>very small</b>

Figure 10. Decision rules

Decision rules in DEXi are shown in Figure 10, where decision rules for the ecological effects of trophic state, environmental parameters, anthropogenic stressors and lake characteristics are presented. Bad conditions are highlighted red and printed in bold and good conditions are highlighted green and printed in bold italic. The asterisk '\*' in the table means any value. The basic decision rules are formulated by a simple "if-then" rule. For example, if the trophic state is low (i.e.

oligotrophic), environmental parameters are *positive*, anthropogenic stressors are *negative* and characteristics are *positive*, **then** the ecological effects are *small*. All together 18 such tables are defined for 18 attributes in the model, each for one parameter. For the determination of these tables, the cooperation of multiple experts is required to improve the scientific value of this model (see Appendix A for more decision rules tables).

## 4. RESULTS AND DISCUSSION

### 4.1 Basic geochemistry

TN and OC concentrations varied from 1.49 to 1.73 % and from 17.9 to 20.3 %, respectively (*Table 5*). C/N ratios ranged from 13.3 to 15.6. Elemental analysis was performed to assess sources of OM i.e., to distinguish between aquatic and terrigenous sources, based on the C/N ratios. This distinction arises from the absence of cellulose in algae and its abundance in vascular plants. Fundamental differences in OM composition also generally survive sinking and sedimentation. The proportions of sedimentary OM that originate from the two general sources can thus be distinguished by their characteristic C/N ratios (Meyers, 2003).

Sediment C/N ratios in the Fifth Triglav Lake were intermediate between the characteristic algal/bacterial (autochthonous) and terrestrial (allochthonous) values, suggesting that both autochthonous and allochthonous sources contribute OM to this lake. Intermediate C/N ratio of 10-20 therefore indicates a mix of aquatic and terrestrial OM. Selective degradation of OM components during early diagenesis has the potential to modify C/N ratios of OM in sediments. This is generally not an issue when interpreting surface sediments, but may be important when interpreting the whole sediment core; C/N ratios tend to increase down the core, reflecting bacterial preference for degrading nitrogen-rich compounds (Fenchel et al., 1998).

Because C/N ratios were measured in several plankton and plant samples in past studies (Vreča, Muri, 2010), I was able to estimate the relative contributions of autochthonous versus allochthonous sources to sedimentary OM in the Fifth Triglav Lake. Vreča and Muri (2010) observed that the average C/N ratio for plankton samples amounted to 7, and that for terrestrial plant samples amounted to 24. The above mentioned values of 7 and 24 were therefore used to characterize autochthonous and allochthonous OM, respectively. Mathematical linear mixing models based on mass balance are commonly used to quantify the proportional contributions of multiple sources to a mixture. The approach for two sources (i.e., autochthonous and allochthonous) can be represented by the following equations:

$$C/N \text{ (surface)} = F_{\text{auto}} \times C/N_{\text{auto}} + F_{\text{allo}} \times C/N_{\text{allo}}$$

$$F_{\text{auto}} + F_{\text{allo}} = 1$$

$$C/N_{\text{auto}} = 7 \text{ and } C/N_{\text{allo}} = 24$$

where C/N (surface) is the measured C/N ratio in the surface sediments, while  $F_{\text{auto}}$  and  $F_{\text{allo}}$  represent the proportions of autochthonous and allochthonous OM in the surface sediments, respectively (Vreča, Muri, 2010).

Allochthonous sources contributed in the Fifth Triglav Lake from 37 to 51 % to sedimentary OM (*Table 5*) and tend to have a relatively lower impact on OM in the Fifth Triglav Lake. Thus, a relatively greater contribution of autochthonous sources to sedimentary OM was observed in the Fifth Triglav Lake contributing from 49 to 63 %. When comparing the data obtained in this study with the data from a recent study (Muri et al., 2013) in the sediments obtained in the deepest part of the Fifth Triglav Lake, a greater contribution of autochthonous OM was observed in the deepest part of the lake contributing up to 85 %, while allochthonous sources could contribute up to 15 %. These data clearly show that outer parts of the lake are relatively more susceptible to inputs of allochthonous OM.

Sample	TN (%)	OC (%)	C/N ratio	AUTO (%)	ALLO (%)
DJ5-I	1.49	20.0	15.6	49.5	50.5
DJ5-II	1.58	19.8	14.5	55.6	44.4
DJ5-III	1.54	17.9	13.6	61.4	38.6
DJ5-IV	1.61	18.4	13.3	62.7	37.3
DJ5-V	1.73	20.3	13.7	60.8	39.2
DJ5-VI	1.55	18.1	13.7	60.8	39.2

**Table 5. Total nitrogen (TN) and organic carbon (OC) concentration and atomic OC to TN ratios (C/N ratios) in the surface sediments of the Fifth Triglav Lake (October, 2011).**

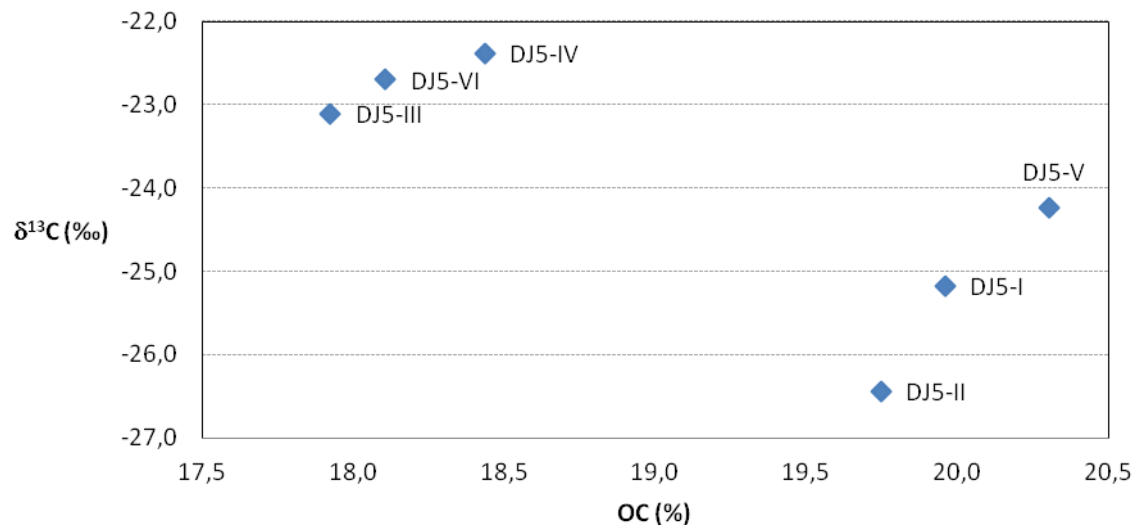
$\delta^{13}\text{C}$  values varied from -22.4 to -26.4 ‰ (Table 6). Together with the C/N values,  $\delta^{13}\text{C}$  values can provide further help to identify sources of OM in lake sediments.  $\delta^{13}\text{C}$  values obtained in this study were lower than the values from the recent study (Muri et al., 2013) where the range from -21.0 to -18.6 ‰ was observed.

Sample	$\delta^{13}\text{C}$ (‰)
DJ5-I	-25.2
DJ5-II	-26.4
DJ5-III	-23.1
DJ5-IV	-22.4
DJ5-V	-24.2
DJ5-VI	-22.7

**Table 6. Stable carbon isotopic composition ( $\delta^{13}\text{C}$  values) in the surface sediments of the Fifth Triglav Lake (October, 2011)**

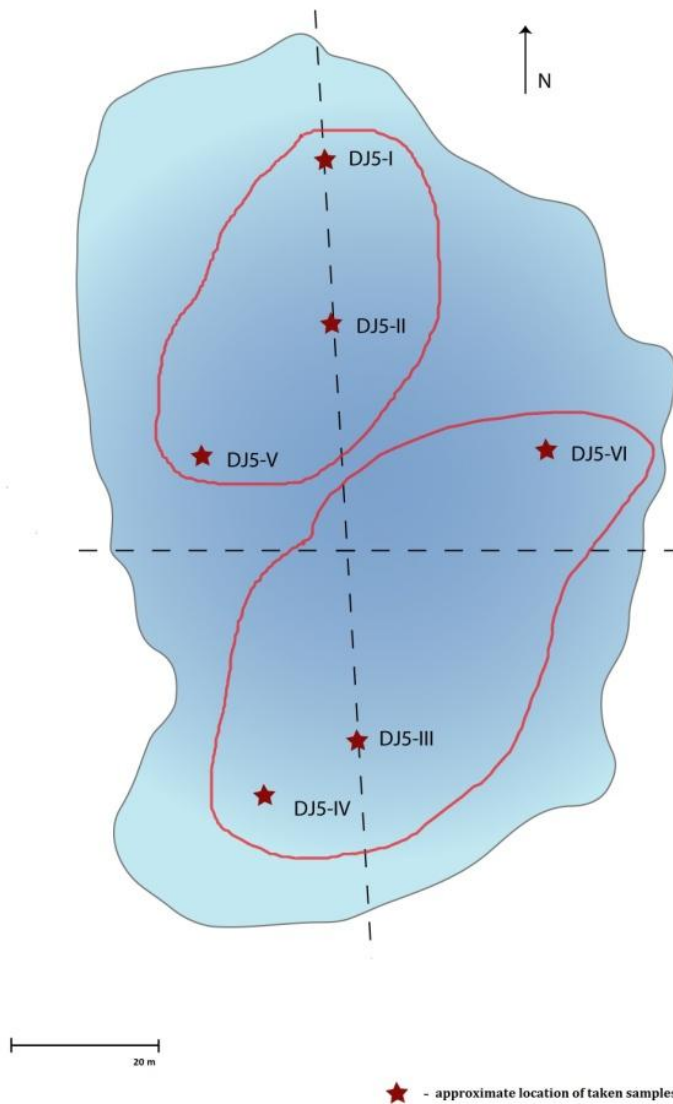
According to the data obtained in this study, it is likely that sources of OM are divided into two groups regarding the sampling locations: those with lower OC concentrations and higher  $\delta^{13}\text{C}$  values (DJ5-III, DJ5-IV, DJ5-VI) indicating that there autochthonous sources tend to have a higher impact on sediment OM, and those with higher OC concentrations and lower  $\delta^{13}\text{C}$  values (DJ5-I, DJ5-II, DJ5-V) indicating that there allochthonous sources tend to have a higher impact on sediment OM (Figure 11).





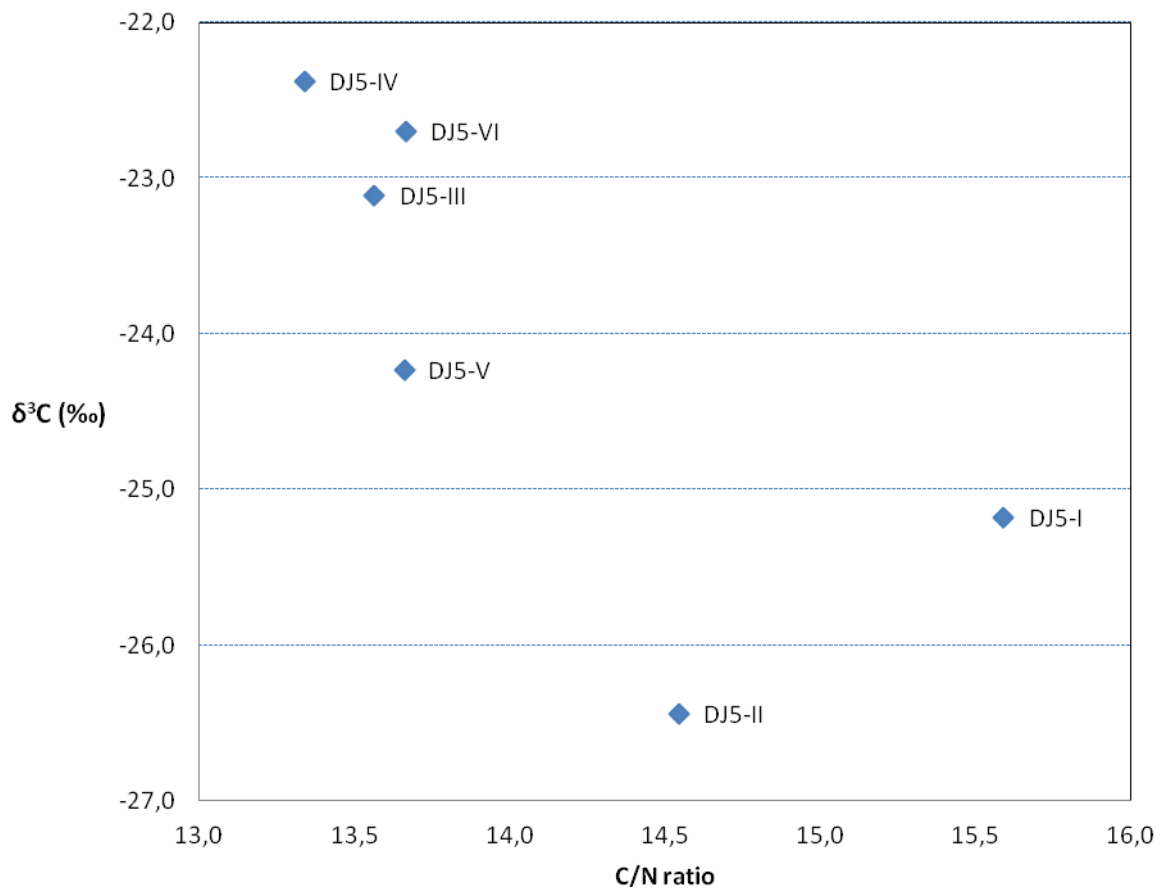
**Figure 11.** Stable carbon isotopic composition ( $\delta^{13}\text{C}$  values) versus organic carbon (OC) concentration in the surface sediments of the Fifth Triglav Lake (October, 2011)

More explicit graphical display shows that the sampling locations with higher impact of allochthonous sources (DJ5-I, DJ5-II, DJ5-V) are located more to the north of the Fifth Triglav Lake and the locations with higher impact of autochthonous sources (DJ5-III, DJ5-IV, DJ5-VI) are located more to the south of the Fifth Triglav Lake (*Figure 12*).



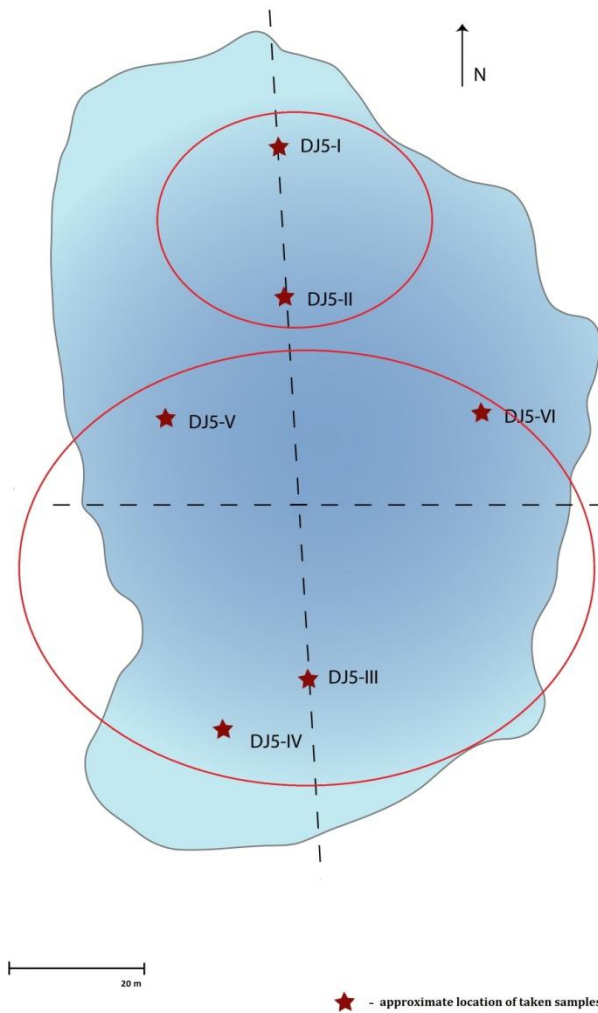
**Figure 12.** Graphical display of grouping of stable carbon isotopic composition ( $\delta^{13}\text{C}$  values) versus organic carbon (OC) concentration across the sampling locations of the Fifth Triglav Lake (October, 2011)

The distribution of contributions of autochthonous versus allochthonous sources to sedimentary OM is slightly changed if comparing  $\delta^{13}\text{C}$  values versus C/N ratio. It is still divided into two groups regarding the sampling locations but now 4 sampling locations are included in one group DJ5-III, DJ5-IV, DJ5-VI, DJ5-V, and have lower C/N ratio and higher  $\delta^{13}\text{C}$  values indicating that there autochthonous sources tend to have a higher impact on sediment OM, while the other 2 locations (DJ5-I, DJ5-II) with higher C/N ratio and lower  $\delta^{13}\text{C}$  values indicate that there allochthonous sources tend to have a higher impact on sediment OM (Figure 13).



**Figure 13.** Stable carbon isotopic composition ( $\delta^{13}\text{C}$  values) versus organic carbon (OC) to total nitrogen (TN) ratios (C/N ratios) in the surface sediments of the Fifth Triglav Lake (October, 2011)

More explicit graphical display shows that the sampling locations (DJ5-I, DJ5-II) with higher impact of allochthonous sources are located in the northern half of the Fifth Triglav Lake while locations with higher impact of autochthonous sources (DJ5-III, DJ5-IV, DJ5-VI, DJ5-V) are located in the central and southern part of the Fifth Triglav Lake (Figure 14).



**Figure 14.** Graphical display of grouping of stable carbon isotopic composition ( $\delta^{13}\text{C}$  values) versus organic carbon (OC) to total nitrogen (TN) ratios (C/N ratios) across the sampling locations of the Fifth Triglav Lake (October, 2011)

The data from the Fifth Triglav Lake were also compared with other lakes in the area (*Table 7*). The following water bodies were included in this comparison: Rjavo jezero (the Second Triglav Lake), Zeleno jezero (the Third Triglav Lake), Jezero v Ledvicah (the Fourth Triglav Lake), Peto jezero (the Fifth Triglav Lake), Šesto jezero (the Sixth Triglav Lake) and Zgornje Kriško jezero. All the lakes are situated in the Julian Alps (NW Slovenia). They are of glacial origin and relatively small and shallow, with surface areas from 0.25 to 4.53 ha and maximum depths from 3 to 18 m. Their elevation range from 1669 to 2150 m. Sediment cores were collected in August/September 2005 from the deepest part of the lakes (Vreča, Muri, 2010).

	OC (%)	TN (%)	C/N ratio	$\delta^{13}\text{C}$ (‰)	AUTO (%)	ALLO (%)	References
<b>Peto jezero</b>	17.6-20.7	1.45-1.76	13.3-15.9	-22.4 – -26.4	49-63	37-51	this study
<b>Rjavo jezero *</b>	7.00	0.80	10.2	-14.1	81	19	#
<b>Zeleno jezero *</b>	6.20	0.70	11.0	-21.1	76	24	#
<b>Jezero v Ledvicah *</b>	12.2	1.30	11.0	-24.7	76	24	#
<b>Peto jezero *</b>	18.8	2.10	10.3	-21.2	81	19	#
<b>Šesto jezero *</b>	8.90	0.80	12.7	-19.1	67	33	#
<b>Zgornje Kriško jezero *</b>	14.3	2.00	8.40	-21.0	92	8	#

**Table 7. Comparison of sedimentary geochemical parameters in the Fifth Triglav Lake with other lakes in the area**

\*: sample collected at the deepest part of the lake

#: data from Vreča, Muri (2010)

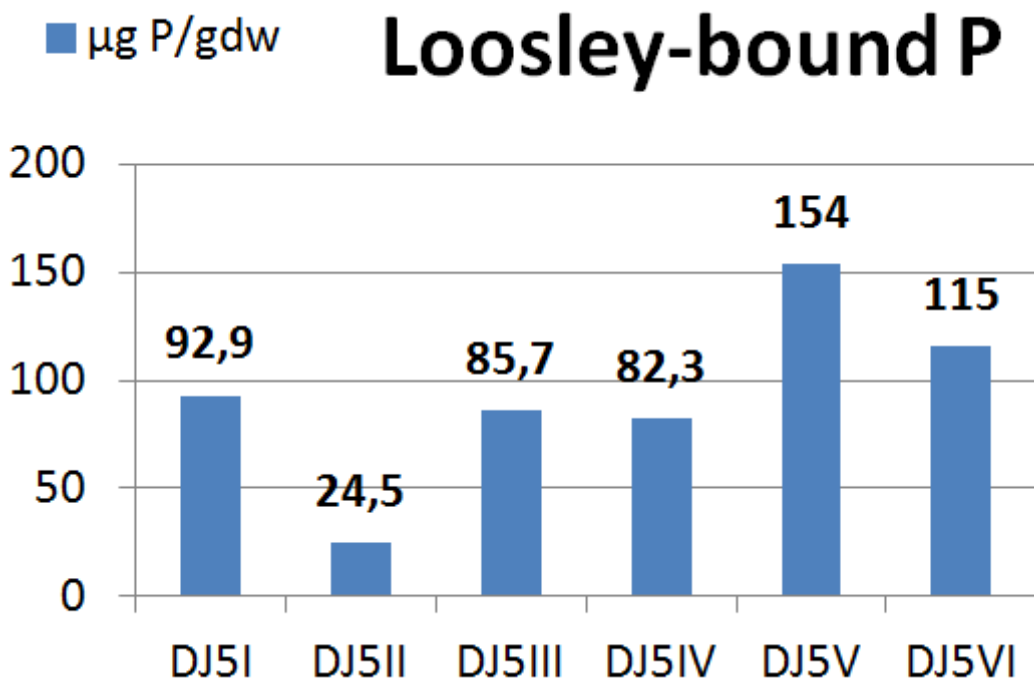
C/N ratios in the surface sediments of the Fifth Triglav Lake were higher than the values in the sediments collected from the deepest part of other lakes in the Julian Alps. A comparison with previous investigations (Vreča, Muri, 2010) shows an increase of C/N ratio from 10.3 to the range between 13.3-15.9. Also, concentrations of OC are higher than the one observed in previous study; they are also significantly higher than in any other lake.

Comparing the sources of OM, the Fifth Triglav Lake exhibited the lowest proportion of autochthonous OM in lake sediment, ranging from 49 to 63 %. Zgornje Kriško jezero sediments had the highest proportion of autochthonous OM, with 92 % while in other lakes, autochthonous contributions were rather similar, ranging from 67 to 81 %. A comparison with previous investigations (Vreča, Muri, 2010) shows that autochthonous contribution was significantly higher in previous study (81 %) than in this study. Nevertheless, it is important to emphasize that surface samples in this study were collected all across the Fifth Triglav Lake, while other surface samples were all collected from the deepest part of the lake. This is reflected in higher proportion of allochthonous OM in my Fifth Triglav Lake samples, since outer parts of the lake are more affected by allochthonous sources.

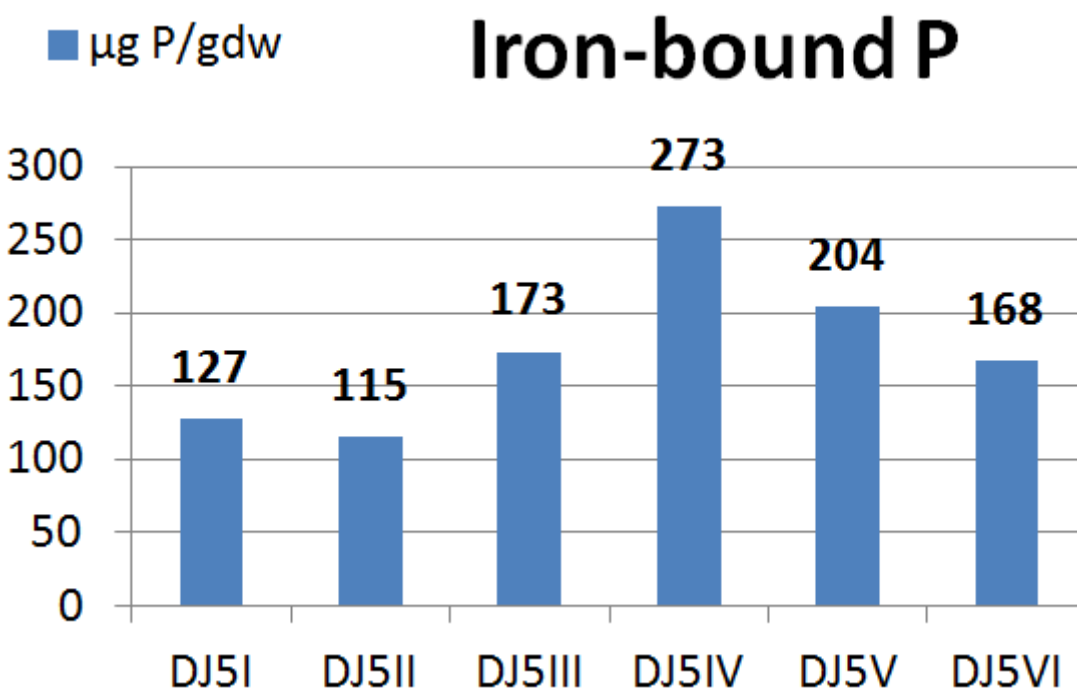
## 4.2 Phosphorous

Concentrations of loosely adsorbed phosphorus compounds ( $\text{NH}_4\text{Cl-P}$ ) range from 24.5 to 154  $\mu\text{g P}$  per gram dry weight sediment ( $\mu\text{g/gdw}$ ) and is highest at the DJ5-V location (*Figure 15*). This fraction is often considered labile (desorbed, hydrolyzed) loosely bound or adsorbed phosphorus. It gives an estimate of the immediately available phosphorus compounds (James et al., 2004). Iron bound (reductant) phosphorus compounds ( $\text{BD-P}$ ) concentrations range from 115 to 273  $\mu\text{g/gdw}$  and is the highest at the DJ5-IV location (*Figure 16*). It is assumed that reductant soluble phosphorus forms are extracted mainly from iron hydroxide surfaces. Iron-bound and redox-sensitive sorption of phosphorus compounds is also considered mobile and can contribute to an internal release (James et al., 2004). Metal oxide (aluminium) bound phosphorus compounds ( $\text{NaOH-P}$ ) concentrations range from 69.7 to 265  $\mu\text{g/gdw}$  and is also the highest at the DJ5-IV location (*Figure 17*). Reactive  $\text{NaOH-P}$  represents phosphate adsorbed to metal oxides (mainly  $\text{Al}_2\text{O}_3$ ) and other surfaces exchangeable against  $\text{OH}^-$  and phosphorus compounds soluble in bases. Iron and aluminium bound phosphorus compounds are exchangeable between the particulate and dissolved phases through sorption processes. Calcium bound phosphorus compounds ( $\text{HCl-P}$ ) concentrations range from 181 to 446  $\mu\text{g/gdw}$  and is also the highest at the DJ5-IV location (*Figure 18*). It represents phosphorus compounds bound to carbonates, apatite-P and phosphorus compounds released by the dissolution of oxides (not adsorbed to the surface). It may contain traces of hydrolyzed organic phosphorus compounds. The fraction is fixed in sediments and may be lost into deep sediments through the burial process (James et al., 2004). The refractory organic phosphorus compounds concentrations range from 331 to 638  $\mu\text{g/gdw}$  and is the highest at the DJ5-IV location (*Figure 19*). The total phosphorus concentrations range from 802 to 1704  $\mu\text{g/gdw}$ . It is also the highest at the DJ5-IV location (*Figure 20*). Total phosphorus includes some or all of the following fractions: crystalline, occluded, adsorbed, particulate organic, soluble organic and soluble inorganic phosphorus compounds.

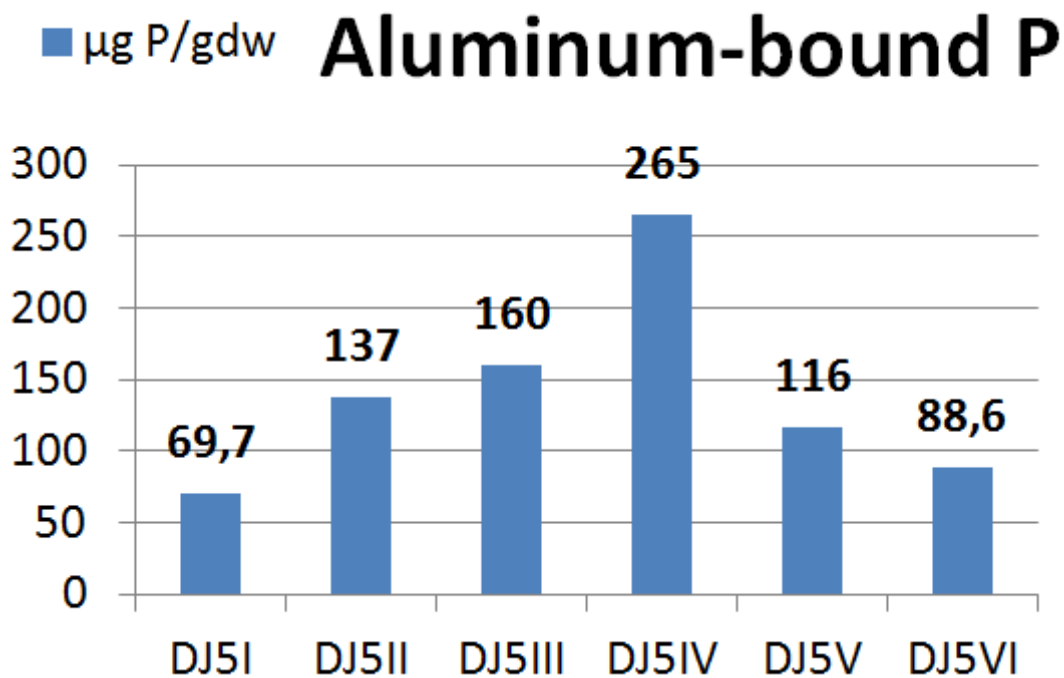
Fractionation of various forms of phosphorus in the sediment usually allows a more precise description of the potentials for phosphorus compounds release from the sediment and can predict its future influence on lake water concentrations. Since the amount of phosphorus compounds release from sediment is called internal phosphorus loading, which can enhance lake eutrophication, the fractionation of sediment phosphorus compounds can be conducive to understanding phosphorus cycling in the aquatic ecosystem. Phosphorus compounds release is a function of the quantity and distribution of phosphorus fractions within the sediments, the degree of saturation of exchangeable phosphorus compounds and of hydrological conditions (Fytianos, Kotzakioti, 2005). The rank order of the different phosphorus forms in the surface sediments of the Fifth Triglav lake is organic phosphorus compounds > Calcium bound phosphorus compounds > Iron bound phosphorus compounds > Aluminum-bound phosphorus compounds > loosely bound phosphorus compounds. In heavily polluted lakes, the rank order of  $\text{NaOH-P}$  >  $\text{HCl-P}$  was found (Lijklema et al., 1993), while in mesotrophic lakes the order was opposite;  $\text{HCl-P}$  >  $\text{NaOH-P}$  (Kaiserli et al., 2002). According to this classification, the Fifth Triglav Lake would not be heavily polluted.



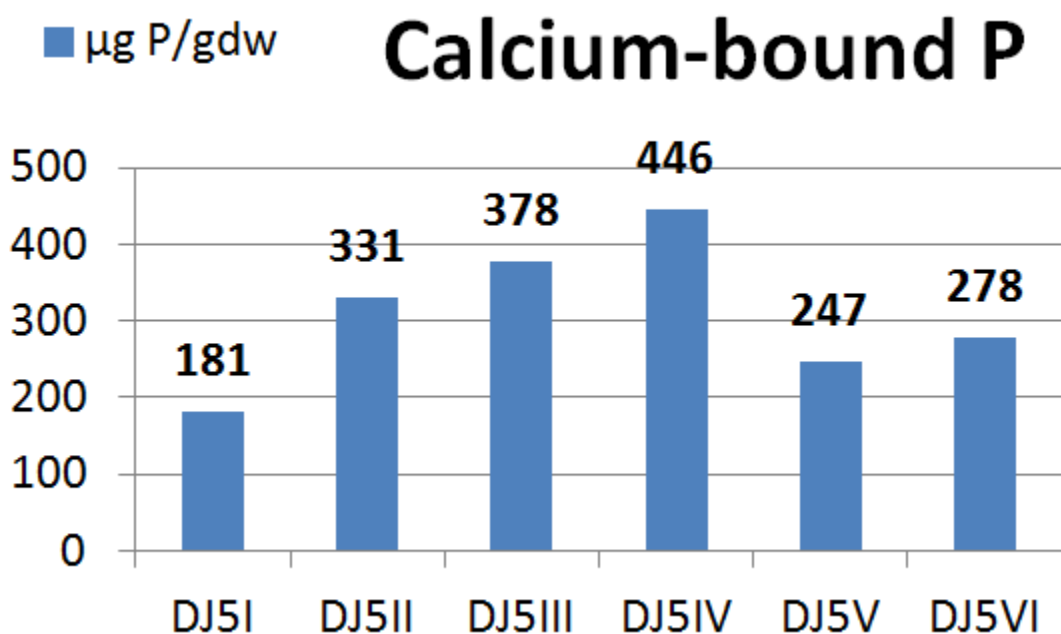
*Figure 15.* Concentrations of loosely-bound phosphorous compounds in the surface sediments of the Fifth Triglav Lake (October, 2011)



*Figure 16.* Concentrations of iron-bound phosphorous compounds in the surface sediments of the Fifth Triglav Lake (October, 2011)



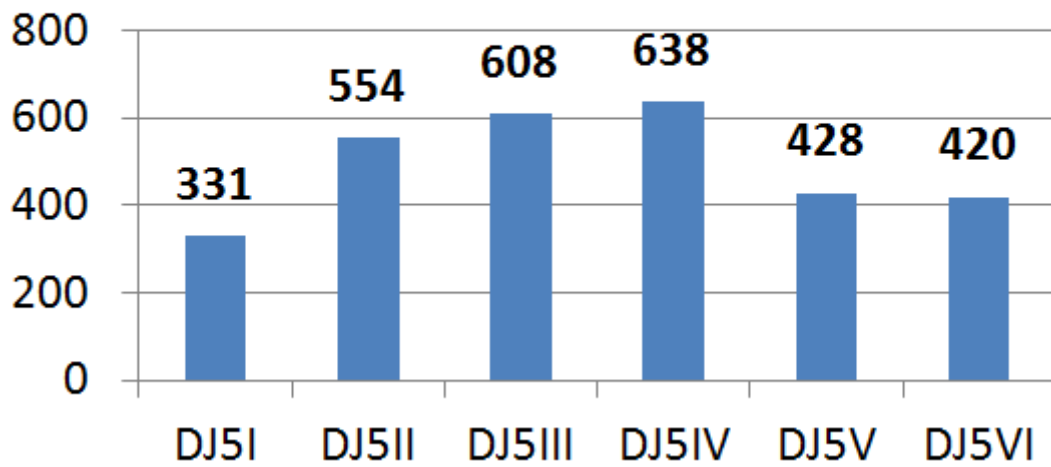
*Figure 17.* Concentrations of aluminum-bound phosphorous compounds in the surface sediments of the Fifth Triglav Lake (October, 2011)



*Figure 18.* Concentrations of calcium-bound phosphorous compounds in the surface sediments of the Fifth Triglav Lake (October, 2011)

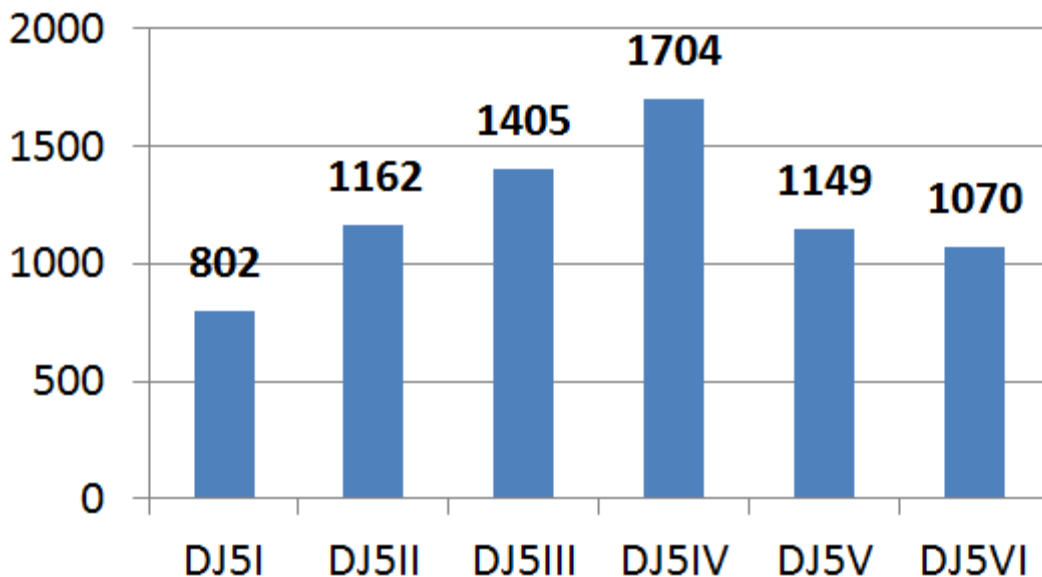


■  $\mu\text{g P/gdw}$  **Organic phosphorus**



*Figure 19.* Concentrations of organic phosphorous compounds in the surface sediments of the Fifth Triglav Lake (October, 2011)

■  $\mu\text{g P/gdw}$  **Total phosphorus**



*Figure 20.* Concentrations of total phosphorous in the surface sediments of the Fifth Triglav Lake (October, 2011)

At the DJ5-IV location where total phosphorus has the highest value, a loosely bound labile phosphorus fraction (NH<sub>4</sub>Cl-P) accounts for only 4.8 % of the total phosphorus (*Table 8*). This fraction is very dynamic and may therefore be a useful indicator of the processes that determine sediment water interactions percentage of the total phosphorus pool (Fytianos, Kotzakioti, 2005). The iron-bound (BD-P) and aluminum-bound (NaOH-P) exchangeable phosphorus compounds account for 16 and 15.6 % of the total phosphorus, respectively. The calcium bound phosphorus compounds (HCl-P) accounts for 26.2 %, while most of phosphorus compounds are in organic form (Org-P; 37.4 %). In contrast, this location exhibits the lowest organic to total phosphorus ratio among all sampling sites (*Table 8*). Concentrations of the total phosphorus vary across the lake. As seen from *Figure 20*, the highest concentration of the total phosphorus is observed at the relatively shallow site DJ5-IV (1704 µg/gdw), but at the same time the DJ5-I location has similar depth as DJ5-IV, but exhibits the lowest concentration of the total phosphorus (802 µg/gdw). This indicates that various biogeochemical processes may be present in the lake also affecting the phosphorus cycle.

It has been shown that the Fifth Triglav Lake is more exposed to direct anthropogenic impacts as other lakes in the vicinity; fish were introduced into the lake and mountain hut is located near the shore to the north (Brancelj, 1999 b; Vreča, Muri, 2010). Regarding mountain hut impact, there is no evidence that locations closer to the hut have higher concentration of the total phosphorus. Even the opposite, the locations DJ5-IV and DJ5-III have the highest concentration but are the most distant. Using the data obtained in this study, it would be difficult to assess the contribution of each anthropogenic factor to the overall condition of the lake.

	% of the Total phosphorus					
	DJ5-I	DJ5-II	DJ5-III	DJ5-IV	DJ5-V	DJ5-VI
<b>NH<sub>4</sub>Cl-P</b>	11.6	2.1	6.1	4.8	13.4	10.8
<b>BD-P</b>	15.9	9.9	12.3	16.0	17.7	15.7
<b>NaOH-P</b>	8.7	11.8	11.4	15.6	10.1	8.3
<b>HCl-P</b>	22.5	28.5	26.9	26.2	21.5	26.0
<b>Org-P</b>	41.3	47.7	43.3	37.4	37.3	39.2

**Table 8. Proportions of individual forms of phosphorus versus total phosphorus in the surface sediments of the Fifth Triglav Lake (October, 2011)**

The data from the Fifth Triglav Lake were also compared with other lakes (*Table 9*). The following water bodies were included in this comparison: Lake Koronia and Lake Volvi, which are located in Northern Greece, about 11.5 km NE of the city of Thessaloniki. Lake Volvi which has mean depth 13.5 m at 37 m altitude is meso-to-eutrophic and Lake Koronia with a mean depth of 2 m and altitude of 75 m is hypertrophic (Fytianos and Kotzakioti, 2005). Lake Erken, Sweden, has maximum and mean depths of 21 m and 9 m. The lake is moderately eutrophic (Rydin, 2000). Myall Lake is situated 75 km North of Newcastle, in the temperate Australian central coast of New South Wales. It has high water clarity and low plankton biomass. The average depth of the lake is about 2.8 m, the deepest part being 4.5 m (Shilla et al., 2008). Lake Brienz, an oligotrophic pre-alpine Swiss lake is located approximately 70 km southeast of Berne, Switzerland. Its surface is at 564 m above sea level and it has a maximum depth of 261 m (Hoyle, 2004).

Concentrations of several phosphorus forms were higher in the Fifth Triglav Lake than the ones in Lake Koronia and Volvi except for organic phosphorus compounds (*Table 9*). Compared to the Sixth Triglav Lake, which is only few meters away, the concentrations are much lower than in the Fifth Triglav Lake. The highest concentrations in the Fifth Triglav Lake are somehow similar to the ones observed in Lake Erken a moderately eutrophic lake, while the lowest tend to be more similar to the concentrations observed in oligotrophic lakes (e.g., Myall Lake and Lake Brienz).

$\mu\text{g/gdw}$	$\text{NH}_4\text{Cl-P}$	$\text{BD-P}$	$\text{NaOH-P}$	$\text{HCl-P}$	$\text{Org-P}$	$\text{TP}$	References
<b>The Fifth Triglav Lake</b>	24.5 - 154	115 - 273	69.7 - 265	181 - 446	331 - 638	802 - 1704	this study
<b>The Sixth Triglav Lake*</b>	4	22	17	190	402	635	data from Muri (unpublished data)
<b>Lake Koronia</b>	8	9	219	95	974	1305	data from Fytianos and Kotzakioti, 2005
<b>Lake Volvi</b>	7	4	250	11	772	1044	data from Fytianos and Kotzakioti, 2005
<b>Lake Erken</b>	27	345	85 - 465	287	606	1814	data from Rydin, 2000
<b>Myall Lake</b>	0.39	84.5	56.4	22.9	622	786	data from Shilla et al., 2008
<b>Lake Brienz</b>			43	433	107	666	data from Hoyle, 2004

**Table 9. Comparison of different forms of sedimentary phosphorus in the Fifth Triglav Lake with other lakes**

\*: sample collected from the deepest part of the lake

### 4.3 Correlations among geochemical parameters

A simple (linear) correlation among OC and TN concentrations, the C/N ratios, stable carbon isotopic composition and different fractions of phosphorus was calculated, in order to determine the degree of relation between these parameters. As seen from *Table 10*, there is no significant correlation between OC and TN suggesting that N is not predominantly associated with OC in the whole lake. TN is negatively correlated with C/N ratios, while OC shows almost no relation with C/N ratios. On the other hand, OC has a relatively strong negative correlation with  $\delta^{13}\text{C}$  values. Also, C/N ratios show a relatively strong negative correlation with  $\delta^{13}\text{C}$  values. These relations can be explained by the intensity of primary production. Intensive primary production is reflected in lower C/N ratios; this OM is also associated with higher  $\delta^{13}\text{C}$  values. When productivity is high, the  $^{12}\text{C}$  pool is relatively depleted and thus a greater fraction of  $^{13}\text{C}$  is incorporated into OM resulting in higher  $\delta^{13}\text{C}$  values (Meyers, 2003).

Total phosphorus, Org-P, HCl-P and NaOH-P fractions have all very high and positive correlations among each other. Probably these fractions of phosphorus are relatively independent of physico-chemical characteristics and/or biogeochemical processes at the studied sampling locations. In contrast,  $\text{NH}_4\text{Cl-P}$  has a negative and low correlation with all forms of phosphorus except for BD-P. There is also no significant correlation between BD-P and several other fractions (e.g., HCl-P and Org-P). This could indicate that reactive forms of phosphorus are more dependent on the sampling site characteristics.

As also seen from *Table 10*, TN is not correlated to any fraction of phosphorus suggesting that their sources differ. In contrast, negative relations between OC and fractions of phosphorus, as well as between the C/N ratio and fractions of phosphorus were observed but the latter correlations were stronger. Lower C/N ratios correlated quite strongly with higher concentrations of phosphorus compounds suggesting that most fractions of phosphorus could originate from autochthonous sources. The distribution of OC furthermore supports this proposition, since lower OC concentrations were found in the sediments where autochthonous sources were relatively more important (*Table 5*, *Figure 11*). On the other hand, the relations between the  $\delta^{13}\text{C}$  values and fractions of phosphorus were all positive but mostly not significant. Higher  $\delta^{13}\text{C}$  values were observed in the sediments where autochthonous sources were relatively more important (*Table 6*, *Figure 13*), and thus positive correlations between the  $\delta^{13}\text{C}$  values and fractions of phosphorus were somehow expected. Nevertheless, only the relation  $\delta^{13}\text{C}$  values versus BD-P was significant indicating that the carbon cycle in the Fifth Triglav Lake is quite complicated, probably due to the influence of complex biogeochemical processes on carbon cycling, as also observed in previous studies (Vreča, Muri, 2010; Muri et al., 2013).

	TN	OC	C/N	$\delta^{13}\text{C}$	$\text{NH}_4\text{Cl-P}$	BD-P	NaOH-P	HCl-P	Org-P	Total P
TN	1									
OC	0.40	1.00								
C/N	-0.51	0.58	1.00							
$\delta^{13}\text{C}$	0.05	<b>-0.76</b>	<b>-0.74</b>	1.00						
$\text{NH}_4\text{Cl-P}$	0.47	0.10	-0.30	0.47	1.00					
BD-P	0.49	-0.34	<b>-0.74</b>	<b>0.76</b>	0.38	1.00				
NaOH-P	0.26	-0.40	-0.60	0.45	-0.26	<b>0.78</b>	1.00			
HCl-P	0.11	-0.63	-0.69	0.47	-0.39	0.61	<b>0.92</b>	1.00		
Org-P	0.14	-0.53	-0.63	0.31	-0.47	0.48	<b>0.87</b>	<b>0.97</b>	1.00	
Total P	0.30	-0.54	<b>-0.78</b>	0.58	-0.16	<b>0.79</b>	<b>0.96</b>	<b>0.96</b>	<b>0.92</b>	1.00

**Table 10. Pearson correlation matrix for measured variables in the surface sediments of the Fith Triglav Lake (October, 2011).**

#### 4.4 Evaluation of ecological effects

For a long time, human in this area has affected the mountain lakes, and so thus the present lake – The Fifth Triglav Lake. The major changes were made by the introduction of fish. In 1991, arctic char was introduced. Arctic char is a predator which reproduces just as rapidly and has destroyed and radically diminished or completely eradicated the original species of zooplankton *Arctodiaptomus alpinus* and *Cyclops abyssorum taticus* in the lake, which previously had no natural enemies (Brancelj, 1999 b). Various new algae species now grow in the lake. One particular problem in that is an underground link between the polluted lake and drinking water sources. Since then, the lake is going through series of changes for which we do not know exactly where they lead. However, there is more and more researches in this field which contribute to clarifying the roles and effects of the presence of fish in the lake ecosystem, which has previously not been inhabited by them (Brancelj et al., 2000; Brancelj, 2002; Muri et al., 2004; Vreča, Muri, 2006; Muri et al., 2013).

Usually, the model is developed by the decision-maker using one of the many decision modeling methods or tools (Bohanec, 2009). The methodology applied in multi-attribute decision-making, and software program DEXi, have proved to be suitable for a systematic and transparent way of decision-making in evaluation of nature and can potentially also be used in cases of other lakes. Modeling is an iterative, dynamic process (Odum 1984; Ford 1999; Grant, Swannack 2008) and environmental models are best developed through an iterative approach where a preliminary conceptual model is developed; then a small section of that conceptual model is quantified and evaluated, addressing challenges or incorporating new ideas as they occur; then a new piece of the conceptual model is quantified and evaluated; and so on, until the entire conceptual model is represented quantitatively.

Model development is most successful when the model is constructed in this manner collaboratively with modelers, subject matter experts, and the eventual end-users of the model. Unfortunately, this iterative approach to model development is seldom documented, but each of the practical activities can be directly related to the three steps mentioned above (conceptualize, quantify, evaluate). As the model development team quantifies each piece of the conceptual model, they are forced to constantly reevaluate the model, both conceptually and quantitatively. Often the pieces that fit well together conceptually do not make sense after performing a quantitative evaluation of those pieces. However, by quantifying and evaluating small pieces of the model separately, the process becomes significantly easier and this provides greater insight into system dynamics and greatly reduces the likelihood of mathematical or logical errors (Swannack et al., 2012).

#### 4.4.1 Model application

##### Description of the options (alternatives)

For alternatives in the model, I chose a variety of situations that could occur in nature and illustrate the description of existing situation of the lake, or the situation that the lake could be. First, the condition of the current situation needed to be determined. The assessment of the current situation was done on the basis of the current knowledge, understanding of the problem and the available data. According on the model results, I evaluated that the ecological effects on the Fifth Triglav Lake are *big*, due to *medium* trophic state (that result from *medium* water column and *medium* sediment characteristics), *negative* environmental parameters (*medium* temperature and *high* precipitation), *negative* anthropogenic stressors (*high* presence of fish and *medium* wastewater inflow) and *neutral* lake characteristics (*short* retention time of the water and *small* volume of the lake) (Figure 21). I wondered how this situation could be improved and what happens if the values of some parameters are changed. So, two more options are added, namely improved situation (better condition of the lake) and declined (worse condition of the lake) situation in order to assess how the current situation could be improved or worsend.

##### Results

The obtained evaluation and analysis results provide the basis for decision-maker's assessment of options and possible choice of the best one.

With multi-attribute models, options are evaluated in the following way:

1. Each option is represented by a vector of basic attribute values.
2. The values of each option are aggregated in a bottom-up way according to the defined structure of the model and corresponding utility functions.
3. The overall evaluation of an option is finally obtained as the value of one or more root attributes of the model.

On this basis, the decision-maker can compare and rank the options, and possibly identify and select the best one. In the evaluation, undefined values of basic attributes, denoted '\*', are interpreted as sets of all possible values that can be assigned to corresponding attributes. There, DEXi evaluates options trying all these values and keeps track of the evaluation results in these cases. Therefore, an evaluation result is not necessarily represented by a single attribute value, but can also be a set of values. In DEXi, results of option evaluation are shown on its Evaluation Page (Figure 21), as well as in charts and reports (Bohanec, 2013). These tables help us explain how and why it came to such results, where the pros and cons of each situation are and how can we reduce environmental impact.

Option	Current situation	Improved situation	Declined situation
<b>Ecological effects</b>	<b>big</b>	<b>medium</b>	<b>very big</b>
.. Trophic state	<b>medium</b>	<b>medium</b>	<b>high</b>
... Water column	<b>medium</b>	<b>medium</b>	<b>bad</b>
.... Chlorophyll a	medium	medium	high
.... Nutrients	medium	medium	high
.... Oxygen	high	high	high
... Sediment	<b>medium</b>	<b>medium</b>	<b>medium</b>
.... C/N ratio	medium	medium	medium
.... Nutrients in sediment	medium	medium	medium
.. Environmental parameters	<b>negative</b>	<b>negative</b>	<b>negative</b>
... Temperature	medium	medium	medium
... Precipitation	high	high	high
.. Anthropogenic stressors	<b>negative</b>	<b>neutral</b>	<b>negative</b>
... Fish	high	low	high
... Wastewater	medium	medium	high
.. Lake characteristics	<b>neutral</b>	<b>neutral</b>	<b>neutral</b>
... Retention time	short	short	short
... Volume	small	small	small

Figure 21. Evaluation results

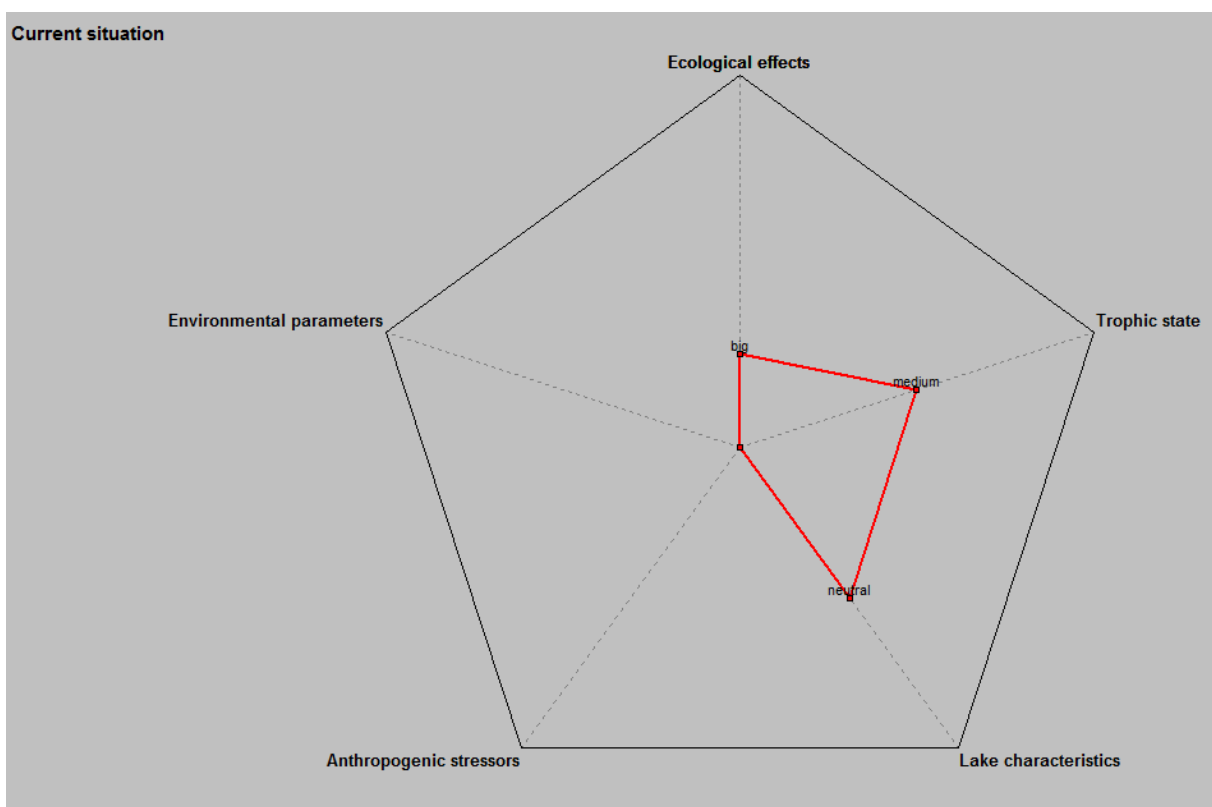
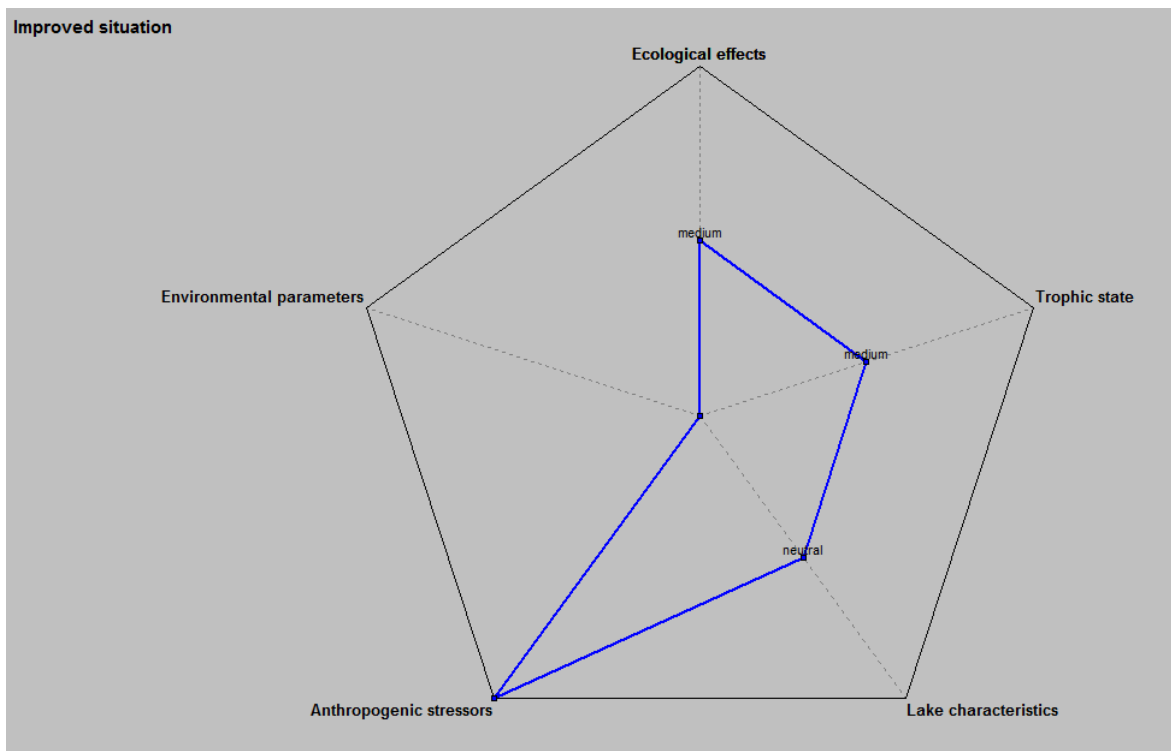


Figure 22. Graphical display of the evaluation – current situation

From the chart (Figure 22), we can see that the **current** ecological effect is **big**, and that one of the factors, which can be modified and we have influence on, is inadequate, and this is the presence of the fish. Likewise, the ecological effect is **big** due to **medium** wastewater inflow, **medium** trophic

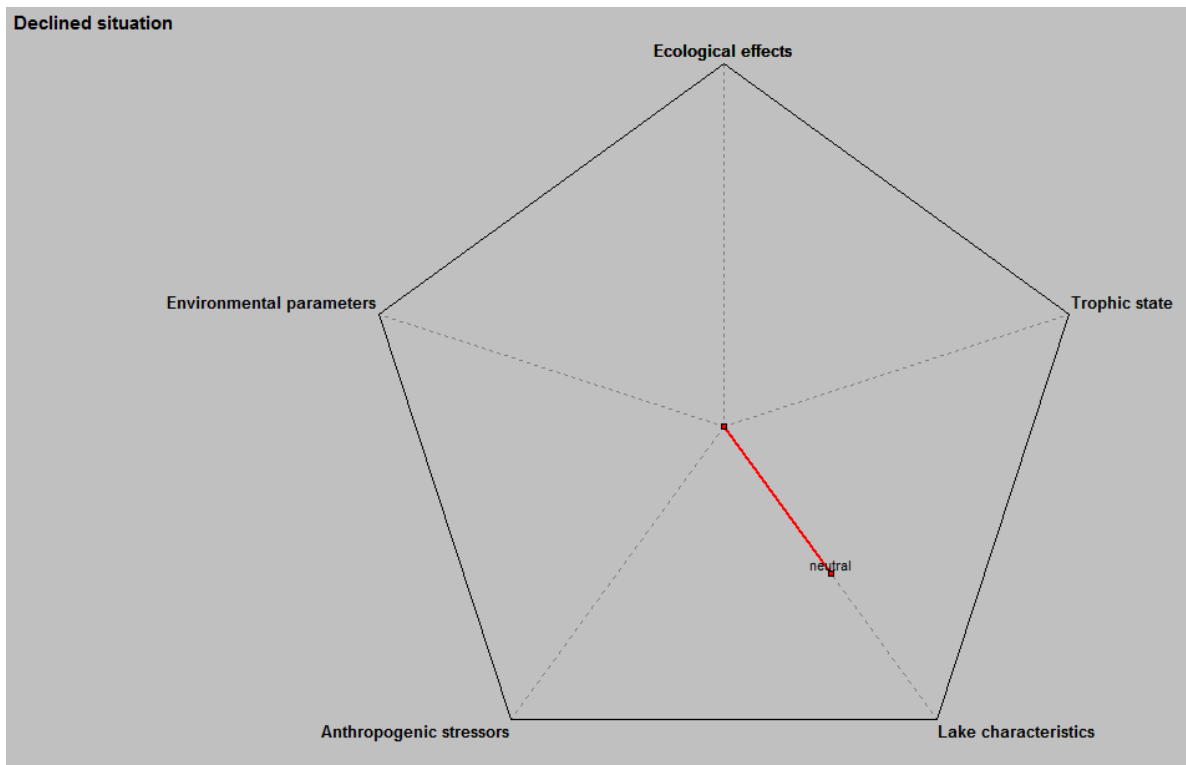
state, *neutral* lake characteristics and *negative* environmental parameters, but on final two we do not have direct impact.



**Figure 23. Graphical display of the evaluation – improved situation**

From the model, I found out that there are two main factors on which we have influence; the presence of the fish and wastewater inflow. I assumed that the wastewater inflow will not change or will even improve, since a wastewater treatment plant was constructed in 2010. On the other hand, the hut on the shore of the Fifth Triglav Lake is there for more than 100 years already. *Medium* ecological effects would thus be achieved when we change the presence of fish from *high* to *low* which results in *neutral* anthropogenic stressors, and they do not have such a great impact on the ecological effects. The graph above shows us *medium* ecological effects and is a part of the **improved** - better situation (Figure 23).





**Figure 24. Graphical display of the evaluation – declined situation**

On the graph above (Figure 24) we see that the ecological effects are *very big*, beside the *high* presence of fish and *high* wastewater inflow, there is also the *high* trophic state, *bad* water quality, and *negative* environmental parameters, as they all affect the increasing ecological effects. So the **declined** – worse situation is showing what could have happened with the state of the lake, if the lake hadn't been properly treated or managed.

## 5. CONCLUSION

OC to TN or C/N ratios together with stable organic carbon isotopic composition ( $\delta^{13}\text{C}$  values) were used to investigate OM sources in the surface sediments of the Fifth Triglav Lake in the Julian Alps. C/N ratios ranged from 13.3 to 15.6. They were intermediate between the characteristic algal/bacterial (autochthonous) and terrestrial (allochthonous) values, suggesting that both autochthonous and allochthonous sources contribute OM to this lake.  $\delta^{13}\text{C}$  values varied from -22.4 to -26.4 ‰ which could also indicate contribution of both autochthonous and allochthonous sources. When comparing  $\delta^{13}\text{C}$  values versus OC concentration, sampling locations with higher impact of allochthonous sources (DJ5-I, DJ5-II, DJ5-V) are located more to the north of the Fifth Triglav Lake, while locations with higher impact of autochthonous sources (DJ5-III, DJ5-IV, DJ5-VI) are located more to the south of the lake. When comparing  $\delta^{13}\text{C}$  values versus C/N ratio, two sampling locations (DJ5-I, DJ5-II) with higher impact of allochthonous sources are located in the northern half of the lake and four locations with higher impact of autochthonous sources (DJ5-III, DJ5-IV, DJ5-VI, DJ5-V) are located in the central and southern part of the lake. A simple (linear) correlation among OC and TN concentrations, the C/N ratios and stable carbon isotopic composition was calculated, in order to determine the degree of relation between these parameters. OC and C/N ratio show a relatively strong negative correlation with  $\delta^{13}\text{C}$  values indicating importance of primary production on sedimentary OM in this lake. When comparing the data obtained in this study with the data from a previous study, C/N ratios in the Fifth Triglav Lake were higher than recently observed and also higher than the ones in other lakes in the Julian Alps. In this study, surface sediment samples were collected all across the Fifth Triglav Lake, also in shallower parts of the lake where allochthonous OM is relatively more important, thus explaining a higher contribution of allochthonous sources to sedimentary OM.

Phosphorus compounds availability is considered as one of the most important factors for determining the water quality of lakes. Most of phosphorus compounds are in organic form, followed by calcium-bound, iron-bound, aluminum-bound and loosely bound phosphorus compounds. Phosphorus compounds are unevenly distributed across the lake, while the locations DJ5-IV and DJ5-III have the highest concentrations but are the most distant from the hut. There is no clear evidence regarding mountain hut impact on the lake. A simple (linear) correlation among the different fractions of phosphorus showed positive and high correlation among total phosphorus, Org-P, HCl-P and NaOH-P ( $r > 0,87$ ). In contrast,  $\text{NH}_4\text{Cl-P}$  and BD-P exhibited much lower correlations indicating that reactive forms of phosphorus are more dependent on the sampling site characteristics. When comparing the data with other lakes, the highest phosphorus compounds concentrations in the Fifth Triglav Lake are somehow similar to the concentrations observed in a moderately eutrophic lake, while the lowest tend to be more similar to oligotrophic lakes.

Program DEXi can be used for assessment, comparison and “what-if” analysis of the current, as well as improved and declined situation, and thus it contributes to a better understanding of the problems of lakes. According to the model results, the presence (amount) of fish is the critical factor affecting the state of the lake. If the amount of fish in the lake had been reduced, ecological effects would have improved from *big* to *medium*, as anthropogenic stressors would have changed from *negative* to *neutral*. In contrast, if inputs of wastewater, as well as nutrient concentrations in the water column had increased, ecological effects would have declined from *big* to *very big*, as the trophic state would have changed from *medium* to *high*. It is important to emphasize that the final result of the evaluation of ecological effect depends not only on making the decision model (i.e., to choose the parameters, determine the scales and related utility functions – decision rules), but it largely depends on the correct, accurate and high-quality data with which we describe the evaluated options (alternatives) of the model. The development of the model and its evaluation is very dependent on a single decision-maker or group of decision-makers and their knowledge of the issue in this field. This model can also be applied to other lakes in the area.

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## 7. APPENDIX A: DECISION RULES TABLES

### DEXi

Ecological effects.dxi

	Water column 50%	Sediment 50%	Trophic state
1	<b>bad</b>	<=medium	<b>high</b>
2	<=medium	<b>bad</b>	<b>high</b>
3	<b>bad</b>	<b>good</b>	medium
4	medium	medium	medium
5	<b>good</b>	<b>bad</b>	medium
6	>=medium	<b>good</b>	<b>low</b>
7	<b>good</b>	>=medium	<b>low</b>

	Chlorophyll a 35%	Nutrients 35%	Oxygen 30%	Water column
1	<b>high</b>	<b>high</b>	*	<b>bad</b>
2	<b>high</b>	<=medium	<=medium	<b>bad</b>
3	<b>high</b>	*	<b>low</b>	<b>bad</b>
4	<=medium	<b>high</b>	<=medium	<b>bad</b>
5	*	<b>high</b>	<b>low</b>	<b>bad</b>
6	<b>high</b>	>=medium	<b>high</b>	medium
7	<=medium	medium	<b>high</b>	medium
8	<b>high</b>	<b>low</b>	>=medium	medium
9	<=medium	<b>low</b>	medium	medium
10	medium	<=medium	<b>high</b>	medium
11	>=medium	<b>high</b>	<b>high</b>	medium
12	medium	medium	*	medium
13	medium	>=medium	<=medium	medium
14	>=medium	medium	<=medium	medium
15	>=medium	>=medium	<b>low</b>	medium
16	<b>low</b>	<b>high</b>	>=medium	medium
17	<b>low</b>	<=medium	medium	medium
18	>=medium	<b>low</b>	<b>high</b>	<b>good</b>
19	<b>low</b>	>=medium	<b>high</b>	<b>good</b>
20	<b>low</b>	<b>low</b>	>=medium	<b>good</b>

	C/N ratio 43%	Nutrients in sediment 57%	Sediment
1	<b>low</b>	<=medium	<b>bad</b>
2	<=medium	<b>high</b>	<b>bad</b>
3	<b>low</b>	<b>low</b>	medium
4	>=medium	medium	medium
5	<b>high</b>	<=medium	medium
6	>=medium	<b>low</b>	<b>good</b>

	Temperature 50%	Precipitation 50%	Environmental parameters
1	<b>high</b>	<=medium	<b>negative</b>
2	<=medium	<b>high</b>	<b>negative</b>
3	<b>high</b>	<b>low</b>	neutral
4	medium	medium	neutral
5	<b>low</b>	<b>high</b>	neutral
6	>=medium	<b>low</b>	<b>positive</b>
7	<b>low</b>	>=medium	<b>positive</b>

	Fish 67%	Wastewater 33%	Anthropogenic stressors
1	<=medium	*	<b>negative</b>
2	*	<b>high</b>	<b>negative</b>
3	<b>low</b>	>=medium	neutral

	Retention time	Volume	Lake characteristics
	57%	43%	
1	<b>long</b>	<=medium	<b>negative</b>
2	<=medium	<b>small</b>	<b>negative</b>
3	<=medium	<b>large</b>	neutral
4	medium	>=medium	neutral
5	<b>short</b>	<b>small</b>	neutral
6	<b>short</b>	>=medium	<b>positive</b>