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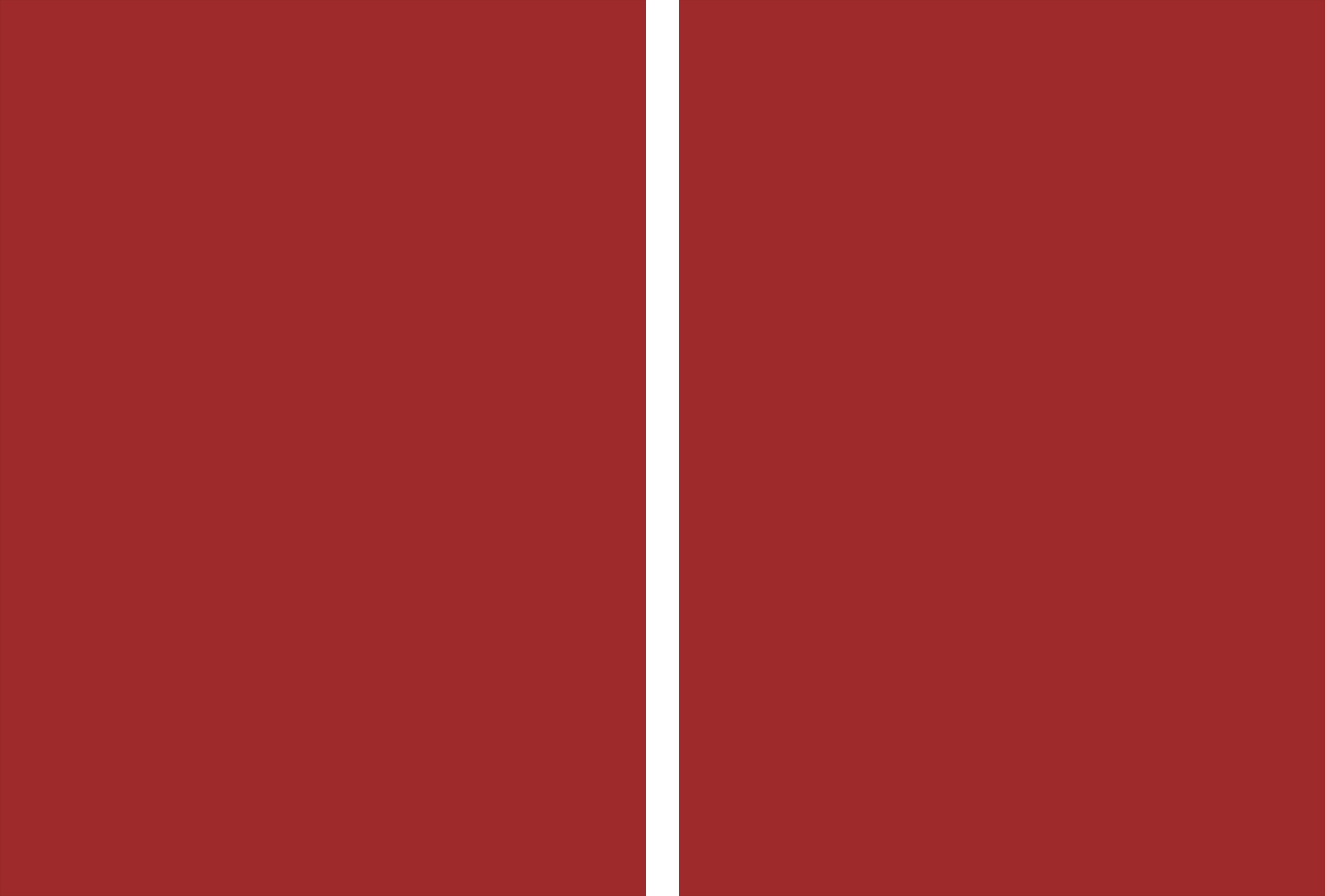
Daniel Cerqueira Ribeiro

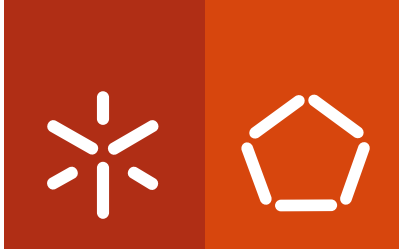
**Phosphorus dynamics in Lake Sediments:
When the sediments act as a sink?**

Daniel Cerqueira Ribeiro Phosphorus dynamics in Lake Sediments: When the sediments act as a sink?

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**Phosphorus dynamics in Lake Sediments:
When the sediments act as a sink?**

Doctoral Dissertation for PhD degree
in Chemical and Biological Engineering

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Abstract

Worldwide anthropogenic activity has hindered the water quality of lakes and reservoirs in the last decades. Highly fertilized land fields leached nutrients (nitrogen and phosphorus) to the water bodies leading to eutrophication and consequently to a bad ecological status. In lakes systems, eutrophication is limited by phosphorus (P) concentration in the water column. Azorean lakes Furnas and Sete-Cidades are examples of eutrophic lakes as consequence of external inputs of nutrients resulting also in P accumulation in the sediments for many years. With the objective of achieving a good water quality and ecological status until 2015, it is essential to implement restoration measures. The reduction of external inputs of nutrients (especially P) is the primary concern in several lakes and reservoirs. But, results from several researchers showed that even reducing external P load, the sediments would continue to release P disabling the recovery process. Thus, the mobility of P in the sediment turned to be one of the most important factors to delineate recovery processes of the lakes' water quality. In this context, the present work has the objectives of exposing several theories for P internal load and of understanding the factors that contribute to P mobility in a geochemical perspective, leading to suggestions for P internal input reduction in a management point of view.

Sediments samples from three Azorean lakes (Fogo, Furnas and Sete-Cidades) were collected and analyzed through a P sequential extraction procedure (PSE) to understand how P was geochemically bound. For lake Fogo (an oligotrophic lake), results showed that the P concentration values increase from the most labile fraction to the most stable fraction (refractory-P). Based on this trend, lake Fogo will not have significant internal P input (concomitant with its present trophic status), unless these P fractions change in the future. In Lake Furnas (eutrophic status) the major P quantity is adsorbed to Al and Fe oxide/hydroxide fractions, with no changes in several years, which can mean that the adsorption capacity might be already saturated for this fraction, leading to P diffusion through the sediment-water interface (SWI). The lake Sete-Cidades (meso-eutrophic status) seems to have the same trend with higher \sim P concentration found in the metallic oxide/hydroxide. The phosphorus maximum solubilization potential (*P-MSA*) was calculated for the three lakes and the higher

value were found in Lake Furnas, which indicates a high potential of P release, turning this lake into the most endangered ecosystem of the three studied lakes.

With the objective of understanding the effect of O₂ concentration with simultaneous change in temperature, sediments from Furnas Lake were placed in a reactor, with temperature and oxygen concentration control. With the aid of microsensors, pH, O₂ and H₂S were monitored in sediment depth. Results showed that variations in O₂ concentration can force changes in pH which will change the equilibrium of P adsorption to metallic minerals. We think that the pH shift is due to microbial activity and adaptation to the aerobic/anoxic conditions, and that this shift can influence P release that is adsorbed to Al minerals.

As *in situ* measuring of changes that happen in the several P-fractions is extremely difficult, we decided to use mathematical models to predict changes in P mobility. The AQUASIM platform was used to model OM mineralization, acid/base equilibrium, precipitation equilibrium as well as P adsorption equilibrium in the sediments. According to the model, the release of P from the dissolution of FeOOH-P complex plus the P released from OM mineralization in anoxic conditions is lower than P release from OM mineralization in aerobic conditions. In addition, during anoxic period Fe(II) is produced in major quantities which leads to phosphate removal as it precipitates in the form of Fe₃(PO₄)₂. Moreover, sulfate reduction activity by bacteria produces hydrogen sulfide (H₂S) that react with Fe(II) precipitating as FeS. This process can permanently remove Fe from the cycle in lower anoxic layers leaving less Fe available to remove P from the pore water as Fe₃(PO₄)₂ or as FeOOH-P when condition at SWI will turn aerobic.

With this entire picture in mind, we can understand that if sediments will act as a sink or not depends largely on the P adsorption capacity of its natural mineral constitution and the time that those mineral remain unsaturated. The presence of H₂S in sediment can reduce the availability of Fe(II) and Fe(III) minerals and consequently reduce the retention capacity of sediments.

Resumo

Nas últimas décadas, a actividade antropogénica tem diminuído a qualidade da água de lagos e albufeiras no mundo inteiro. Lixiviados com elevadas concentrações de nutrientes (azoto e fósforo) provenientes de campos altamente fertilizados são drenados para as massas de água conduzindo à eutrofização e a um mau estado ecológico. Em sistemas lagunares, a eutrofização é limitada pela concentração de fósforo (P) na coluna de água. Nos Açores, as lagoas das Furnas e de Sete-Cidades são exemplos de lagos eutrofizados como consequência de entradas externas de nutrientes, tendo acumulado P nos sedimentos por vários anos. Com o objectivo de se atingir o bom estado ecológico e de qualidade da água até 2015, medidas de restauração devem ser implementadas numa perspectiva de gestão ambiental. A redução das entradas externas de nutrientes (com foco no P) é a primeira preocupação em vários lagos e albufeiras. No entanto, resultados de vários investigadores mostraram que mesmo reduzindo as cargas externas de P, os sedimentos continuam a libertar P dificultando o processo de recuperação. Assim, a mobilidade do P nos sedimentos é de elevada relevância para delinear processos de recuperação da qualidade da água de lagos. Neste quadro, o presente trabalho tem como objectivo expor teorias sobre entradas internas de P e entender os diferentes factores que influenciam a mobilidade deste, conduzindo a soluções para a redução das cargas internas.

Amostras de sedimentos de três lagos açorianos (Fogo, Furnas e Sete-Cidades) foram recolhidas e analisadas através de um procedimento de extracção sequencial (PSE) para entender a distribuição geoquímica do P. Para a lagoa do Fogo (estado oligotrófico), os resultados indicam que a concentração de P aumenta desde a fracção mais lábil até a fracção mais estável (P refractário). Baseado nesta tendência, prevê-se que a lagoa do Fogo não terá entradas significativas de P interno (concomitante com o seu estado trófico actual), excepto se ocorrerem futuras alterações nas fracções analisada. Na lagoa das Furnas (estado eutrófico) a maior quantidade de P está adsorvida a óxidos e hidróxidos metálicos sem grandes alterações nos últimos anos, indicando a saturação da capacidade de retenção desta fracção, resultando na difusão de P através da interface sedimentos-água (SWI). A lagoa das Sete-Cidades (estado meso-eutrófico) apresenta a mesma tendência que a lagoa das Furnas.

O potencial de máxima solubilização de fósforo (*P-MSP*) foi calculado para as três lagoas sendo superior na lagoa das Furnas, sendo por isso o ecossistema mais ameaçado.

Com o objectivo de entender o efeito da variação concentração de O_2 e temperatura (T), sedimentos da lagoa das Furnas foram colocados num reactor, com T e concentração de O_2 controlados. Com o auxílio de microsensores, o pH, O_2 e H_2S foram monitorizados em profundidade nos sedimentos. Os resultados mostram que a variação da concentração de O_2 pode influenciar a alteração do pH o que altera o equilíbrio na adsorção de fósforo aos minerais metálicos. Pensa-se que a mudança de pH deve-se à actividade microbiana em adaptação às mudanças de condições aeróbias/anóxicas, e que esta mudança pode influenciar a libertação de P adsorvido principalmente aos minerais de Al. Visto que a medição *in situ* de alterações que acontecem nas diferentes fracções de fósforo é extremamente difícil, usou-se um modelo matemático para entender os processos de mobilidade do fósforo. O AQUASIM foi usado como plataforma de modelação, incluindo os processos de mineralização da matéria orgânica (OM), equilíbrio ácido/base, equilíbrio de precipitação, assim como equilíbrio de adsorção.

Segundo o modelo, a libertação de P por dissolução do complexo FeOOH-P mais o P libertado pela mineralização da MO em condições anóxicas é inferior ao P libertado pela mineralização da OM em condições aeróbias. O P é igualmente removido por reacção com Fe(II), em condições anóxicas, precipitando na forma de $Fe_3(PO_4)_2$ o que induz a remoção de P dissolvido. Por outro lado, a redução do sulfato por actividade bacteriana produz H_2S que reage com Fe(II) precipitando como FeS removendo permanentemente Fe nas camadas anóxicas, diminuindo o Fe disponível para remover P na forma de $Fe_3(PO_4)_2$ e de FeOOH-P.

Com este quadro em mente, os sedimentos actuam como sumidouro de P dependendo da proporção de minerais de Al e Fe presentes e do tempo que estes permanecem insaturados. A presença de H_2S nos sedimentos pode reduzir a disponibilidade de minerais compostos por Fe(II) e Fe(III) e conseqüentemente reduzir a capacidade de retenção dos sedimentos.

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Abbreviations

ADP – Adenosine di-phosphate

Al – Aluminium

AlOOH – Aluminium oxi-hydroxide

ATP – Adenosine tri-phosphate

BD – Bicarbonate -dithionite

Ca – Calcium

dw – Dry weight

Fe – Iron

Fe(II) – Ferric iron (Fe^{2+})

Fe(III) – Ferrous iron (Fe^{3+})

$\text{Fe}_3(\text{PO}_4)_2$ – Iron phosphate (Vivianite)

FeOOH – Iron oxi-hydroxide (Ghøetite)

FeS – Iron sulfide

H – Length of control volume (in water)

h – Length of control volume (in sediments)

HCl – Hydrochloric Acid

H_2S – Hydrogen sulfate

Mn – Manganese

$m_{\text{P, sed}}$ – Phosphorus mass in sediments

Myr – Million year(s)

N – Nitrogen

NaOH – Sodium hydroxide

NH_4 – Ammonium

NH_4Cl – Ammonium chloride

NO₃ – Nitrate

NRP – Non reactive phosphorus

OM – Organic matter

O₂ – Molecular oxygen

P – Phosphorus

PP – Particulate phosphorus

HPO₄²⁻ – Phosphate

P-MSP – Phosphorus maximum solubilization potential

PSE – Phosphorus sequential extraction

POP – Particulate organic phosphorus

phytate-P – Phytate-phosphate

poly-P – Poly-phosphate

SRP – Soluble reactive phosphorus

TP – Total phosphorus

ρ_{sed} – Sediment density

Φ – Total sorption capacity

SWI – Sediment/Water interface

SO₄²⁻ – Sulfate

θ – Sediment porosity

WFD – Water frame directive

Preface

This thesis is based on research for a PhD project undertaken at the IBB - Institute for Biotechnology and Bioengineering, Centre for Biological Engineering, University of Minho, from February 2006 to January 2011. This thesis is based on scientific research that resulted in three articles that are published or submitted to scientific journals and one article in preparation for submission.

Ribeiro, D.C., Martins, G., Nogueira, R., Cruz, J.V., Brito, A.G., (2008). Phosphorus fractionation in volcanic lake sediments (Azores - Portugal), *Chemosphere* 70, 1256–1263.

Ribeiro, D.C., Martins, G., Brito, A.G., Nogueira R., (2012). Phosphorus mobility in lake sediments - A review. (submitted).

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Publications co-authored and closely related to the topic of the thesis, but not explicitly comprised here are listed below. It includes several publications in scientific journals, one book chapter and several presentations at international and national conferences.

Articles in Scientific Journals

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Oliveira, M., **Ribeiro, D. C.**, Nobrega, J. M., Machado, A. V., Brito, A. G., Nogueira, R. (2011). Removal of phosphorus from water using active barriers: Al₂O₃ immobilized onto polyolefins. *Environ Technol.*, 32(9-10):989-95.

Martins, G., Henriques, I., **Ribeiro, D.C.**, Correia, A., Bodelier, P.L.E., Brito, A.G., Nogueira, R., (2009). Biogeochemical characterization of lake sediments: a prerequisite to establish a restoration plan for eutrophic Azorean lakes. *Aquatic Microbial Ecology* (submitted).

Martins, G., Terada, A., **Ribeiro, D.C.**, Brito, A.G., Smets, B.F., Nogueira R., (2009). Sediment bacterial structure and activity in Azorean volcanic lakes. *FEMS Microbiology Ecology* (submitted).

Martins, G., Peixoto, L., **Ribeiro, D. C.**, Parpot, P., Brito, A. G., Nogueira, R., (2010) Towards Benthic Microbial Fuel Cell implementation in Volcanic Eutrophic lakes: bacterial electrochemical activity assessment in Lake Furnas (Azores) – Portugal. *Bioelectrochemistry*, 78, 67–71.

Martins, G., **Ribeiro, D.C.**, Pacheco, D., Cruz, J.V., Cunha, R., Gonçalves, V., Nogueira, R., Brito, A.G., (2008) Prospective scenarios for water quality and ecological status in Lake Sete Cidades (Portugal): the integration of mathematical modelling in decision processes. *Applied Geochemistry*, 23, 2171-2181.

Book Chapter:

Martins, G., **Ribeiro, D.C.**, Terada, A., Smets, B.F., Brito, A.G., Nogueira, R., (2011). Phylogeny and activity of Proteobacteria in lake sediments. In *Proteobacteria: phylogeny, metabolic diversity and ecological effects*; Sezena., M.L., Ed.; Nova Science Publishers, Inc., ISBN: 978-1-61761-198-8.

Oral Presentation and Posters

Ribeiro D.C., A. G. Brito, Nogueira R., “Phosphorus Mobility in Lake Sediments” 2nd meeting of the IBB, 23-24 October 2010, Braga - Portugal.

Martins, G., **Ribeiro, D.C.**, Terada, A., Henriques, I., Peixoto, L., Bodelier, P.L., Correia, A., Cruz, J.V., Parpot, P., Brito, A.G., Smets, B.F., Nogueira, R., (2010). Eutrophication-threatened aquatic ecosystems: sediment biogeochemical processes towards nutrients

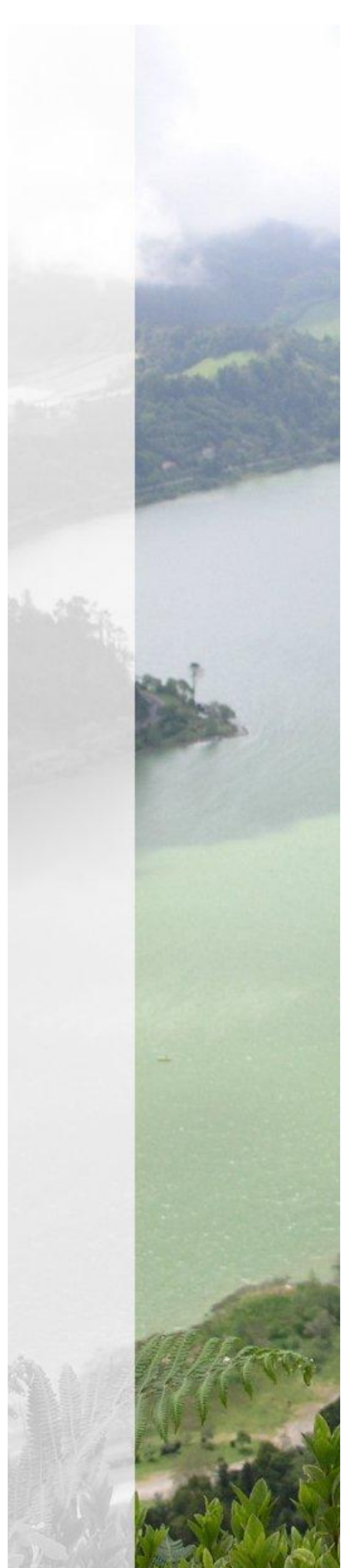
control. 14th International Conference, IWA Diffuse Pollution Specialist Group: Diffuse Pollution and Eutrophication. September 12-17, Québec - Canada.

Martins, G., Terada, A., Henriques, I., **Ribeiro, D.C.**, Correia, A., Brito, A.G., Smets, B.F., Nogueira, R., (2010). Sediment bacterial community structure and activity in Azorean volcanic lakes. XV AIL Congress, July 4-9, Ponta Delgada, Portugal.

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Chapter 1.

Motivation and Objectives



For centuries water seemed to be an unlimited renewable resource for mankind and all other living things in the ecosystems. But in the last century, aquatic environments turn to be one of the most endangered habitats and are in direct need of protection and conservation. Monitoring programs were started worldwide aiming the assessment of ecological communities and the environmental factors that can interfere with their sustainability. In September 2000, the European Parliament approved a new Directive known as the Water Framework Directive (WFD) that outlines a legal structure for the assessment of all types of water bodies in Europe (2000/60/EC; European Commission 2000). The Directive defines the framework for the community actions with the purpose of protection and/or restoration of surface waters, coastal and groundwater aiming a good ecological status until 2015.

Eutrophication of lakes and reservoirs is a growing problem in Portugal as well as in many other countries. This is mainly due to anthropogenic activity, especially as a consequence of nutrient leaching from the highly fertilized land fields to the water bodies (INAG, 2005). The Portuguese archipelago of Azores has several islands with eutrophic lakes, due to diffuse pollution from the cultivated watershed (DROTRH/INAG, 2001). The Azores is a volcanic archipelago situated in North Atlantic Ocean and belongs to the Macaronesia. From the nine islands of the Azorean archipelago, this thesis will focus on S. Miguel Island as the studied lakes are located there. The “Green Island” is how S. Miguel is several times recorded, due to the extensive grass fields that cover the land, once occupied by a widespread laurel forest type. Industrial massive deforestation happened in the last decades, in order to extend the availability of fertilized grass field for cattle rising. The newly fertilized fields have hastened the eutrophication process, as nutrients were drained into the lakes (Santos *et al.* 2004, 2005; Medeiros, 2004). Among the several lakes of S. Miguel, this study is mainly concerned with the ecological status of three lakes, namely Fogo, Furnas and Sete Cidades.

In aquatic systems, nitrogen (N) and phosphorus (P) are the most important nutrients for eutrophication enhancement, as they are both needed for primary producers' growth (Conley *et al.*, 2009). Aquatic plants and phytoplankton are examples of primary producers that will excessively increase in number if those nutrients are largely available. Particularly, cyanobacteria blooms will increase leading to cyanotoxin release and the decrease of water quality. Thus, the control of nutrients concentration in aquatic ecosystems is crucial to prevent

the eutrophication process. However, in lake systems, microbial denitrification can permanently remove N from a lake (McCarthy *et al.* 2007) leaving P (mainly in phosphate form) as the limiting nutrient for the algae growth, as there is no similar process for P removal. To find solutions for decreasing the eutrophication rate or even reverse it, one should look to the P cycle in lakes and attempt to reduce P availability in the water column.

The first and most evident approach would be to understand the effect of external P load reduction. This procedure was applied in several lakes worldwide while modeling was used for others (Jeppesen *et al.*, 2005; Søndergaard *et al.*, 2005; Martins, G., *et al.* 2008). The results of those procedures demonstrated that if external P load is not decreased eutrophication will persist. The results also showed that for some lakes, even if the external P load is reduced, eutrophication will continue to happen as the P buried in the sediments will continue to be a source of P to the water column (Søndergaard *et al.*, 2007). Thus, the study of the P cycle in the sediments is highly relevant to understand when those are acting as a sink or as a source of P, and to define which procedures could ensure P retention in the sediments.

Since 1936 that P release from the sediments is being studied and related with redox potential changes (Einsele, W., 1936; Mortimer, C. H., 1941, 1942.) Einsele and Mortimer were the first researchers that related P release with iron (Fe) minerals reduction where P was adsorbed to. Since then, internal P load has been linked to the hypolimnetic oxygen depletion resulting in Fe reduction and consequently to P release (Mortimer, C. H., 1971). In this context, hypolimnetic oxygenation and artificial destratification were implemented in several lakes (Grochowska, J. and Gawrońska, H., 2004) including the Azorean lake Furnas. However, the improvement of water quality as a result of these techniques was not evident. The results of several trials led to the conclusion that although the classical paradigm is valid, other factors play an important role in P retention, even when redox potential changes happen. For instance, in some lakes the P flux from the sediments to the water column does not increase even when hypolimnium is anoxic; the Plešné lake is an example of this phenomenon (Kopáček *et al.* 2005, 2007). This fact is related to the presence of metallic oxides or hydroxides that are redox non-sensitive and continue to trap P during anoxia. Another reality is that in some lakes P is released from the sediments even when there is no

O₂ stratification. This fact has been related to the presence of hydrogen sulfide (H₂S) interactions with iron in the sediments' deepest layers (Gächter, R., and Müller, B. 2003).

Thus a complex network of biological and geochemical reactions takes place in sediments, and influences the mobility of P. In Azores, the problem of eutrophication is well documented, especially of the processes on the water column (Santos *et al.* 2005). In addition, monitoring of water quality is continuously made by Regional Department of Water Resources and Land Planning (DROTRH) resulting in several reports every year. However, no sediment diagnose was made to understand the contribution of internal P to the Azorean lakes' eutrophication problem. Research toward biological screening of species in sediments and their contribution to P release was recently made for these lakes (Martins, G. *et al.* 2010). Moreover, P mobility has also a strong relationship with the inorganic mineral composition of the sediments (Ribeiro, D. C. *et al.* 2008). As this information was lacking, the present work aims to give insight mainly in the geochemical aspect P mobility and to deliver knowledge to define the elements that one could influence to mitigate P internal release. The specific aims of the present work were as follow:

- to assess the biogeochemical distribution of P in the sediments;
- to apply a sequential extraction procedure as a tool to forecast the exhaustion of the P retention capacity;
- to evaluate the dynamics of P mobility and understand how environmental factors can influence it;
- to use mathematical modeling to determine the factors that can influence P retention
- to suggest remediation measures based on the present work results.

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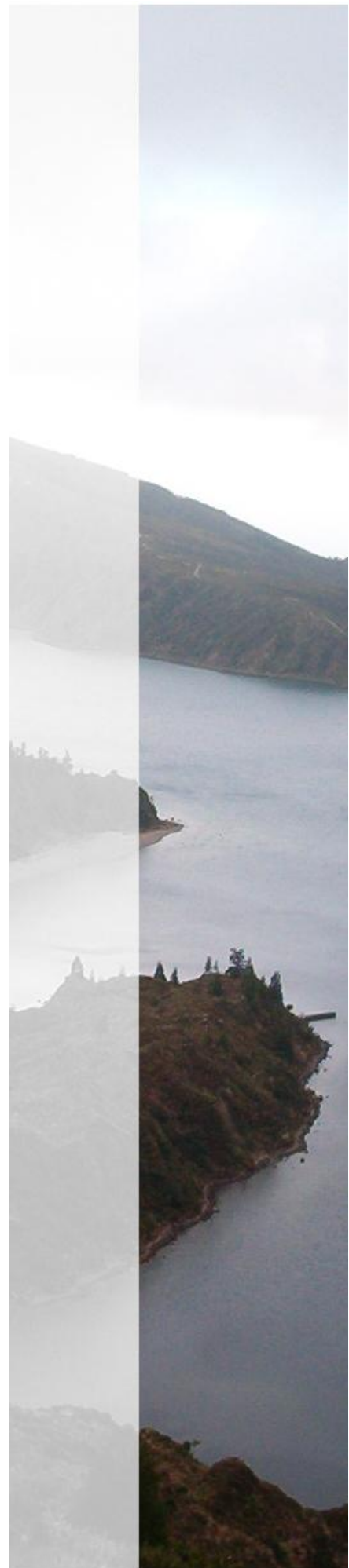
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Chapter 2.

Thesis Overview



After defining the motivation and objectives of this project in Chapter 1, the internal structure of the thesis is presented as follow:

Chapter 3 addresses a revision of the literature related with the mobility of P in sediments. It establishes the key terminology of P fluxes that are used in this work and highlights the main controversial aspect on that subject. It discusses the interaction of geochemical components and microbiological species in P retention capacity of sediments. Strong evidence that P retention is dependent on several geochemical and microbial aspects is demonstrated leaving the classic limnological paradigm valid only in particular cases.

Chapter 4 is mainly focused on sediments characterization in terms of P content. It describes an extraction procedure of P that was applied to sediments of three lakes (Fogo, Furnas and Sete-Cidades) in Azores archipelago. It shows the relation between different lake's trophic state and the P fractions in the sediments. The concept of maximum P solubilization potential is also addressed in this chapter.

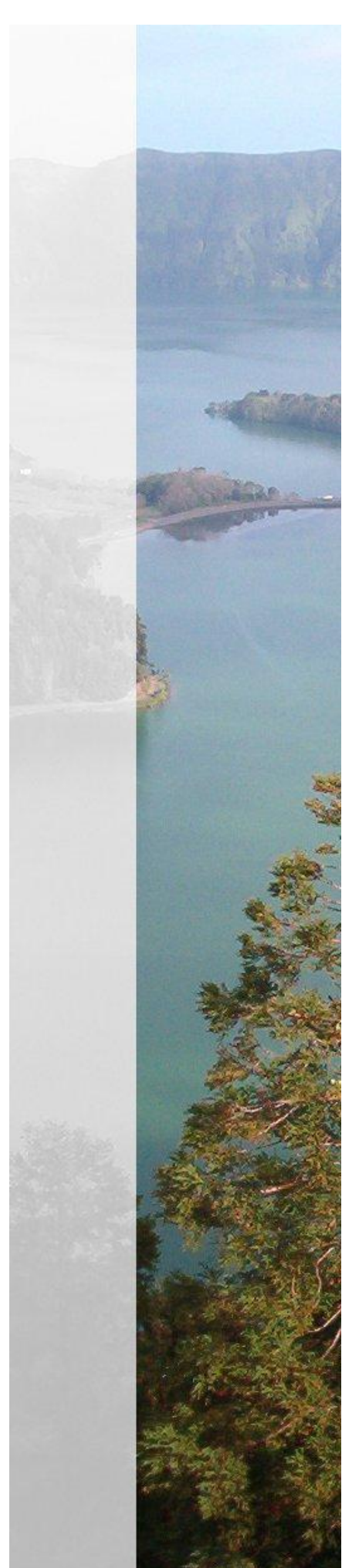
Chapter 5 presents the results of a microcosm experiment with sediments from the eutrophic Lake Furnas. Microsensors and P sequential extraction procedures were used to evaluate the mobility of P as function of oxygen concentration.

Chapter 6 describes the results of the mathematical modeling study of the phosphorus mobility in sediments due to changes in sediments metallic characteristic, H₂S presence and variation of O₂ concentration. The AlOOH:FeOOH ratio is assessed as a mean of retention capacity evaluation.

Chapter 7 summarizes the results obtained during this thesis and provides future perspectives of the present study.

Chapter 3.

Theoretical Basis



Phosphorus Mobility in Lake Sediments – A review

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Redrafted from: Journal of Soils and Sediments, submitted

For a long time that phosphorus release in sediments has been almost exclusively related with the absence of oxygen in the hypolimnium. This paradigm was firstly stated with the pioneer work of Einsele (in 1936) and Mortimer (in 1941), demonstrating the relation between the reduction of Fe(III) and phosphorus release in anoxic sediments. Although the theoretical statements matched the experimental findings, these could not be generalized since several field observations and laboratory experiments lead to other conclusions. In fact, according to this paradigm, restoration measures were applied using hypolimnetic aeration, but with few or no results in eutrophication control. This acquired experience has led to a need of deeper understanding of factors that influence the phosphorus mobility, leaving the old paradigm applicable only in special cases. Enumerating some of the factors, studies have shown that phosphorus release is largely influenced by the phosphorus retention capacity of the lake due to the sediments' geochemical characteristics. The presence of metallic oxides and hydroxides (specifically of aluminium and iron) in the sediment structure enhance retention, even in anoxic conditions. Phosphorus can also be released by microbial mediation in processes like organic matter mineralization, iron and sulphate reduction. Bacteria can also impel a pH and redox variation that consequently leads to geochemical change liberating phosphorus. In contrast, some bacteria have the capability of storing phosphorus. A review of these processes leads to a better understanding of factors that controls phosphorus mobility in natural waters.

3.1. Introduction

For several decades, limnologists have accepted that the release of phosphorus (P) from lakes' sediment is strongly related with the seasonal anoxic conditions that these are exposed. The idea that dissolved oxygen is the key factor to P release was firstly proposed by Einsele (1936) and later demonstrated by Mortimer (1941, 1942). The chemical basis behind this theory is related with the high capacity for iron (Fe) oxides and hydroxides to adsorb phosphorus, and that this iron-phosphorus complex can be dissolved when the sediments are under reduced conditions due to low oxygen concentration.

It is observed that hypolimnetic P concentration rises when there is oxygen depletion, giving an apparent correlation between P release and low oxygen concentration. With these findings in mind, hypolimnetic aeration/oxygenation was applied in several lakes as a restoration measure. Although the expected P concentration reduction was reported for some lakes, others that were also submitted to aeration continued to release P from the sediments (Gächter and Wehrli, 1998; Schauser and Chorus, 2007). Even more astonishing is the fact that some lakes that were anoxic in some period of the year released an extremely low amount of P, in contradiction to the accepted theory (Driscoll *et al.*, 1993; Kopáček *et al.*, 2005). These deviations from the theoretical statements raised doubts against the validity that "oxygen concentration is the key factor to control P release from sediments", and that other key factors are in the role (Boström *et al.* 1988; Hupfer and Lewandowsky, 2008).

Focussing on the oxygen depletion there are at least two possible approaches for P release from sediments. Oxygen consumption by microorganisms during mineralization will consequently release P, while low oxygen concentration will cause inorganic P release that was bounded to Fe minerals. As both reactions occur, it is difficult to determine whether oxygen depletion is the consequence or the cause of P release. Other studies showed that the presence of sulphate and its chemical reaction with Fe can reduce the P retention capacity of the sediments (Caraco *et al.*, 1993). The sediments mineral composition must be taken into account as it has a strong relationship with its retention capacity (Kopáček *et al.*, 2005; Ribeiro *et al.* 2008). Thus, there are several others variables that can influence the P binding to the sediments, demonstrating that this is a complex problem that cannot be simplified to the statement that oxygen controls P release, leaving it valid only in particular cases.

The aim of this work is to review the overall variables that can interfere with P concentration in the water column, focusing mainly in the biogeochemical processes that control internal P load.

3.2. Definition of external and internal phosphorus loads: setting the reference system

A lake is a natural open system with mass and energy exchange with the surroundings. In our case, we are interested in the mass flux of P through the boundary. Depending on where the boundary is set, there are different approaches for the lake systems (Hupfer and Lewandowski, 2008; Moosmann *et al.*, 2006). In this article, we will focus on the process approach.

The process approach set the boundary at the water limit with the basin – the system is the water column. Thus, mass exchange in the sediment-water interface (SWI) is taken into account as illustrated in Figure 3.1. With this in mind, it is now important to define the variables that are related with the P mobility. The need of a consensus in the use of technical expressions is essential, as different terms are used to define the same variable, or even more confusing when the same term has different meanings depending on the viewpoint. In the following, the terms related with the P flux in the lake will be explained depending on the viewpoint and author's citation, in a way to delineate a consensual key terminology.

It is a general agreement that “*external P load*” refers to the dissolved and particulate P that enters the lake by water inflow (e.g. river, pluvial waters). More controversial is the term “*internal load*” in which we will focus in the next discussion. Hakanson has defined internal load of any chemical element (including P) as “*the sum of advective (resuspension) and diffusive transport from the sediments*” (Hakanson, 2004). This defines internal P load (P_{int_L}) as the sediment's particulate P (PP_{int_L}) plus the soluble reactive P (SRP_{int_L}) as a “*P flux from the sediment back into the water column*” (Moosmann *et al.*, 2006). Thus, internal load can be defined as:

Equation 3.1:
$$P_{int_L} = PP_{int_L} + SRP_{int_L}$$

and is also identified by some authors as “gross release”. At this moment, it is important to state that for deep lakes, internal load is mainly ortho-phosphate release (SRP_{sed}) while in shallow lakes, where the water column is well vertically mixed PP_{sed} resuspension will have a higher contribution to total phosphorus (TP) than in deep lakes (Sondergaard *et al.*, 2005). For this reason and as suggested by Nürnberg (2009), internal load should be analysed as TP and not only the SRP fraction because this could lead to an underestimation of internal load.

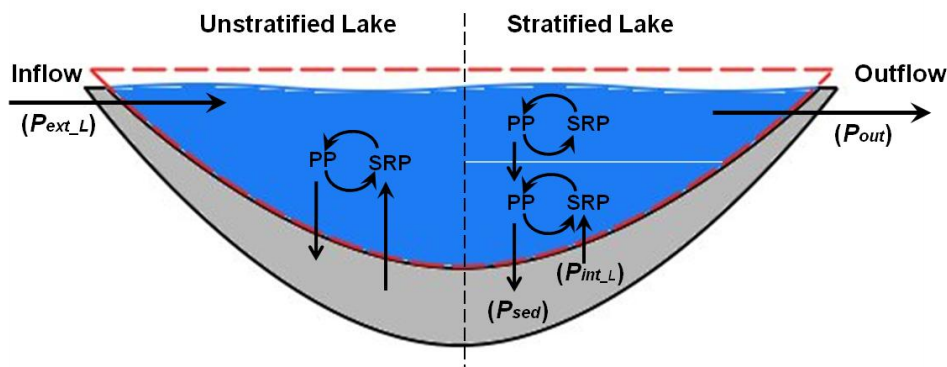


Figure 3.1 - Boundary settings of the lake system for the process approach.

In contrast, as depicted in Figure 3.1, there is also an opposing downward flux to P_{int_L} , which consists of settling of particulate P (PP) composed by organic and inorganic P. This flux is also known as “gross sedimentation”, defined as the “P flux from the epilimnion to the stratified deep water” (Moosmann *et al.*, 2006). To comprise deep and shallow lakes, we will define gross sedimentation as the P flux from the water column to the sediment (P_{sed}). Some authors define *internal load* as the net flux from the sediment ($P_{net_int_L}$), being the difference between gross release and sedimentation:

Equation 3.2:

$$P_{net_int_L} = P_{int_L} - P_{sed}$$

In this article we will define it as “net internal load” (also called “*net release*” - Nürnberg, 2009) to avoid disagreement with the term “internal load” defined above. If $P_{net_int_L}$ is positive then it means that there is more P going into the system than leaving it across the SWI, and vice-versa.

Table 3.1 – Review of terminology (note: all variables represent fluxes of P per lake area on an annual basis)

Term	Also Called	Definition	Mass balance (steady-state)
External Load	–	Total P that enters the lake by external inflows	$P_{ext_L} = P_{out} + P_{sed} - P_{int_L}$
Internal Load	Gross Release	Total P release from the sediments to the water column (re-suspension and diffusion process) – Eq. 3.1	$P_{int_L} = P_{out} + P_{sed} - P_{ext_L}$
Net Internal Load	Net Release	Difference between Internal load and gross sedimentation – Eq. 3.2	$P_{net_int_L} = P_{out} - P_{ext_L}$
Gross Sedimentation	–	Total P flux from the water column to the sediment (downward flux)	$P_{sed} = P_{ext_L} - P_{out} + P_{int_L}$
Net Retention	Net Sedimentation	Amount of TP that remains permanently in the sediments after sedimentation – Eq. 3.3	$P_{net_R} = P_{ext_L} - P_{out}$

An additional term defined differently depending on the viewpoint is *P retention*. Moosmann *et al.* (2006) defined “*net sedimentation*” as “*the amount of deposited P that remains permanently in the sediment*” (in a steady-state). This definition has the same meaning as “the difference between gross sedimentation and gross release”, and has been defined as “*net retention*” (Søndergaard *et al.*, 2003):

Equation 3.3:
$$P_{net_R} = P_{sed} - P_{int_L}$$

The absolute value of net retention (P_{net_R}) is equal to the absolute value of net internal load ($|P_{net_R}| = |P_{net_int_L}|$) and in a steady-state is equal to the difference between P external load and TP export via outflow (P_{out}).

To determine the internal load of a lake system by a mass balance, gross sedimentation must be known (Nürnberg, 2009). The problem is that direct determination of gross sedimentation can be inaccurate (James and Barko, 1997). Thus, Nürnberg (2009) suggested that this parameter should be determined through models, in order to calculate internal load.

The determination of which is the main contributor to lake’s P budget, between external and internal load, is still controversial. While some authors state that the enhance of P external load will cause a higher P sedimentation rate that will exceed P retention capacity of the sediments, leading to internal load (Hupfer and Lewandowski, 2008), others showed that even after P external load is reduced, there is a continuous release of P from the sediments

(Søndergaard *et al.*, 2005). Some authors declared that in some cases (depending on lake's characteristics), internal loading can endure for 10 to 20 years after external load reduction (Jeppesen *et al.*, 2005; Søndergaard *et al.*, 2007). Modelled scenarios with external P load reduction lead to the same conclusion (Martins *et al.*, 2008). Thus, next section will make an overview of the internal processes in sediments that can change the P retention capacity leading to P release.

3.3 Sediment's mineral composition as the chemical key to phosphorus retention

The sediments retention capacity is mainly related with its geochemical composition that depends primarily on the type of soil of the catchment area. Thus, geological characteristics of soil set the natural P adsorption capacity of the sediments (Kopáček *et al.*, 2005 and 2007; Ribeiro *et al.* 2008). If external load of P exceeds this capacity, internal load will occur. Even if natural retention capacity is not exhausted by external load, environmental conditions like pH, redox potential, and presence of sulphur compounds have an important role in the dissolution of the minerals that can adsorb SRP in the sediments.

Since the early work of Mortimer (1941, 1942), the P retention capacity of sediments has been related mainly to the presence of iron oxides (Fe_2O_3), oxyhydroxide (FeOOH) and hydroxides ($\text{Fe}(\text{OH})_3$) in which P adsorbs as represented in Figure 3.2 (Mortimer 1971; Skoog and Arias-Esquivel, 2009; Wauer, 2005). In Mortimer's experiment, the sediments were maintained aerated while the settling of OM was stopped. In these conditions, P adsorbed to Fe(III) oxides and hydroxides in the top sediment layer. In accordance with these findings, real scale hypolimnetic aeration was made in some lakes to hinder ferric (hydr)oxides minerals dissolution, consequently raising P retention capacity. However, the results were not reproducible for all lakes that were submitted to hypolimnetic aeration and/or mechanical destratification. Some authors reported reduced internal loads of P (Beutel and Horne, 1999; Grochowska and Gawronska, 2004), while others did not observe any change in internal P load (Gächter and Wehrli, 1998; Gächter and Müller 2003; Schauser and Chorus, 2007). The lake Sempach is an example of more than two decades of artificial oxygenation with neither reduction of P internal load nor higher retention capacity (Gächter and Müller 2003). The geochemical processes taking place in deeper sediment layers seem to be the key to understand these results. As consequence of sedimentation, the oxic layer of sediments will

be buried and turn anoxic at a certain moment. Thus, P adsorbed to ferric minerals will be released as a result of Fe reduction and consequent dissolution of ferric minerals. The concentration of Fe(II) and phosphate in the pore water can exceed the solubility product of ferrous phosphate minerals leading to precipitation (for example) of vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$]. Thus, vivianite will enclosure P and Fe in the suboxic layer (Equation 3.4).



As redox potential decreases as a result of additional burial, sulphate is reduced to H_2S that can react with Fe(II) resulting in FeS precipitation, as demonstrated in Equation 3.5 (Giordani, G., *et al.*, 1996). The consumption of Fe(II) in the pore water imbalances the solubility equilibrium of vivianite, contributing to its dissolution and P release (reverse reaction of Equation 3.4). The precipitation of FeS is a permanent sink of Fe in lake sediments as oxygen is unable to reach deeper sediment layers, which hinders Fe(II) oxidation. This will permanently limit the possibility of further Fe (oxy)hydroxides production in oxic sediment layers, as Fe(II) remains in deeper layers as FeS. Consequently, accumulated phosphate will diffuse to upper sediment layers and finally to the water column. Thus, increased available oxygen (by aeration) in top sediment layers will not enhance P retention unless sulfide production rate is lower than the production rate of Fe(II) in anoxic sediment layers (Gächter, 2003). This means that, if Fe(II) is totally precipitated as FeS, leaving no Fe(II) available to diffuse to upper layers and re-oxidize forming Fe-P complexes, than aeration will not increase P retention capacity.



Differently than Fe (oxy)hydroxides, aluminium hydroxide [$Al(OH)_3$] is stable under anoxia. In sediments with a naturally high concentration of Fe and Al the P retention capacity is largely enhanced because Al minerals are not redox-sensitive (Hansen *et al.*, 2003; Kopáček *et al.* 2007). Kopáček *et al.* (2005) established that $Al(OH)_3:Fe(OH)_3$ molar ratio > 3 prevents P release from sediments. Lakes with natural input of aluminium from their watershed and bedrock will form sufficient $Al(OH)_3$ to re-capture P that is released from $Fe(OH)_3$ in anoxic conditions (Kopáček *et al.*, 2001, 2007). The lake Plešné is an example of P retention by Al

minerals during anoxic periods. It has been strongly acidified between 1900 and 1980, and had high inorganic Al import from the watershed. The results of P extraction from the sediments showed that SRP was mainly bound to Al (more than 90% - graphically estimated) in the first 15 cm of sediments. Similar results were obtained in the 15-270 cm layers, showing that natural Al precipitation occurred in this lake for thousands of years and resulted in a P trap, even in anoxic periods (Kopáček *et al.*, 2007). This explains the low internal P load observed in anoxic condition. In a management perspective, the Al:Fe ratio can be used to predict the tendency of the sediments to release P during anoxia (Kopáček *et al.*, 2005). Al compounds are often used in restoration measures in lakes with low retention capacity. Nevertheless, in such cases, $AlSO_4$ should be avoided as it will lower Fe availability to P retention (formation of FeS) and pH must be controlled as low values will reduce Al minerals sorption capacity and induce the formation of toxic Al compounds as $Al(OH)_2^+$ and Al^{3+} (Cooke *et al.*, 1993). Thus, artificial load of aluminium hydroxide and oxide (Al_2O_3) should be taken into account, in a restoration perspective (Oliveira *et al.*, 2010).

The calcium (Ca^{2+}) concentration is also of importance in concern to P retention capacity by the sediments. Hardwater lakes seem to behave differently than softwater lakes, in the chemical subject. High concentration of Ca^{2+} in the water column can deposit as calcium carbonate ($CaCO_3$). Phosphate can adsorb to $CaCO_3$ or even react with Ca^{2+} in order to create $CaHPO_4$, $Ca_2(PO_4)_2$, or an even more thermodynamically stable mineral like hydroxyapatite [$Ca_5(PO_4)_3OH$] (Figure 3.2).

It has been demonstrated that hypolimnetic oxygenation, in lakes with a high external source of Ca^{2+} , does not prevent P release but, on the contrary, can enhance its release (Driscoll *et al.*, 1993). The rise on oxygen concentration can enhance aerobic mineralization and consequently produce CO_2 and diminish the pH (at least in a microenvironment scale). It is important to have in mind that other authors say that anoxic conditions will also lead to a decrease in pH, causing Ca- PO_4 minerals to dissolve. Which condition between oxic and anoxic has the highest contribution to organic matter mineralization is still controversial.

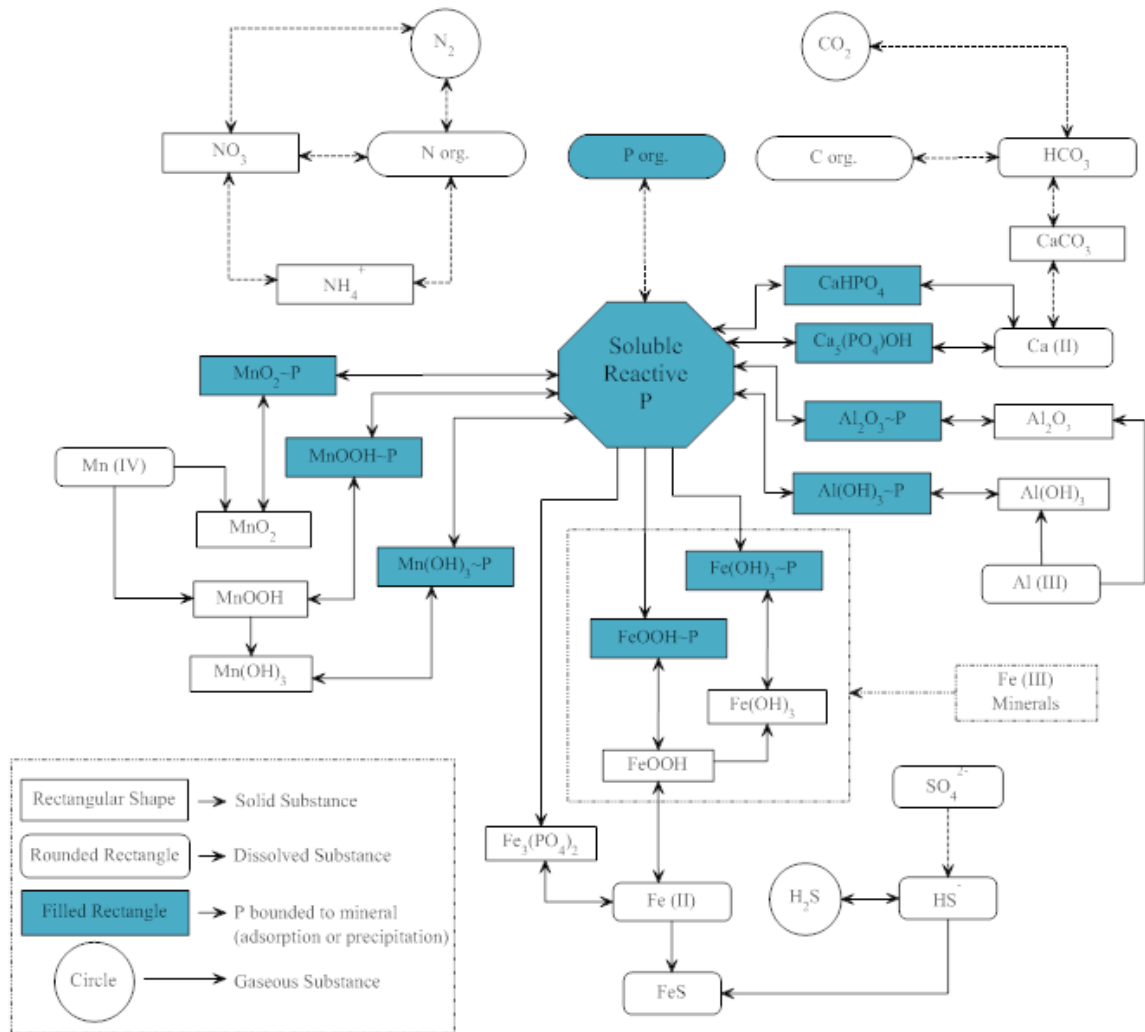


Figure 3.2 - Chemical interaction between metallic (Ca, Mn, Fe and Al) oxides and hydroxides with P (not all minerals are presented). Biological contribution, in this scheme, is only described in mineralization of organic matter and sulphate reduction (sketched lines).

Golterman states that mineralization will increase with anoxia, as there is a need to consume a higher quantity of organic matter to obtain the same amount of energy that would be obtained in aerobic conditions (Golterman, 2001). In contrast, Bastviken *et al.* (2003) showed that organic carbon mineralization rate is higher in aerobic conditions. Nevertheless, it is consensual that at low pH, Ca-PO₄ minerals will dissolve increasing the SRP concentration in pore water that will diffuse into the water column. Thus, pH has an important role controlling the release of P in hardwater lakes, as low pH values will enhance the dissolution of Ca-PO₄ minerals while high pH (even in anoxia) will raise their stability.

It is then evident that the presence of Fe, Al and Ca minerals has higher importance in internal load control. Figure 3.2 shows the complex interactions of these minerals with P. In

sediments where Fe is the main metal, Fe reduction is by far the most important reaction in controlling P release (Hansen *et al.*, 2003). For P retention on Al and Ca mineral, pH is the most important factor, as these minerals are redox non-sensitive. Simmons (2010) has conducted a laboratory experiment testing P adsorption onto Fe, Al and Mn hydroxides, showing the optimal pH range for P adsorption for each mineral. His results showed that Fe-P stability is less controlled by pH than Al-P and Mn-P compounds.

At last, it is important to say that several of the above cited interactions are microbial mediated. Thus bacterial activity related to P release will be discussed in the following section.

3.4 Environmental and Biological pathways to phosphorus release

Although organic matter (OM) mineralization occurs in the water column, it is in the sediments that this process is more pronounced. The mineralization of OM can happen in the presence or absence of oxygen. It has been discussed that in oxic condition, although there is better decomposition efficiency comparing with anoxic condition, P can be uptaken by bacteria rather than being released to the water column (Florenz *et al.*, 1984; Gächter and Meyer, 1993). Several bacterial species have the ability to store PO_4^{3-} in the polyphosphate (poly-P) form when PO_4^{3-} is in excess. When the shift from oxic to anoxic conditions happens, bacteria will no longer be able to obtain energy from glucose during anoxia, then the cleavage of poly-P bounds will provide P to ATP synthesis from ADP (Gächter and Meyer, 1993; Wentzel *et al.*, 1986). In this case, intracellular PO_4^{3-} concentration raises leading to diffusion of inorganic P to the exterior of the cell raising P concentration in the pore water..However, earlier findings on the release of P from poly-P showed that this process does not seem to have a major contribution on the P flux in the SWI. Huppfer and Rube (2004) results demonstrate that, even though P released from poly-P could be re-captured by adsorbing to sediment's minerals, there was no evidence that this process was happening, suggesting that poly-P remains as a non-reactive P (NRP) fraction during microbial transformation. Moreover, the relative importance of P flux regulation by benthic organisms cannot yet be assessed as there is not only P accumulation as poly-P in benthic microorganisms but there is also a large contribution of poly-P by planktonic and settling seston. In addition, Golterman *et al.* (1998) agrees with the fact that P from poly-P will be released in sewage sludge experiments and in

culture experiments in anoxic condition, but states that this process is not clear in natural lake systems, thus setting the possibility of the P release being from phytate-P instead of poly-P.

There are several pathways of OM mineralization depending on the availability of the final electron acceptor (O_2 , NO_3^- , Mn^{4+} , Fe^{3+} , SO_4^{2-}). For example, if O_2 is absent, then NO_3^- will be the preferred as the final electron acceptor. Even more, in contrast with O_2 that will be depleted in the first 2 mm of sediments to complete absence, NO_3^- can diffuse deeper in the sediments substituting O_2 as oxidant. This can explain why in some cases, even in anoxic condition, Fe-P is not released from the sediments (Hansen *et al.*, 2003; Wauer, 2005). Since denitrification takes place as result of the anoxic conditions of the sediment, NO_3^- concentration will decrease and consequently Mn and Fe will be used as final electron acceptors. Several bacterial species have been identified with the ability to transfer electrons from organic carbon to metals during mineralization (Lovley *et al.*, 1986; Martins *et al.*, 2010). Lovley *et al.* (2004) have also demonstrated that, in opposition to the idea that Fe(III) reduction in sediments is minor comparing with the reductive potential of OM present there (Jones *et al.*, 1984), OM can be completely mineralised with Fe(III) as final electron acceptor. From their results, we can understand that products of fermentative organisms can be completely metabolized with Fe(III) reduction, leading to the conclusion that there is the possibility to occur a significant electron transfer to Fe(III) while OM complete mineralization takes place, particularly if Fe oxyhydroxide is in the amorphous form (Lovley *et al.*, 1986). In this case, as shown previously, Fe reduction will lead to P desorption and diffusion to the water column. However, if highly crystalline Fe forms are present (non-amorphous Fe form), the transfer of electron from OM to Fe will be minor during fermentation. Moreover, microbial Fe reduction activity is temperature dependent with the optimum value at 30 °C (Jones *et al.*, 1984). Then, the efficiency of microbial Fe reduction during OM mineralization in natural lake systems will change seasonally and will also depend on the crystallinity of the Fe minerals present in the sediments.

Sulfate is also used by microorganisms as oxidant during OM mineralization. It is reduced to hydrogen sulfide (H_2S) and can react with Fe(II) forming FeS (Figure 3.2 and 3.3), thus lowering the Fe(III) concentration and consequently the Fe:P ratio (Caraco *et al.*, 1993). This reaction happens in the deep anoxic sediment layer and can consequently release P to the

pore water and then through the sediment-water interface by molecular diffusion, as explained before. However, it is important to remark that this mechanism is usually more intense in marine sediments than in lake sediments. Recently, Nielsen *et al.* (2010) suggested that the oxygen in the oxic layers could oxidize H₂S in deep sediment layers (more than 12 mm below the oxic layer). One mechanism proposed was that bacteria could drive electrons through a microbial network connected with nano-wires from H₂S in the deep anoxic sediment layer to oxygen in the upper oxic layers (Kenneth H., 2010; Nielsen *et al.*, 2010). The importance of these findings is that Nielsen *et al.* (2010) results show that besides fast H₂S consumption, a raise in pH near the oxic-anoxic interface occurred. This would promote the stability of Al and Ca minerals leading to P adsorption. However, these findings need more experimental support for lake sediments as they were conducted with marine sediments.

The P can also be permanently buried in the sediments. Part of the organic material in sediments is decomposed in an extremely slow rate (in a time scale of some hundred years) that it can be considered refractory (Gächter and Meyer, 1993). Humic acids have been identified as being more recalcitrant than other organic compounds (Reitzel *et al.*, 2007; Rodrigues *et al.*, 2008) and thus may be considered a sink of P, although they can be decomposed at a very slow rate (Reitzel *et al.*, 2007; Rodrigues *et al.*, 2010).

3.5 Can the sediment phosphorus release be controlled by one key factor?

In summary, internal P load is not controlled by a single key factor, like hypolimnetic oxygen concentration. There are several other factors that influence P release from the sediments. Redox potential, pH, temperature and microbial activity may influence the direction of the P mobility either as sink or a source to the water column. Although the high complexity of the SWI system does not allow describing all the processes in a single picture, Figure 3.3 reiterates a conceptual model for some of the biogeochemical interactions, in three different cases. In aerobic conditions, Fe(III) minerals are available and SRP from OM mineralization will be adsorbed on these (Figure 3.3 – A). Al and Ca minerals will also adsorb P if their adsorption capacity is not exhausted. In this case, as the retention capacity is high, there is a low diffusion (net internal load) across the SWI. When anoxic conditions are set in the hypolimnium, Fe(III) is reduced to Fe(II) decreasing the availability of Fe-minerals and

releasing P. The P that desorbs from Fe-minerals is re-adsorbed by the remaining capacity of Al and Ca minerals (Figure 3.3 – B).

While the overall retention capacity is not exhausted, P diffusion across the SWI will not raise despite of the anoxic period. However, as mineralization of OM continues to occur and the metallic minerals reach their maximum adsorption capacity, retention capacity of all metallic minerals will be exhausted (Figure 3.3 – C) for a certain moment. This will lead to a high net P internal load. In this case (Figure 3.3 – C), both anoxic or oxic conditions are represented, including lakes that are in oxic state or that were exposed to aeration and continue to have high net internal loads of P.

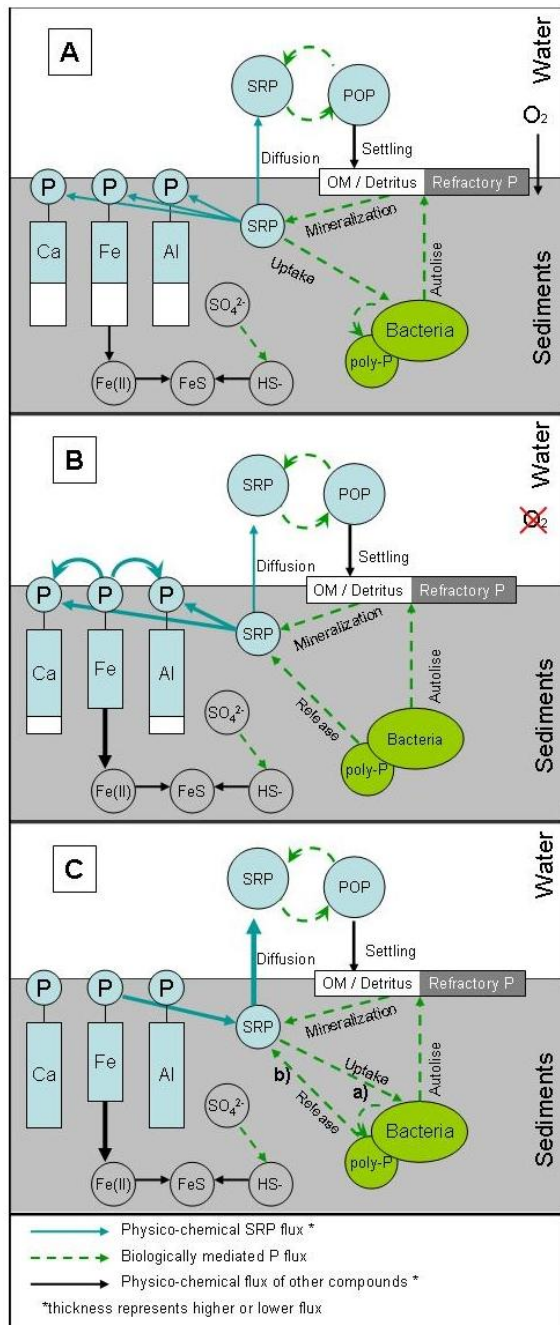


Figure 3.3 - Summary for internal P load (only by diffusion) considering bacterial uptake and storage, P adsorption by metallic minerals at different redox conditions and iron reaction with hydrogen sulfide.

The interaction of sulfide with Fe (that would happen in deeper anoxic layers) was included in Figure 3.3, showing that Fe minerals availability can be reduced by this reaction. The processes of bacterial storage of P as poly-P in aerobic conditions and the release of it in anoxic conditions were also included in Figure 3.3. Nevertheless, we must stress that this represents a small fraction of the P fluxes compared with those produced by the geochemical reactions. Finally, it is important to reiterate that the management of external P loads is crucial to prevent retention capacity exhaustion, while natural or anthropogenic adding of non-redox sensitive minerals will enhance P retention capacity of the sediments, even in anoxic conditions.

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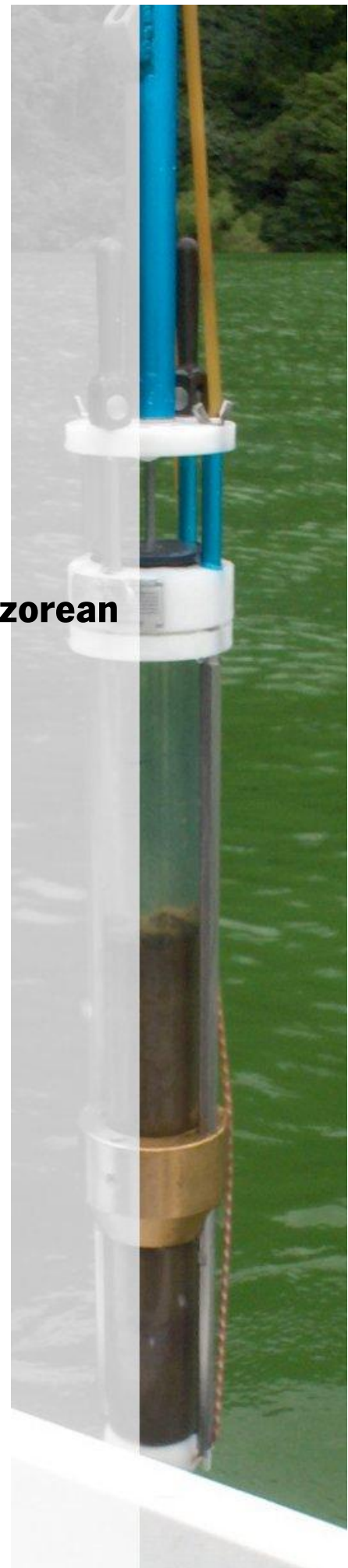
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Chapter 4.

Geochemical Characterization of Azorean Lake Sediments



Phosphorus fractionation in volcanic lake sediments (Azores – Portugal)

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The phosphorus distribution in volcanic sediments of three lakes that are under different anthropogenic pressures in São Miguel Island (Azores – Portugal) was evaluated using a sequential extraction scheme. The P-fractionation scheme employs sequential extractions of sediment with NH_4Cl , bicarbonate-dithionite (BD), NaOH (at room temperature), HCl and NaOH (at 85 °C) to obtain five P-fractions. The P-Fractionation shows that in lakes with higher trophic status (Lake Furnas and Lake Sete-Cidades), the NaOH extracted P is the dominant fraction, that contribute with more than 50% to total sedimentary phosphorus. The rank order of P-fractionation for these two lakes was $\text{NaOH} > \text{NaOH (85 °C)} > \text{HCl} > \text{BD} > \text{NH}_4\text{Cl}$ for Furnas lake and $\text{NaOH} > \text{HCl} > \text{NaOH (85 °C)} > \text{NH}_4\text{Cl} > \text{BD}$ for Sete-Cidades lake. On the other hand, the trend of P contribution of the oligotrophic lake Fogo shows that the most inert P pools have the higher concentration, with more than 50 % of the P contribution in the last extraction step (NaOH at 85 °C). For this lake, the rank order of P-fractionation was $\text{NH}_4\text{Cl} > \text{BD} > \text{NaOH (45 °C)} > \text{HCl} > \text{NaOH (85 °C)}$. The *Phosphorus Maximum Solubilization Potential (P-MSP)* was also calculated and the results show that for the more bio-available P fractions (first and second extraction step), the *P-MSP* values for Furnas and Sete Cidades lakes are sensibly higher than the results obtained in Fogo lake, an indication of the non-point diffuse load discharged in the first ones

4.1 Introduction

Biological productivity in lakes is strongly related to the concentration of phosphorus (P) in the water column. It has been shown that the sediment of the lakes can act as an internal source of phosphorus for the overlying water (Lijklema, L., *et al.*, 1993; Ramm and Scheps, 1997; Zhou *et al.*, 2001). This is especially important when the external nutrient sources are controlled. In this context, many studies in the past years have been made to understand the factors that affect P release from the sediments. Temperature, redox reactions, pH, dissolved oxygen concentration, nitrate, sulfate and bacterial activity are pointed as the major controlling factors (Kim *et al.*, 2003; Jin *et al.*, 2006).

Phosphorus is present in sediments in several chemical forms (Gonsiorczyk *et al.*, 1998). Thus, prediction of future internal P-loading requires more than the knowledge on the total concentration of phosphorus. Soil P fractionation has been investigated since 1957 and later applied to lake sediments to overcome the limited information that total P analysis can provide (Zhou 2001). Since then, several procedures for phosphorus extraction in sediments have been proposed in order to suit studies of different sediment mineral phases. (Psenner and Pucsko, 1988; Ruttenberg, 1992; Ruban *et al.*, 1999). These sequential extraction schemes made possible, in several studies, to characterize the diverse forms in which P is distributed in sediments, classified as labile P, reductant P, metal bound P, occluded P and organic P (Psenner and Pucsko, 1988). These fractions have been also classified as water-soluble P, readily desorbable P, algal available P or ecologically important P (Pettersson *et al.*, 1988; Zhou *et al.*, 2001).

The aim of this research is to define P speciation and profile in the sediments of three lakes, in São Miguel, as a tool for understanding the potential mobility of P from sediments to the overlying water and corresponds to the first study to apply phosphorus speciation to characterize in these lake sediments. In the present study we used a modified Psenner scheme (Psenner and Pucsko, 1988), as already proposed by Romero-González (Romero-Gonzalez *et al.*, 2001). This procedure allows the partial separation of P iron-bond fraction from aluminium and calcium-bond fraction.

4.2 Material and Methods

4.2.1 Study Site

The three studied lakes are located in the island of São Miguel which belongs to the archipelago of Azores (Portugal), located between the parallels 36° 45' – 39° 43' of latitude North and meridians 24° 45' – 31° 17' of longitude West (Figure 4.1). The eutrophic shallow lake Furnas is located in East side of the island. The Sete-Cidades lake is located in the Western part of São Miguel and it is composed by two interconnected lakes, the so-called Azul and Verde lakes. The Azul lake is at meso-eutrophic state but the Verde lake is already classified as eutrophic. The third studied lake is Fogo, an oligo-mesotrophic lake, located in the central part of the island. The morphometric and geochemical characteristics of the lakes are presented in Table 4.1.

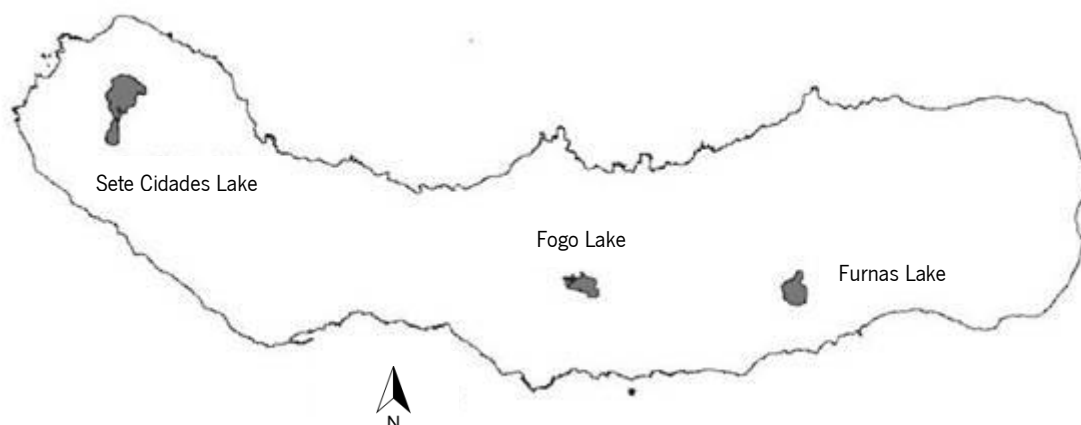


Figure 4.1. Location of the studied lakes in S. Miguel Island.

The three studied lakes are in the bottom of large calderas, located in the three volcanic centers that dominated São Miguel geology. These centers correspond to the major active trachytic central volcanoes of Fogo, Sete Cidades and Furnas, linked by rift zones.

During the last 5 000 years the activity of these three active central volcanoes is shown by 57 volcanic eruptions, with an output of 4.6 km³ of dense rock (Booth *et al.*, 1978). For the whole island of São Miguel it is possible to estimate an overall erupted volume of 400 km³ in the past 4 Myr., at an average volume of at least 0.01 km³ per century. The majority of these eruptions presented were explosive, resulting in pumice deposits, of acid character, that cover

the volcanoes flanks. Therefore, in the bottom of the lakes it is expected that sediments present a close relation with these pumice deposits.

Table 4.1. Physical and Chemical properties of the studied lakes

	Lake Furnas	Lake Sete-Cidades	Lake Fogo
<i>Physical Description</i> ⁽¹⁾			
Surface Area (km ²)	1.9	4.35	1.48
Max. Depth (m)	12	33	30
Volume (m ³)	9 212 500	47 760 500	18 040 800
Volcanic Setting	Caldera	Caldera	Caldera
<i>Chemical and trophic parameters</i>			
pH ⁽¹⁾	7.36	7.46	6.68
EC (μS cm ⁻¹) ⁽¹⁾	142.78	113.67	47.50
HCO ₃ (mg L ⁻¹) ⁽¹⁾	49.01	28.28	6.20
Ca (mg L ⁻¹) ⁽¹⁾	2.88	1.43	0.48
Mg (mg L ⁻¹) ⁽¹⁾	2.27	1.32	0.80
Dissolved CO ₂ (mg L ⁻¹) ⁽¹⁾	10.33	5.98	2.97
Soluble Reactive Phosphorus (μgP L ⁻¹) ⁽²⁾	11	3	-
Total Phosphorus (μg L ⁻¹) ⁽²⁾	45	21	-
Chla (mg m ⁻³) ⁽²⁾	17.85	10.43	2.73
Secchi disc Transparency (m) ⁽²⁾	0.8	2.3	-
Trophic Clasification	Hypertrophic	Meso-Eutrophic	Oligotrophic

⁽¹⁾ Data from Cruz *et al.*, 2006

⁽²⁾ Data from water monitoring network from regional government.

During the last 5 000 years the activity of these three active central volcanoes is shown by 57 volcanic eruptions, with an output of 4.6 km³ of dense rock (Booth *et al.*, 1978). For the whole island of São Miguel it is possible to estimate an overall erupted volume of 400 km³ in the past 4 Myr, at an average volume of at least 0.01 km³ per century. The majority of these eruptions presented were explosive, resulting in pumice deposits, of acid character, that cover the volcanoes flanks. Therefore, in the bottom of the lakes it is expected that sediments present a close relation with these pumice deposits.

São Miguel Island is also called “The Green Island” which definitely is its dominant colour, due to the fact that the area is occupied by grass fields. The lakes’ basins are also occupied with highly fertilized grass fields. As so, in some periods of the year in Azores, the large quantity of rainfall drains nutrients from the fields into the lakes. The major part of the small rivers present in this island is not of constant flow. Their flows depend mostly on the rainfall.

However, sometimes rainfall is so intense that large amounts of water and soil particles are discharged into the lakes, with the dissolved nutrients from the grass fields.

Besides the nutrient input due to agriculture, secondary manifestations of active vulcanism may also contribute to water composition in these studied lakes, through seepage of thermal waters or gaseous compounds. At the fumaroles field located in the north margin of Furnas lake the discharge of boiling SO_4^{2-} rich waters occurs convected to a steam-heating mechanism (Cruz and França, 2006) and in the field surface runoff to the lake is observable. Therefore it is not excluded that these steam-heated waters are a supplementary SO_4^{2-} source into the lake.

4.2.2 Water/Sediment Sampling and analysis

One sediment sample was collected in February 2006, at the deepest locations of each of the three lakes. For the Sete-Cidades Lake, the core was made in the deepest site of the Verde lake. A gravitational Uwitec-corer was used, which enabled collecting undisturbed sediment cores, in the soft sediments of the studied lakes. The Uwitec-corer tubes, with a diameter of 60 mm, and 600 mm length, had penetrated about 220 to 440 mm in the sediments, and collected also the overlaying water. The sediment samples with the water were sealed *in situ*, in the core tubes. After a very delicate transportation into the laboratory, the water from the sampling core tubes was recovered, sealed in glass flasks and preserved at 4 °C until the analysis. The sediment of each core tube was cut in five slices with an Uwitec Mechanical cutting apparatus. Each slice was homogenized, dried at 105 °C, sealed and conserved frozen in plastic Petri dishes, until the analysis.

Water Analysis

The analyzed chemical parameters of the water were phosphate (PO_4^{3-}), nitrate (NO_3^-), and sulfate (SO_4^{2-}), after filtration with a 0.45 μm membrane. Phosphate was analyzed by spectrophotometric method by the molybdenum blue/stannous chloride method, nitrate by ultraviolet spectrophotometric screening method, and sulfate by turbidimetric method (APHA *et al.*, 1995).

Phosphorus Fractionation

The phosphorus fractionation method used in the present work was the Psenner *et al.* (1984) scheme, with minor modifications. This extraction method draws the conclusion on the P-binding forms in the sediments (Table 4.2), and is also useful to predict bioavailability of P.

Table 4.2. Extraction procedure used in the present work, adapted from Psenner *et. al.* (1984) extraction scheme (SRP – Soluble Reactive Phosphorus; NRP – Non Reactive Phosphorus; TP-Total Phosphorus).

Step	Solvent	P-Fraction	P bounding forms
1	NH ₄ Cl	SRP	Loosely bound P: Pore water soluble phosphate and sediment surface loosely adsorbed phosphate, algal available phosphate.
2	BD (0.11M) (Bicarbonate – Dithionite) 40 °C	SRP	Reductant Soluble P: Redox-sensitive P, mainly bound to Fe-hydroxide and Mn-hydroxide.
		NRP	Redox-sensitive organic P
3	NaOH (1M) (Sodium Hydroxide) 25 °C	SRP	Metallic Oxide bound P: Phosphate bound to metallic (Hydr)oxide (mainly Al), soluble inorganic P-compounds in alkaline solution.
		NRP	P in micro-organisms, detritus, humic compounds, poly-P, P-lipid.
4	HCl (0.5M) (Hydrochloric Acid)	SRP	Apatite and CaCO₃ bound P
		NRP	Organic P sensible to acid
5	NaOH (1M) 85 °C	TP	Organic Refractory P

After each extraction step, samples were centrifuged at 7000 rpm, for 20 min., and the supernatant was filtrated through a 0.45 µm membrane. The analysis of SRP was made by molybdenum blue/stannous chloride method (APHA *et al.*, 1995). The total-P (TP) analysis was achieved by an acid digestion of the samples, with nitric and sulfuric acids at 250 °C, and further analyzed as a SRP sample. The NRP fraction is defined as the difference between TP and SRP. With this extraction procedure, as shown in Table 4.2, phosphorus is fractionated in labile P (NH₄Cl), redox-sensitive P (bicarbonate-dithionite), metal oxide bound-P (NaOH-SRP), organically bound P (NaOH-NRP), Ca-bound P (HCl), refractory/residual P (hot NaOH).

4.2.3 Phosphorus Maximum Solubilization Potential (P-MSP): definition and presumptions

We define phosphorus *Maximum Solubilization Potential (P-MSP)* as a hypothetical concentration of phosphorus in the water column, in the case of total dissolution of the P present in the sediments, for each chemical form. Naturally, this hypothetical event is extremely improbable, as it depends on many complex chemical and biological processes. However, the purpose of this calculation is to estimate the maximum input limit of P from the sediments to the overlaying water.

This theoretical parameter is calculated from the results of P concentration obtained by the sequential extraction procedure applied in the sediments of the studied lakes. For this evaluation, several presumptions have been assumed:

- All the sediment area of the lake has the same environmental conditions as well as the same phosphorus chemical forms concentration.
- A water and sediment control volume is defined and all the lakes' water body and sediments have the same physical and chemical behavior of the respective control volumes.
- Only vertical diffusion of P is considered and the water column is homogeneous (no thermal or chemical gradients).
- The sediment control volume is homogeneous with a mean concentration value for each of the P forms, calculated by the results obtained in the P fractionation procedure.

Only the values at approximately 50 mm depth have been used for the determination of the mean P concentration in the sediments.

The control volumes for each sediment and water column have the same area, which is the one made by the corer in the sediments. Therefore, the control volume V_C for each sediment ($i=sed$) or water column ($i=wat$) is cylindrical, with a circular base area (A). The length of the cylindrical control volume for the sediments (h) considered was 50 mm. This means that, for all this 50 mm length control volume, the sediment is homogeneous and has P concentration equal to the mean value calculated from the results of P-fractionation. For the water body, the

length of the control volume (H) depends on the length of the deepest location of the lake (Table 4.1). The Equations 4.1 and 4.2 shows the calculation of the control volume for the sediments and water column.

Equation 4.1:
$$V_{C_{sed}} = A \times h = \frac{\pi}{4} d^2 \times h$$

Equation 4.2:
$$V_{C_{wat}} = A \times H = \frac{\pi}{4} d^2 \times H$$

The density (ρ_{sed}) and porosity (θ) of the sediments are 2.439 kg L^{-1} and 0.90 respectively. The control volume of the sediments ($V_{C_{sed}}$) is the sum of the sediments volume (V_{sed}) and volume occupied by the interstitial water ($V_{W_{sed}}$) present in the sediments (Equation 4.3). With the combination of Equations 4.3 and 4.4 we can obtain the sediments volume (Equation 4.5).

Equation 4.3:
$$V_{sed} = V_{C_{sed}} - V_{W_{sed}} \Leftrightarrow V_{W_{sed}} = V_{C_{sed}} - V_{sed}$$

Equation 4.4:
$$\theta = \frac{V_{W_{sed}}}{V_{C_{sed}}}$$

Equation 4.5:
$$V_{sed} = V_{C_{sed}} \cdot (1 - \theta)$$

The exact sediment mass (m_{sed}) can be calculated by multiplying the sediment volume and the sediment density, as demonstrated by the Equation 4.6. With the results of P concentration in the sediments ($C_{P,sed}$) obtained in the applied sequential extraction procedure and with the calculated sediment volume, we can determine the P mass present in the sediment ($m_{P,sed}$), for each P chemical forms (Equation 4.7).

Equation 4.6:
$$m_{sed} = \rho_{sed} \cdot \frac{\pi}{4} \cdot d^2 \cdot h \cdot (1 - \theta)$$

Equation 4.7:
$$m_{P,sed} = C_{P,sed} \cdot m_{sed}$$

Equation 4.8:

$$\begin{aligned}
 P-MSP &= \frac{m_{P, sed}}{V_{C_{wat}}} = \frac{C_{P, sed} \cdot m_{sed}}{\frac{\pi}{4} \cdot d^2 \cdot H} \Leftrightarrow P-MSP = \frac{C_{P, sed} \cdot \rho_{sed} \cdot \frac{\pi}{4} \cdot d^2 \cdot h \cdot (1-\theta)}{\frac{\pi}{4} \cdot d^2 \cdot H} \Leftrightarrow \\
 &\Leftrightarrow P-MSP = \frac{C_{P, sed} \cdot \rho_{sed} \cdot h \cdot (1-\theta)}{H}
 \end{aligned}$$

The concentration of P in the water control volume, if hypothetically all the P mass from the sediment control volume would dissolve into it, is given by the Equation 4.8, and represents the *P-MSP* theoretical parameter. The results of *P-MSP* for each lake and P forms are presented in Table 4.3.

4.3 Results**4.3.1 Water at the Interface**

Despite the fact that several chemical parameters were analyzed, the most important in the present work is the phosphate analysis. As so, the results for the water analysis will focus only in the soluble phosphate concentration.

The SRP concentration in the sediments' overlaying water for Fogo, Furnas and Sete Cidades core site was 23.5, 17.0 and 47.4 $\mu\text{g P L}^{-1}$ respectively. The highest SRP concentration is found in Sete Cidades lake. In contrast of what would be expected, hypereutrophic lake Furnas has the lowest concentration of SRP. Lake Fogo has a slightly higher concentration than Lake Furnas, although Fogo is at lower trophic status.

4.3.2 Sediment

Although TP analyses for each step were performed, in the present work only SRP analysis results will be showed and further discussed. The main reason is that this work is specially focused in a geochemical approach. Therefore, these results are the most accurate for the assessment of bioavailability of P, in a chemical point-of-view. Further work in a more biological approach will be made, and NRP pool (which is mainly organic-P) will be

considered, as well as specific biological processes of degradation. The results are next presented for each lake.

Lake Fogo

The mean value of the sum of SRP concentration, for all extraction steps (and depth) is $86 \mu\text{g P g}^{-1} \text{ dw}$. However, the distribution of P in sediments is not linear, as the higher amount of SRP is located in the first 50 mm of the studied sediment core (Figure 4.2).

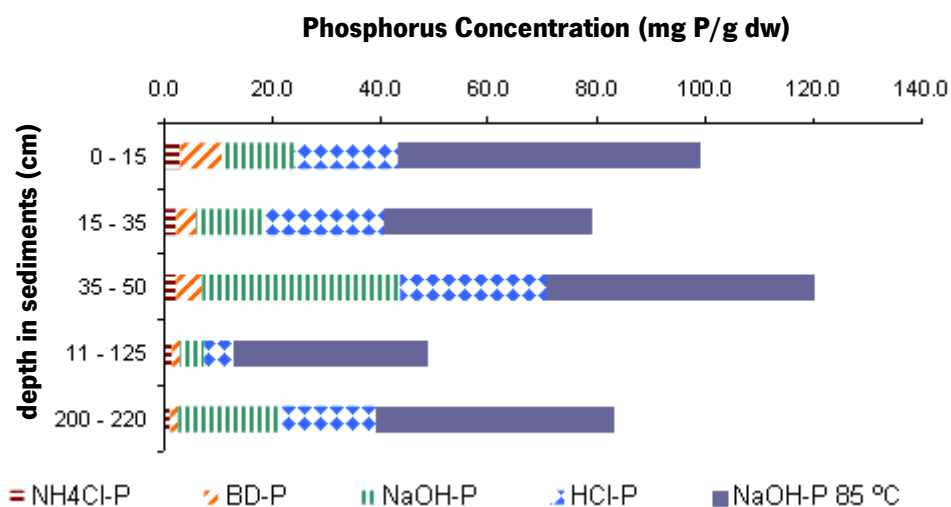


Figure 4.2. SRP concentration in each extracted fractions, at different sediment depth, for Lake Fogo.

For all the samples, the major part of the phosphorus has been extracted in step 5, with NaOH at 85 °C. The most bio-available P, which is extracted in the first step (NH₄Cl-P), is present at low concentration in the sediment of this lake ($2 \mu\text{g P g}^{-1} \text{ dw}$).

The P bound to Fe-hydroxide and Mn-hydroxide (BD-extraction step) is also in low concentration ($4 \mu\text{g P g}^{-1} \text{ dw}$), in comparison with the other extraction steps. Results also demonstrate that in loosely bound-P and redox sensitive P (extracted in the first two steps), SRP is more concentrated at the upper part of the sediment, decreasing with depth.

Lake Furnas

In Furnas Lake, the mean SRP concentration in the analyzed samples is $325 \mu\text{g P g}^{-1} \text{ dw}$, which is almost four times higher comparing with Lake Fogo. In this case, the most extracted P was verified in the third step (NaOH). The fifth step, also performed with NaOH (at 85°C),

highly contributed to the sedimentary phosphorus (54.2%). Thus, the both extraction with NaOH, which extract the P bound to oxide metals (mainly Fe and Al) and organic-P compounds, has the major SRP contribution in the sediments from this lake (Figure 4.3).

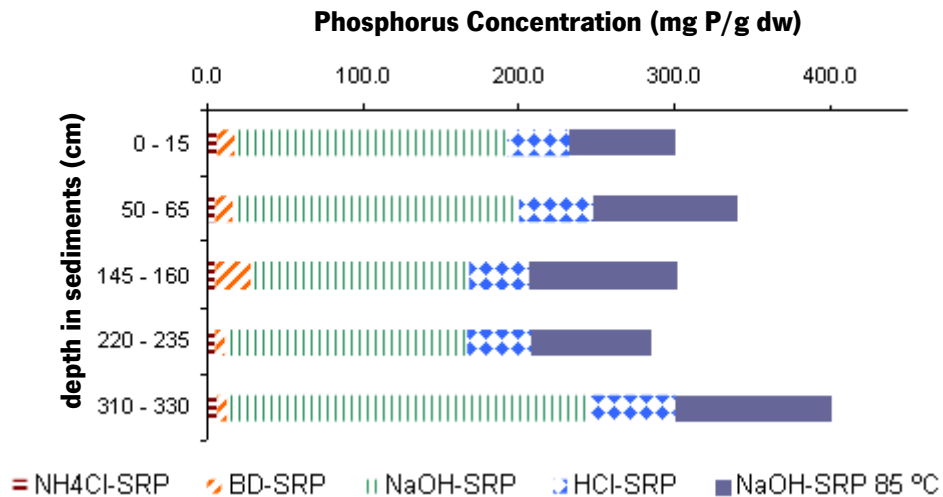


Figure 4.3. SRP concentration in each extracted fractions, at different sediment depth, for Lake Furnas.

The loosely bound-P is almost constant along the core, and has a relatively low concentration. The BD-P concentration reaches his maximum in the middle of the sediment core, but still in relatively low concentration. The HCl-P contribution shows it to be more or less constant along the analyzed core.

Lake Sete-Cidades (Verde Lake)

The sediment P-fractionation of the Verde lake, shows that the extraction step that most contributed to P concentration was the cold NaOH extraction (third step). The loosely bound-P fraction has higher concentrations in the upper sediment zone (interface zone), as shown in Figure 4.4. The P contribution by the NH₄Cl, HCl and hot NaOH extraction steps is similar (Figure 4.5).

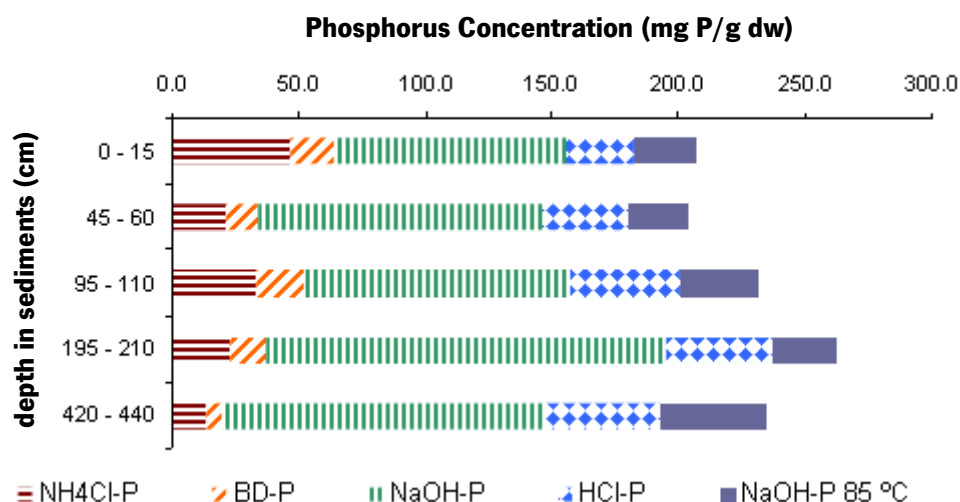


Figure 4.4. SRP concentration in each extracted fractions, at different sediment depth, for Lake Sete Cidades.

The mean concentration of SRP of the sum of all extractions (for all samples), is $228 \mu\text{g P g}^{-1}$ dw in this lake. The higher SRP concentration is observable in 195 to 210 mm depth interval.

4.3.3 Phosphorus Maximum Solubilization Potential

The *P-MSP* results are demonstrated in Table 4.3 with the maximum values for each lake in *bold type*.

Table 4.3. Values of *P-MSP* for each lake and P extracted form (in brackets are the standard deviation values).

	$\mu\text{g P L}^{-1}$				
	NH ₄ Cl-SRP	BD-SRP	NaOH-SRP 45 °C	HCl-SRP	NaOH-SRP 85 °C
Fogo	1.0 (\pm 0.2)	2.2 (\pm 0.9)	8.6 (\pm 5.6)	9.2 (\pm 1.6)	19.5 (\pm 3.6)
Furnas	5.9 (\pm 1.0)	11.7 (\pm 0.0)	181.8 (\pm 6.3)	44.3 (\pm 6.1)	81.2 (\pm 18.0)
Sete Cidades	12.6 (\pm 6.7)	5.5 (\pm 1.3)	37.6 (\pm 5.5)	11.3 (\pm 1.8)	9.0 (\pm 0.2)

Fogo lake has the higher P potential in the fifth extraction step (NaOH at 85 °C) while Furnas and Sete Cidades lake shows to have the P higher potential in the third one (NaOH at 45 °C).

4.4 Discussion

4.4.1 Loosely Adsorbed Phosphorus (NH₄Cl-P)

The immediately available P in sediments corresponds mostly to soluble inorganic P, which is mainly orthophosphate. Therefore, the loosely adsorbed P (also called Water Soluble Phosphorus – *WSP*) is the best parameter for assessment of bioavailability of P (Zhou *et al.*, 2001). Analytical results suggests that NH₄Cl-P concentration in Sete Cidades lake is between 59.4 and 13.3 $\mu\text{gP}\cdot\text{g}^{-1}\text{dw}$, with the higher values in the upper sediment layers. In comparison with the other two lakes, Sete Cidades has the higher concentration value of NH₄Cl-P. This means that loosely adsorbed P will be easily available to algae, promoting consequent blooms. The SRP concentration in the sediment's overlaying water is also higher in Lake Sete Cidades. A comparison between the Fogo and Furnas lake in terms of NH₄Cl-P extraction shows that Furnas has concentrations 2.3 to 5.4 times higher than Fogo. The decrease of the NH₄Cl-P concentration with depth, for the three lakes, might be explained by the decrease of pH with depth, which enhance desorption of P (Gonsiorczyk *et al.*, 1998).

4.4.2 Reductant Soluble Phosphorus (BD-P)

The reductant SRP is assumed to be bound to Fe-hydroxide and Mn compounds. For all the studied lakes, this form of P is present in relatively low concentrations, (Figure 4.5). For Lake Sete Cidades reductant P is the smallest contributor for the total amount of SRP. Nevertheless, when the hypolimnium is in reductive state, due to low oxygen concentration, this P-metal hydroxide bound might be released. However, the widely accepted hypothesis of phosphate release from anoxic sediments due to FeOOH-P complex reduction has been questioned (Golterman, 2001).

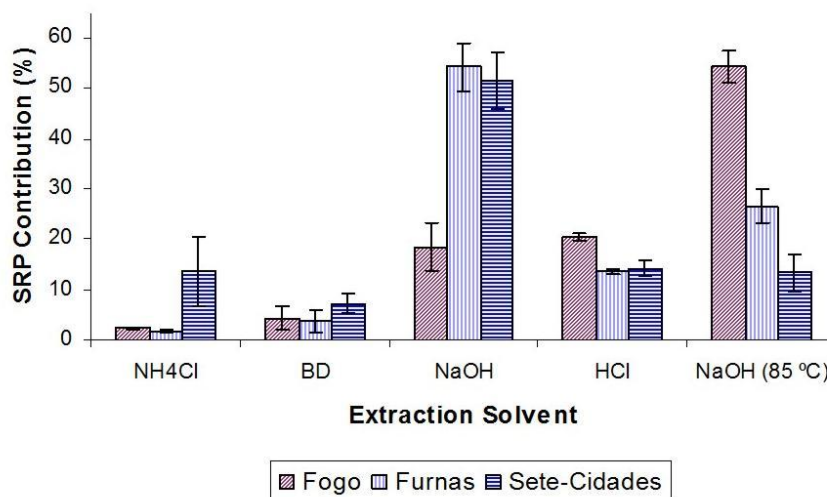


Figure 4.5. Relative contribution of P from each extraction step for all the core of the three lakes.

Golterman (2001) has also shown by calculation (for an hypothetical shallow lake) of the reduction capacity, that the BD-P contribution from the sediments to the overlaying water is low, and that small changes in Fe(OOH) concentration will have no impact in P release (Golterman, 2001). Further work over samples collected along the present study, including specific rate flux calculation, will be done to investigate the role of BD-P pool in the eutrophication problem.

4.4.3 Metallic Oxide bound Phosphorus (NaOH-P)

The quantity of metallic (Fe and Al) oxide bound P is much higher in the two eutrophic lakes than in the Lake Fogo (oligo-to-mesotrophic). The NaOH-P amount in Lake Furnas is about six times higher than Lake Fogo. This extraction step is the major contributor to SRP concentration for both Lake Furnas and Sete Cidades (Figure 4.5). Lake Furnas has also the highest concentration of dissolved iron in the water ($241 \mu\text{g L}^{-1}$ at deepest site, and an average of $100 \mu\text{g L}^{-1}$) of all the three lakes, as shown by Cruz *et al.* (2006). Therefore, Lake Furnas presents the highest value of NaOH-P concentration. It has been shown that NaOH extractable P is significantly correlated with 2-days and 14-days available P for an alga named *Selenastrum capricornutum* (Zhou *et al.*, 2001). This specie is present in some lakes in the Azores archipelago, but hasn't been identified in the studied lakes. However, several species from de *Selenastrum* sp. gender are now included in the *Ankistrodesmus* sp. and *Monoraphidium* sp. genders. In the Furnas and Sete Cidades lakes, several species from the *Ankistrodesmus* sp. and *Monoraphidium* sp. genders were identified. This means that, the

NaOH-P could be available for these algal species. The NaOH extractable P has also been suggested to be used for estimation of short and long-term available P in the sediment, and is a measure of algal available phosphorus (Zhou *et al.*, 2001). In this context, we can say that, both Lake Furnas and Sete Cidades have a highly potential available P for algae, which is undesirable for the eutrophication control.

As shown by Xiangcan Jin *et al.* (2006), NaOH-P might be released by the change of pH to higher values. In this case, pH control is very important, as this is the main potential pool for P-release in the studied lakes. However, this extraction step has been criticized because it seems that it is not so specific for metallic oxide bound P, as it is claimed to be. Golterman (2001) has shown that phosphate extraction with NaOH is time and concentration dependent and will also extract phytate phosphate and org-P as well. Therefore, the use of this extraction step will be pondered and more deeply studied in further research.

4.4.4 Apatite and CaCO₃ bound Phosphorus (HCl-P)

The three studied lakes are from volcanic origin and are soft-water lakes, with total hardness of 16.67 mg L⁻¹, 9.08 mg L⁻¹ and 4.53 mg L⁻¹ for Furnas, Sete Cidades and Fogo lakes respectively. Therefore, Ca and Mg are present in low concentration in these waters (Table 4.1). This might be the reason why, in these lakes, the HCl-P concentration is much lower than the NaOH-P fraction, when compared with other hard-water lakes that has high HCl-P concentrations (Gonsiorczyk *et al.*, 1998; Kaiserli *et al.*, 2002). Apatite-P (which is mainly extracted by HCl) is assumed to be an inert fraction (Psenner and Pucsko, 1988). Thus, the concentration of P in this extraction step will not be bio-available so easily, being considered permanent burial (Jin *et al.*, 2006).

4.4.5 Labile Organic and Refractory P (NaOH-P at 85°C)

This extraction step also seems to be an inert P-fraction resulting from soils, terrestrial plant material and dust, loaded into the lakes by inflows, wind and precipitation (Psenner and Pucsko, 1988). This is the main P-pool in Fogo Lake. As demonstrated in Figure 4.5, P-contribution at Fogo lake increase from the first to the next extraction steps. This is desirable in terms of potential P release to the overlaying water, because it means that the higher P

concentration pools are the most inert ones. So, the P release will not occur easily in this lake, preventing eutrophication. However, a question is proposed when looking to the results for the other two lakes (Figure 4.5): is it possible that hot-NaOH-P pool would be partially transformed into NaOH-P pool, by biological activity? If these two P-pools can be biologically related, then this would explain why NaOH-P pool is much higher than hot-NaOH-P pool, for Furnas and Sete-Cidades Lakes. This would also be a concern for the future trophic status of Lake Fogo. Therefore, more research in this area is needed.

4.4.6 Phosphorus Maximum Solubilization Potential

The results, in Table 4.3, show that the *P-MSP* value in Fogo lake is higher in the most inert fraction (NaOH-SRP at 85 °C). Even for the more bio-available P fractions (first and second extraction step), the *P-MSP* values are under 2.2 $\mu\text{g P L}^{-1}$, which would not have any impact. In fact, the sum of all *P-MSP* values for the Fogo lake is 40.5 $\mu\text{g P L}^{-1}$.

On the other hand, looking at the *P-MSP* values for Furnas and Sete Cidades lake, algal bloom risk is evident. Although *P-MSP* is in relatively low concentration for the most bio-available P forms (under 12.6 $\mu\text{g P L}^{-1}$), the *P-MSP* values for the P-NaOH (45 °C) fraction are 181.8 and 37.6 $\mu\text{g P L}^{-1}$ for Furnas and Sete Cidades respectively. Thus, it is expected that these two lakes could suffer a more intense eutrofication process in a short term.

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Chapter 5.

Sediment microenvironment changes as forcing function to phosphorus mobility



The mobility of phosphorus in a sediment microcosm experiment under different redox potentials

P mobility in lake sediments was assessed in a microcosm experiment. Sediments from Lake Furnas (Portugal) were analyzed through a P sequential extraction procedure previously to the experiment, setting the reference value (initial conditions). Two other P sequential extractions were made before and after a shift in redox potential achieved by means of O₂ concentration variation. Microsensors were used to measure pH and O₂ concentration in the sediments, during oxic and anoxic periods. The sediments that were under anoxic conditions released P from Fe minerals (BD fraction) compared with the initial conditions. The P bounded to Al minerals remained approximately the same comparing with the initial conditions (NaOH fraction), indicating that this fraction remains stable with redox potential changes. When the microcosm was exposed to O₂, Fe minerals re-adsorbed P which is consistent with the classical paradigm. However, we found that Al minerals released P in the oxic phase of the experiment leading to an increase of the P concentration in the water column. The reason was not directly related to the O₂ concentration but to an increase in pH. A possible explanation is related with the recent findings that oxygen in the oxic layers could oxidize hydrogen sulfide in deeper sediment layers through a microbial network connected with nano-wires from the deep anoxic sediment layers to the upper layers, with concomitant pH increase.

Calcium minerals bounded to P remained stable between anoxic and oxic conditions (HCl fraction), as well as the refractory pool (NaOH 85 °C). P bounded to Al and Fe represents the most mobile fraction and is an indicator of exhaustion of sediments' retention capacity.

5.1 Introduction

In lakes with eutrophication problems, phosphorus (P) is in most cases the limiting nutrient of algae blooms. The provenience of P can be external to the water body or internal by inputs from the sediments. When the temperature raises and the lake stratifies thermically, the oxygen concentration in the hypolimnium decreases leading to a redox potential change and in some cases to P release.

Still controversial is the chemical and/or biological pathways of phosphate release from the sediments (Boström, B., *et al.*, 1988; Hupfer, M. and Lewandowski, J., 2008; Ribeiro, D. C. *et al.*, 2012). Some authors state that oxygenated sediments retain P by fixation to Fe(III) while reduced sediments release phosphorus by reduction of iron and subsequent dissolution of iron-phosphorus complexes – a model proposed by Einsel (1938) and Mortimer (1941). In reality the process of P release from sediments is more complex, as several oxygenated lakes continue to release phosphorus with no major changes in the eutrophication state of the lakes (Gächter, R., and Wehrli, B., 1998; Schauser, I., and Chorus, I., 2007). The Portuguese lake Furnas in Azores Island is an example of this case. Also interesting to observe is that in some lakes with anoxic hypolimnium, the P release rate is not significantly different comparing with the oxic period of the hypolimnium (Driscoll, C. T., *et al.*, 1993; Kopáček, J., *et al.*, 2005). Other authors showed that pH has an important role in P release. Lower pH levels lead to phosphorus release in calcareous lakes while higher pH values promote the release of P in non-calcareous lakes (Lake, T., *et al.*, 2006). Microorganisms can also change the sediments' environment conditions. Recently, some authors proposed that electro-active bacteria are capable of oxidize hydrogen sulfide and change the pH of the water at the sediment/water interface (SWI) as a result of oxygen reduction (Nielsen, L. P., *et al.*, 2010; Kenneth H., 2010). Sediments with electrochemical activity mediated by bacteria are now well documented (Martins, G., *et al.*, 2010; Lovley, D. R., *et al.*, 2004). It has also been showed that the P release can be mediated by iron-reducing bacteria (Lovely, D. R., *et al.* 1986).

In sediment there are several different chemical P forms that, during early diagenetic process, can move from one form to another and shift from organic to inorganic and vice-versa (Ribeiro, D. C., *et al.* 2012). P can be bounded to chemical elements by ionic and covalent bonds or even just by physical adsorption. It can also be uptake by bacteria or released from

organic matter by mineralization. Understanding *which chemically bounded P is being released from the sediment* under different redox potential can provide the knowledge needed to overcome the seasonal release of this element to the water body, in a recovery process perspective.

With the objective of understanding the P mobility in sediments as a result of environmental changes (redox potential and temperature), a phosphorus sequential extraction (PSE) scheme was used as well as microsensors to monitor pH, O₂ and ΣH₂S (which means total sulfide and is expressed as: ΣH₂S = [H₂S] + [HS⁻] + [S²⁻])^{*} concentration in the sediment pore water.

5.2 Materials and Methods

5.2.1 Sediment Sampling

The collected sediments belong to the shallow lake Furnas, located in the archipelago of Azores (Portugal). Morphometric and geochemical characteristics of the lake can be found in Ribeiro, D. C., *et al.* (2008). The sediment samples were collected at the deepest locations of the lake (which is approximately 12 m). A gravitational Uwitec corer was used to collect undisturbed sediment cores in the soft sediments of the studied lake. The Uwitec corer tubes, with a diameter of 6 cm, and 60 cm length, penetrated about 18 to 40 cm in the sediments. After transportation into the laboratory, the sediment was homogenized and preserved at 4 °C. The fresh sediment was used in a microcosm experiment.

5.2.2 Microsensor Profiling

Profiles of pH, O₂ and ΣH₂S concentration in the interstitial water of the sediment were made with microsensors. A level III microprofiling set up from Unisense was used. This includes a micromanipulator (MM33-2) with a motor controller (MC232) to precisely control the vertical movement of the microsensors. All the data was acquired by computer using an analogical/digital converter (ADC216). The analog signal from the amperimetric microsensors (e.g oxygen sensor) was amplified with a picoameter (PA2000) and then converted to a digital signal, as shown in Figure 5.1.

^{*} The single species distribution of total sulfide system is pH dependent. In this thesis, we will use the term ΣH₂S as total sulfide.

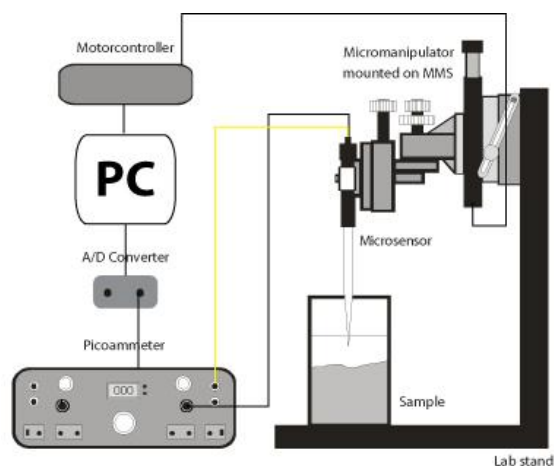


Figure 5.1. Micro manipulator stage scheme used in the experiment.

The profiles were made in the first 20 mm of the sediment and in the water 10 mm above the sediment. The vertical resolution used in this experiment was 250 μm (80 measured points in the sediments). In the following sections, the term *microprofiling* will be used in reference to the procedure explained in this section.

5.2.3 Phosphorus analysis

Samples with Soluble Reactive Phosphorus (SRP) were analyzed by the molybdenum blue/stannous chloride method (APHA *et al.*, 1995). The total-P (TP) analysis was achieved by an acid digestion of the samples with nitric and sulfuric acids at 250 °C and further determination as SRP.

5.2.4 Phosphorus extraction scheme

The phosphorus fractionation method used in the present work was the Psenner and Pucsko (1988) scheme, but only the SRP fractions were determined. This extraction method evaluates the P-binding forms in the sediments (Table 5.1) and is also useful to predict bioavailability of P.

After each extraction step, samples were centrifuged at 7000 rpm, for 20 min., and the supernatant was filtrated through a 0.45 μm membrane. The analysis of SRP was made by the molybdenum blue/stannous chloride method (APHA *et al.*, 1995).

Table 5.1. Phosphorus forms extracted with the different solvents in the sequential extraction procedure.

Step	Solvent	P-Fraction	P bounding forms
1	NH ₄ Cl	SRP	Pore water soluble phosphate and sediment surface loosely adsorbed phosphate, algal available phosphate.
2	BD (0.11M) (Bicarbonate – Dithionite) 40 °C	SRP	Redox-sensitive P, mainly bound to Fe-hydroxide and Mn-hydroxide.
3	NaOH (1M) at 25 °C	SRP	Phosphate bound to metallic oxide (mainly Al), soluble inorganic P-compounds in alkaline solution.
4	HCl (0.5M)	SRP	Carbonate and Apatite- P
5	NaOH (1M) at 85 °C	TP	Organic Refractory P

5.2.5 Microcosm experiment

The term *microcosm* is used to describe a pseudo-scale down experiment analogous to a lake's SWI. Aiming to describe the mechanism of release of P from the sediments in different redox conditions, the sediments were placed in three tubes inside a parallelepiped reactor filled with water. Two equal reactors were connected allowing the water to circulate in a closed loop from one reactor to the other (Figure 5.2). The water temperature of the reactors was controlled with a Nüve BS302 refrigerating system.

The experiment was divided in five different phases as depicted in Table 5.2 and schematized in Figure 5.2. In the **first phase**, the three tubes of each reactor were filled with sediments, leaving approximately 1 cm of head space in each tube. A small amount of homogenized sediment was taken for phosphorus sequential extraction (PSE) setting the initial. Both reactors were filled gently with distilled water and the circulation between them was started with a peristaltic pump. The water circuit was from the first reactor passing through a serpentine in the temperature controlling system getting in the second reactor and finally completing the circuit leaving the second reactor and entering the first one (Figure 5.2). The temperature set for the first and second phases was 20 °C. Both reactors were sealed in order to prevent oxygen diffusion to the water.

After 24 h, all the sediment settled and the **second phase** started with a microprofiling of the sediment in the first 20 mm. Every time the reactors were opened for microprofiling, nitrogen was bubbled in order to remove oxygen and keeping the reactors in an anaerobic state.

Table 5.2 – Description of the phases of the microcosm experiment.

	Phase 1	Phase 2	Phase 3	Phase 4	Phase 5
Phase Name	Initial Conditions	Anaerobic Conditions	Transition Conditions	Aerobic Conditions	Final Conditions
Time	1 day	21 days	5 days	21 days	1 day
Operation	Two Reactors	Two Reactors	One Reactor	One Reactor	One Reactor
Water Analysis			o-Phosphate		o-Phosphate
Sediment Analysis	Microprofiling; PSE	Microprofiling	Microprofiling; PSE	Microprofiling	Microprofiling; PSE
Temperature	[Graph showing a dashed line that starts at a high level, drops during Phase 2, and then gradually rises through Phase 3 and Phase 4, ending at the initial level in Phase 5.]				
Oxygen Concentration	[Graph showing a dashed line that starts at a low level, drops further during Phase 2, and then rises through Phase 3 and Phase 4, ending at the initial level in Phase 5.]				

In the **third phase**, one of the reactors was unplugged from the system for water/sediment analysis. For the overlying water, SRP was determined. For the sediment, a microprofiling was performed just before unplugging the reactor. After that, a sediment sample was taken from each tube (approximately 2 g of wet sediment) for PSE. The reactor that continued in the experimental system was opened to air allowing the diffusion of oxygen into the water. The temperature was set to 15 °C and maintained until the end of the experiment. The temperature variation was made to mimic the seasonal temperature shift of the lake.

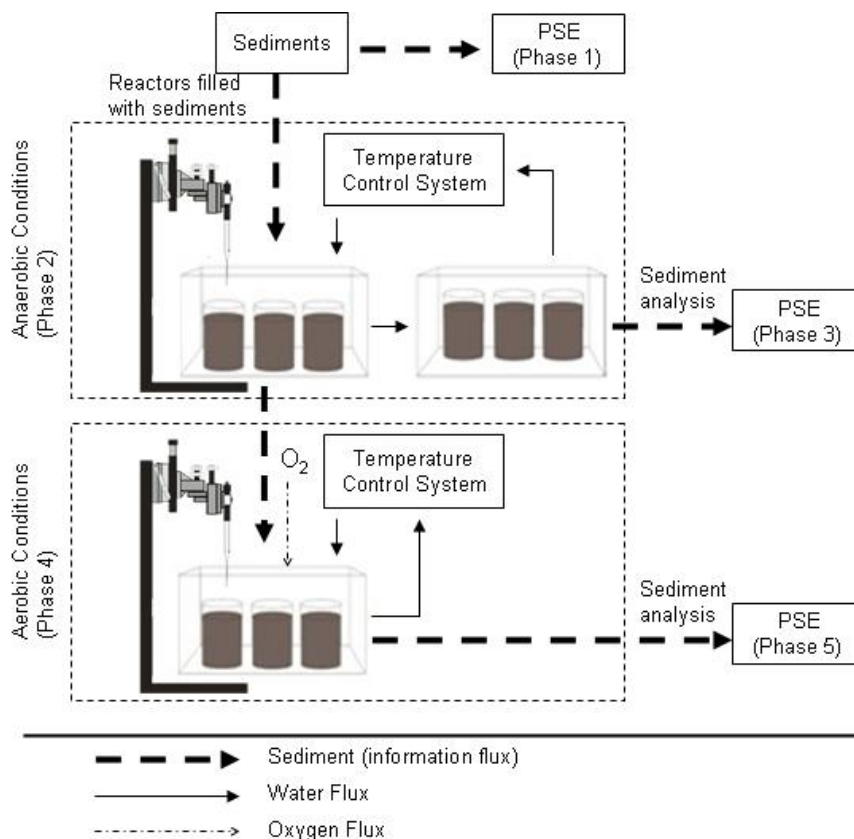


Figure 5.2. Representation of the experimental setup as well as the shift from phase to phase.

The **fourth phase** was executed exactly the same way as the second phase, with the only difference of keeping the reactor open in order to allow the aerobic conditions at the SWI.

The **fifth phase** was performed in the same way as the third phase. The SRP in the water was determined and the PSE was performed for the sediments. A sample (approximately 2 g) of wet sediment was taken from each tube.

5.3 Results and discussion

The sediments that were under anoxic conditions (Figure 5.2 – Phase 2) released P from Fe oxides/hydroxides compared with the initial conditions as a result of reduction of Fe(III) to Fe(II) leading to solubilization of Fe mineral complexes (Figure 5.3 - BD fraction). When the reactor was exposed to O₂, Fe minerals re-adsorbed P (concomitant with the higher concentration in the BD fraction) which is consistent with the paradigm that O₂ controls P retention/release through changes in Fe oxidic state. A parallel reaction that contributes to P release from Fe minerals is due to the presence of sulfide (Figure 5.4) that reacts with Fe producing FeS, exhausting the availability of Fe complexes for P binding. The presence of ΣH₂S in anoxic conditions was detected from the top sediment layers to deep layers, contributing to FeS production in the entire sediment column. However, when the reactor was exposed to O₂, ΣH₂S oxidation happened in the top sediment layers reducing drastically its concentration in the first 9 mm, as demonstrated in Figure 5.4.

The P bounded to Al minerals (NaOH fraction) remained approximately the same comparing with the initial conditions in the anoxic phase, indicating that Al-P complex remains stable with redox potential changes. However, we found that Al minerals released P in the oxic phase of the experiment (Figure 5.3 – NaOH fraction) leading to a P concentration increase in the water column. The reason was not due directly to O₂ concentration change but to an increase in pH in the oxic phase (Figure 5.4). P binding to Al hydroxides is pH dependent as hydroxyl ions compete with phosphate at high pH. It has been demonstrated that the pH range between 5 and 8 is optimal for P binding to Al hydroxides (Simmons, J. A. 2010; Lijklema, L., *et al.*, 1980). In the oxic phase, pH increased above 8.7 which explain the partial P release that was bounded to Al hydroxides.

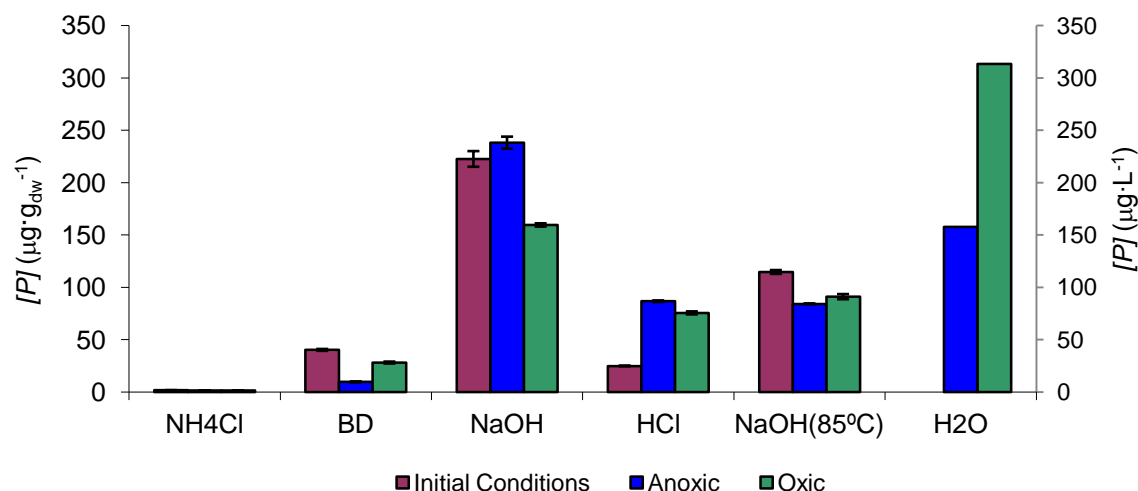
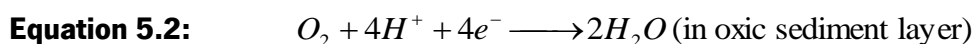
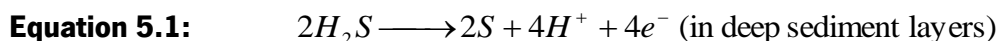


Figure 5.3. Results of PES for initial conditions, anoxic and oxic conditions. The P-HPO_4^{2-} concentration in the water column of the reactor is also presented in the graph.

A possible explanation for pH increase in the oxic phase can be related with the recent findings that oxygen in the upper layers could oxidize $\Sigma\text{H}_2\text{S}$ in deep sediment layers (Nielsen, L., P., *et al.* 2010). It was proposed that bacteria could drive electrons through a microbial network connected with nano-wires from $\Sigma\text{H}_2\text{S}$ in the anoxic layers to oxygen in the upper sediment layers (Nielsen, L., P., *et al.* 2010; Kenneth, H., 2010). The redox reactions are represented in Equations 5.1 and 5.2.



Among several microorganisms capable of driving electrons is *Geobacter* (Lovley, D., R., *et al.*, 2004) that was found to be present in these sediments (Martins, G., *et al.*, 2010). This reaction increases the pH above 8 leaving the Al-P complex unstable, and consequently will release P by diffusion, increasing its concentration in the water column (Figure 5.3 – H₂O). In the other hand, the oxidation of H₂S (Equation 5.1) could be responsible for the drop in pH in the deeper layers, as demonstrated in Figure 5.4.

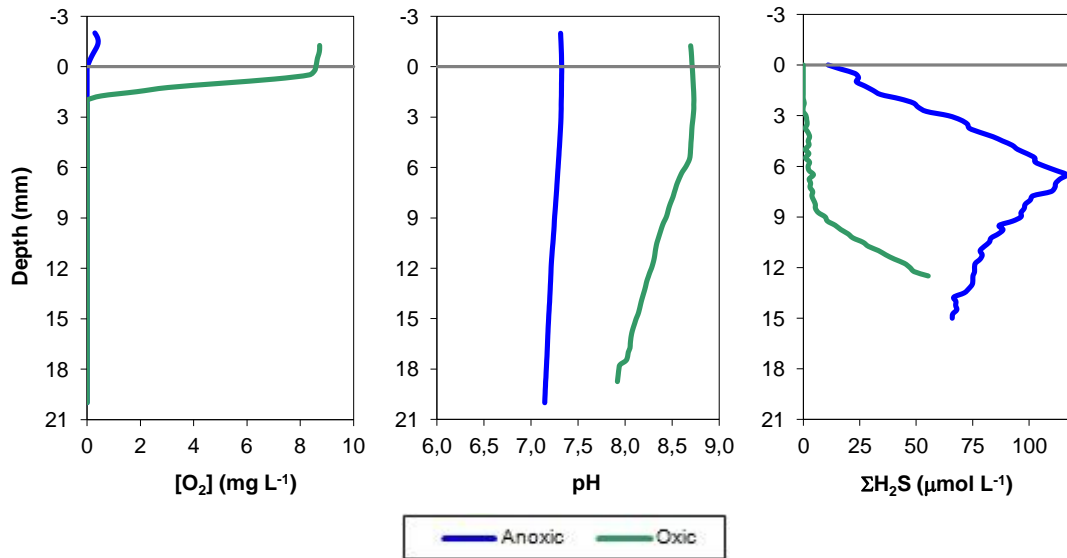


Figure 5.4. Microprofiling results, for pH, O₂ and H₂S concentration, in oxic and anoxic conditions for the first 20 mm.

Calcium minerals bounded to P proved to be a non-redox sensitive fraction as the maximum adsorption occurred during the anoxic phase (Figure 5.3 – HCl). The refractory pool (NaOH 85 °C) remained stable between anoxic and oxic conditions. It was noticed that the P content of this fraction in the initial conditions was higher comparing with anoxic and oxic phases. Although this fraction represents P in refractory organic matter, we believe that a small part of it was degradable and was mineralized during the anoxic phase with concomitant P release to the water column.

As an overview of these results, we can conclude that, in the presented conditions, P bounded to Fe and Al minerals represents the most mobile fraction, and that they depend on redox conditions and pH, respectively. These fractions can be used as an indicator of exhaustion of sediments retention capacity for P. It has been demonstrated in laboratory experiments (Oliveira, M., *et al.* 2010) as well as in soil geochemistry research field (Arlene, K., *et al.*, 2000) that Al minerals play an important role in P retention capacity as long as its sorption capacity has not reach the limit. As shown in previous work (Ribeiro, D. C., *et al.*, 2008), when comparing the sediments quality of eutrophized and oligotrophic lakes with the same geological characteristics, it is desirable that the NaOH-P fraction concentration remains low in the sediments, reflecting a non-exhausted P retention capacity.

5.4 Conclusion

The reduction of Fe (hydr)oxides happens during the anoxic phase with concomitant P release, proving once again that this phenomenon is dependent on the redox potential. However, it was also demonstrated that the concentration of Al (hydr)oxides bound to P do not change during the redox potential shift, which reveals that Al minerals are important in the improvement of P retention in the sediments.

Nevertheless, a shift in pH was detected after going from anoxic to oxic condition in the reactor. Consequently, part of the P adsorbed to Al minerals was dissolved, revealing that the P retention in these minerals is pH dependent. In addition, although the pH shift was not fully understood, we believe that it can be related with the biological reduction of hydrogen sulfide in deep sediment layers with simultaneous pH raise at the SWI.

We conclude that the mobility inorganic P is mainly related with Al and Fe minerals that depends on the pH and redox condition change; that is mostly driven by biological activity. Due to the complexity of the biological and chemical interactions in the sediments, we strongly suggest that microcosm or *in situ* experiments should be additionally supported by mathematical modelling.

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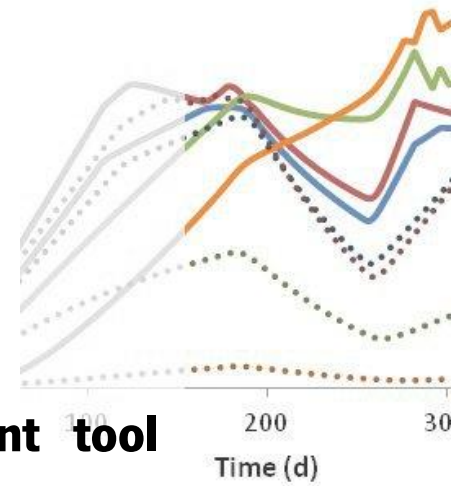
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$$\frac{\partial(\theta S_i)}{\partial t} = \frac{\partial}{\partial z} \left(\theta D_{S_i} \frac{\partial S_i}{\partial z} \right) + r_{S_i}$$

$$\frac{\partial X_i}{\partial t} = -\frac{\partial(v_{sed} X_i)}{\partial z} + \frac{\partial}{\partial z} \left(D_{B,X_i} \right)$$

Chapter 6.

Mathematical models as assessment tool toward restoration measures

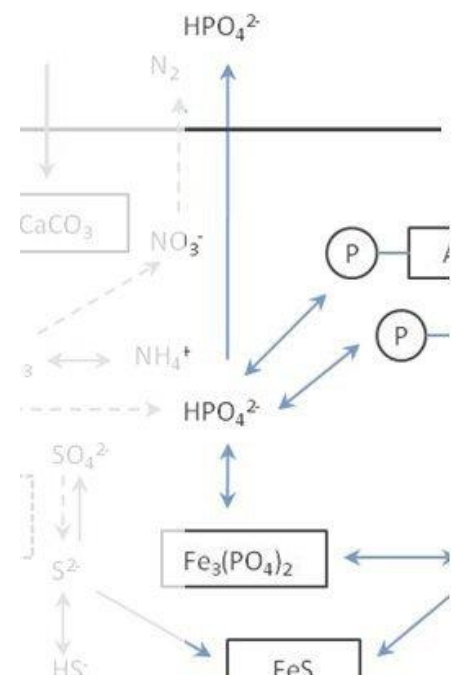


$$\frac{C_{O_2}}{K_{deg_O_2}} X_{org_deg}$$

$$\frac{C_{NO_3}}{K_{deg_NO_3}} \frac{K_{deg_O_2}}{K_{deg_O_2} + C_{O_2}} X_{org_deg}$$

$$\frac{C_{FeOOH}}{K_{deg_FeOOH} + C_{FeOOH}} \frac{K_{deg_O_2}}{K_{deg_O_2} + C_{O_2}} X_{org_deg}$$

$$\frac{C_{SO_4}}{K_{deg_SO_4} + C_{SO_4}} \frac{K_{deg_FeO}}{K_{deg_FeOOH} + C_{FeOOH}} X_{org_deg}$$



The role of mineral composition in P retention in sediments: an analysis through mathematical modeling.

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Redrafted from: Environmental Modelling & Software (2012) - Submitted

To understand the complex biological and geochemical relationships in the diagenetic system is of much interest as it has a large contribution in the water body quality state. Particularly, if one is interested in the contribution of phosphorus (P) internal input in the eutrophication problem, then understanding the mobility of P is of great concern. However, tracing changes in the several P type concentrations, that is, in organic form (refractory or degradable), adsorbed to metallic minerals or precipitated as salt (mineral), is extremely difficult to perform *in situ*. Thus, a mathematical model (in AQUASIM platform) was used to understand the mobility of P, when changes in O₂ concentration happens in the sediment-water interface (SWI). The importance of the AlOOH:FeOOH ratio in P retention was also studied through the model. The model conception included processes of organic matter mineralization (OM), acid-base equilibrium, precipitation and adsorption. For calibration purpose, microprofiling of O₂, P sequential extraction and determination of total Fe (TFe) and total Al (TAI) concentration were performed in natural sediments from the Azorean volcanic lake Furnas - Portugal. The model results showed that the P released during O₂ depletion was lower than the one released during the aerobic period. Although P adsorbed to FeOOH mineral was released when sediment were anoxic, this quantity was largely exceeded by mineralization of OM in the oxic period, as P adsorption happens only in 1.5 % of the Fe present in FeOOH. In addition, dissolved P can be removed from the pore water precipitating as vivianite if Fe(II) is available; a condition that is largely dependent on the concentration of hydrogen sulfide. Even with high AlOOH:FeOOH ratio the presence of hydrogen sulfide can decrease significantly the P retention capacity, by inducing early saturation of this metallic minerals.

6.1 Introduction

In the environmental field, several models have been applied to predict or understand changes in biogeochemical systems. Water quality of lakes has been modeled in order to determine the factors that can induce the eutrophication problem as well as to establish restoration measures.

It is known that external input of phosphorus (P) will enhance the eutrophication status of a lake. However, results obtained from restoration procedures revealed that even after a reduction of external P load, the eutrophication problem may continue to develop (Søndergaard, M., *et al.*, 2005) due to P release from the sediments (internal P load). Modeled scenarios also show that despite the reduction of external P load, the P flux from the sediments may be sufficient to maintain the eutrophic status of the lake for more than 10 years (Martins, G., *et al.*, 2008), which corroborates the field work of others researchers (Jeppesen, E., *et al.*, 2005; Søndergaard, M., *et al.*, 2007). Thus, as internal P load may delay the recovery of the water quality of eutrophized water bodies, it is important to understand what influence has the sediments in the eutrophication problem.

Geochemical processes that take place in the sediments are complex and influenced by environmental changes. As biological and chemical reaction rates are temperature dependent, diagenetic processes are largely controlled by temperature variations. The lack of oxygen in the hypolimnion due to bacteria uptake as a result of organic matter (OM) mineralization is more pronounced during stratification and will lead to redox changes in sediments. As a consequence of these processes, P is released from redox sensitive minerals (e.g. iron minerals) to the pore water and across the sediment-water interface (SWI). This is the classical paradigm for P release from sediments (Einsel, W., 1934, Mortimer, C., H., 1941, 1942). But some authors reported a low P flux at the SWI during anoxic periods, proposing exceptions to the classical paradigm (Hansen, J., *et al.*, 2003; Kopáček, J., *et al.* 2007). It has been demonstrated that this phenomena was related with the mineral composition of the sediment. Lakes with $\text{Al}(\text{OH})_3:\text{Fe}(\text{OH})_3$ molar ratios above 3 presented low diffusion of P across the SWI during anoxia (Kopáček, J., *et al.*, 2005, 2007). The presence of aluminium

(hydr)oxide* in the sediments can enhance P retention as these minerals are not redox sensitive. In contrast, iron (hydr)oxide is redox sensitive and will release P during anoxic periods. Thus, the mineral composition of sediments has an important role in controlling P internal load (Ribeiro, D. C., *et al.* 2012; Hupfer, M., and Lewandowsky, J., 2008; Moosman, L., *et al.* 2006; Boström, B., *et al.* 1988)

Modeling the mobility of P in the sediments can predict changes in P retention capacity of a lake, or if restoration is possible by changing the mineral composition of the sediments to improve P retention. The objective of this work is to deliver clarifications of the effect of aerobic/anoxic cycles and the presence of H₂S in P retention. In addition, P retention capacity was assessed as a function of the mineral composition of sediments.

6.2 Methods

6.2.1 Sediments Metal Analysis

The sediments were collected in the deepest site of Lake Furnas, in the archipelago of Azores – Portugal. This is a volcanic lake in São Miguel Island, located between the parallels 36 ° 45' – 39 ° 43' of latitude north and meridians 24 ° 45' – 31 ° 17' of longitude west. An Uwitec gravitational sediment corer (with 6 cm in diameter and 60 cm in length) was used for the sediment sampling. The first 25 cm of sediments were collected and homogenized. Then triplicates samples of homogenized sediments were digested with a mixture of nitric acid and sulfuric acid, according to the standard methods of examination of waters and wastewaters (Method: 4500-P, B4 - APHA *et al.*, 1995) and used for total Al and Fe (TAI and TFe) analyses. The atomic absorption spectroscopy was used for the metal analysis (APHA *et al.*, 1995).

6.2.2 Oxygen profile in sediments

Sediments were placed in a glass cylinder with approximately 6 cm in diameter and 15 cm length (Figure 6.1). The cylinder was filled with distilled water leaving a headspace of 1 cm approximately. The setup was left untouched for 24 hour to allow the sediment to settle and to achieve the air/water equilibrium. Oxygen profiles were made in the sediments by means of a Unisense automated profiling system (Figure 6.1). Vertical profiles of O₂ concentration

* In the present text, the term aluminium “(hydr)oxide” include aluminium oxides (Al₂O₃), hydroxides (Al(OH)₃) and oxy-hydroxide (AlOOH). The same reasoning will be used is for iron “(hydr)oxide”.

were made with a resolution of 250 μm for the first 2 cm depth. The sensor used was the oxygen glass microsensor (Ox25) from Unisense.

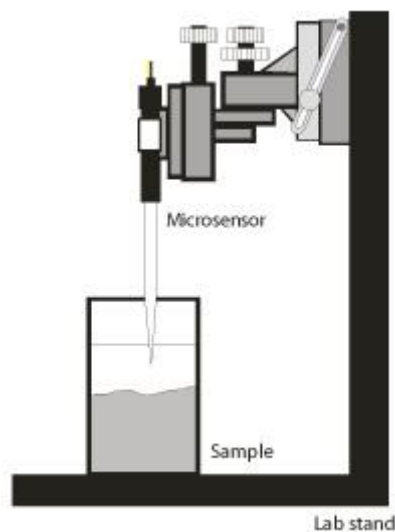


Figure 6.1. Experimental setup of the microprofiling system for the vertical profiles of oxygen concentration in sediments.

6.2.3 Model Conception

Biogeochemical Processes

To model biogeochemical reactions present in the sediments including OM mineralization, precipitation of salts, acid-base reactions and adsorption/desorption of P to metallic minerals, a dynamic model was created in the AQUASIM platform. The processes considered in the model are depicted in Figure 6.2 and Table 6.1. As shown in Table 6.1, OM is oxidized by a cascade of electron acceptors (oxygen, nitrate, iron hydroxide and sulfate)^{*}. In all processes of OM mineralization, CO_2 is produced and will be converted into carbonic acid (Table 6.1: AB₂) that will be integrated in the carbonate system equilibrium (Table 6.1: AB₃₋₄) and will influence the calcium carbonate precipitation equilibrium (Table 6.1: P₁). When O_2 is present, OM mineralization will also produce nitrate (nitrification reaction embedded – Table 6.1: OM₁). In absence of O_2 , ammonium will be produced instead of nitrate (Table 6.1: OM₃₋₄). The nitrate produced in the oxic sediment layer will diffuse downward to the anoxic layer and

^{*} The MnO_2 is also used as last electron acceptor if iron (hydr)oxide is not available, but to simplify the model, this reaction was not included.

will be used for denitrification (Table 6.1: OM₂). Phosphate is also produced in all processes of OM oxidation and is integrated in the acid-base equilibrium of phosphate (Table 6.1: AB₆₋₇).

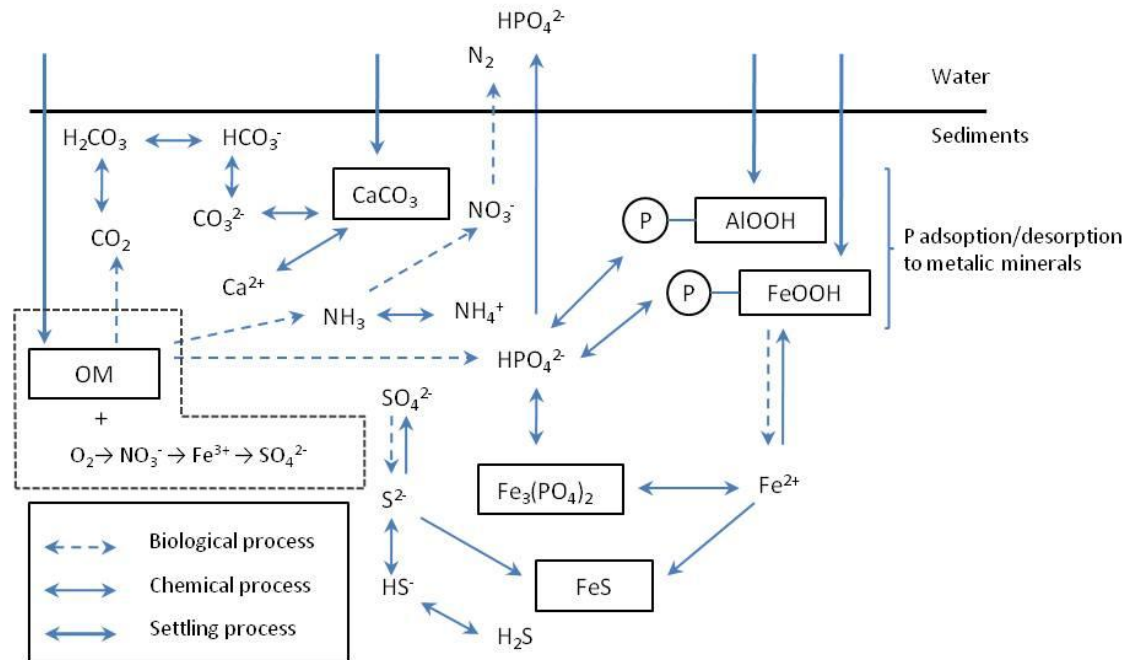


Figure 6.2. Representation of the conceptual model. (Framed compounds are in solid state and unframed ones are soluble compounds).

Iron reducing bacteria can use FeOOH as final electron acceptor (Martins *et al.* 2010; Lovley *et al.* 2004; Jones *et al.* 1984) during OM mineralization (Table 6.1: OM₃) producing Fe (II) that will react with phosphate (Table 6.1: P₂) to produce vivianite (Fe₃(PO₄)₂) if its solubility product is exceeded (Gachter and Müller, 2003). As HSO₄⁻ is reduced to HS⁻ in deeper anoxic layers (Table 6.1: OM₄), S²⁻ can react with Fe(II) precipitating as FeS (Table 6.1: P₃) which is a permanent sink of Fe as oxygen cannot diffuse in the sediments' deeper layers to re-oxidize Fe(II) to Fe(III). Thus less Fe(III) will not be available to precipitate as FeOOH. These processes can intensify the HPO₄²⁻ release to the pore water as FeOOH is less available to re-adsorb it (Table 6.1: AD₁ - reverse reaction). If AlOOH has not reached the maximum P adsorption capacity, P will be retained (Table 6.1: AD₂) avoiding its diffusion to the pore water and across the SWI (Kopáček *et al.* 2007).

All OM mineralization reactions are driven by bacterial activity and were mathematically expressed by a Monod-type equation as presented in Table 6.2 (OM₁₋₄). As the presence of

some oxidants may inhibit some reactions (e.g. the presence of oxygen inhibits OM degradation with Fe(III) as final electron acceptor), an inhibition term is added to the Monod equation in order to simulate the OM mineralization by a cascade of electron acceptors (Dittrich, M., *et al.* 2009; Soetaert, K., *et al.*, 1996). The bacteria concentration is considered constant in the model and implicit in the rate constant of Monod equation.

Precipitation and dissolution of CaCO_3 , Fe_3PO_4 and FeS are considered in the model and mathematically expressed as presented in Table 6.2. The acid/base equilibrium reactions included in the model are the carbonates, phosphates, ammonium and sulfide equilibrium, mathematically expressed in Table 6.2.

Adsorption of P in metallic mineral is included in the model only for FeOOH and AlOOH . These reactions were expressed as a Langmuir-type isotherm (Table 6.2). No temperature variation was applied in the model and it was set constant at 10°C .

The constants related to OM mineralization, precipitation equilibrium and acid/base equilibrium were obtained from Dittrich *et al.* (2009). The constants in the adsorption/desorption equations were obtained from Li and Stanforth (2000) for the iron FeOOH adsorption, and from Tanada *et al.* (2003) for the AlOOH adsorption.

Products	Reactants*	Reactions
OM mineralization:	OM _{1:1} : OM + 138 O ₂	→ 106 CO ₂ + 16 NO ₃ ⁻ + HPO ₄ ²⁻ + 18 H ⁺ + 122H ₂ O
	OM _{2:2} : OM + 94 HNO ₃	→ 106 CO ₂ + 55 N ₂ + HPO ₄ ²⁻ + 86 H ₂ O + 90 HO ⁻
	OM _{3:3} : OM + 424 FeOOH + 846 H ⁺	→ 106 CO ₂ + 16 NH ₃ + 424 Fe ²⁺ + HPO ₄ ²⁻ + 742 H ₂ O
	OM _{4:4} : OM + 53 HSO ₄ ⁻	→ 106 CO ₂ + 16 NH ₃ + 53 HS ⁻ + H ₃ PO ₄ + 106 H ₂ O
Precipitation Equilibrium	P _{1:1} : Ca ²⁺ + CO ₃ ²⁻	↔ CaCO ₃
	P _{2:2} : 3Fe ²⁺ + 2HPO ₄ ²⁻	↔ Fe ₃ (PO ₄) ₂ + 2H ⁺
	P _{3:3} : Fe ²⁺ + S ²⁻	↔ FeS
Acid/Base Equilibrium	AB _{1:1} : H ⁺ + HO ⁻	↔ H ₂ O
	AB _{2:2} : CO ₂ + H ₂ O	↔ H ₂ CO ₃
	AB _{3:3} : H ₂ CO ₃	↔ HCO ₃ ⁻ + H ⁺
	AB _{4:4} : HCO ₃ ⁻	↔ CO ₃ ²⁻ + H ⁺
	AB _{5:5} : NH ₄ ⁺	↔ NH ₃ + H ⁺
	AB _{6:6} : H ₂ PO ₄ ⁻	↔ HPO ₄ ²⁻ + H ⁺
	AB _{6:6} : H ₂ PO ₄ ⁻	↔ HPO ₄ ²⁻ + H ⁺
	AB _{7:7} : HPO ₄ ²⁻	↔ PO ₄ ³⁻ + H ⁺
	AB _{8:8} : H ₂ S	↔ HS ⁻ + H ⁺
	AB _{9:9} : HS ⁻	↔ S ²⁻ + H ⁺
Adsorption ^α / Desorption	AD _{1:1} : 2FeOOH + H ₂ PO ₄ ⁻	↔ (FeO) ₂ -PO ₄ ⁻ + 2H ₂ O
	AD _{2:2} : 2AlOOH + H ₂ PO ₄ ⁻	↔ (AlO) ₂ -PO ₄ ⁻ + 2H ₂ O

* OM is the organic matter as reactant with the general molecular formula: (CH₂O)₁₀₆(NH₃)₁₆(H₃PO₄)

^α The adsorption mechanism on Goethite (α-FeOOH) is still controversial. Thus, for modeling purpose we assume that adsorption happens through a binuclear bound, as it is one of the most accepted mechanisms (Li and Robert Stanforth, 2000). In this case the hydroxyl anion of two FeOOH molecules is replaced by two oxygen atoms of the phosphate molecule, as described next: (FeO)₂-(OH)₂ + H₂PO₄⁻ = (FeO)₂-(O)₂PO₄⁻ + 2H₂O. We assume that phosphate adsorption on AlOOH follows the same mechanism, only with different coefficient values in the Langmuir isotherm equation.

Table 6.2. Reaction rates of all reactions included in the mathematical model.

OM mineralization	
$OM_1 = k_{deg_O_2} \frac{C_{O_2}}{K_{deg_O_2}} X_{org_deg}$	
$OM_2 = k_{deg_NO_3} \frac{C_{NO_3}}{K_{deg_NO_3}} \frac{K_{deg_O_2}}{K_{deg_O_2} + C_{O_2}} X_{org_deg}$	
$OM_3 = k_{deg_FeOOH} \frac{C_{FeOOH}}{K_{deg_FeOOH} + C_{FeOOH}} \frac{K_{deg_NO_3}}{K_{deg_NO_3} + C_{NO_3}} \frac{K_{deg_O_2}}{K_{deg_O_2} + C_{O_2}} X_{org_deg}$	
$OM_4 = k_{deg_SO_4} \frac{C_{SO_4}}{K_{deg_SO_4} + C_{SO_4}} \frac{K_{deg_FeOOH}}{K_{deg_FeOOH} + C_{FeOOH}} \frac{K_{deg_NO_3}}{K_{deg_NO_3} + C_{NO_3}} \frac{K_{deg_O_2}}{K_{deg_O_2} + C_{O_2}} X_{org_deg}$	
Precipitation Equilibrium	
$P_1 = k_{CaCO_3} \frac{C_{Ca^{2+}} C_{CO_3^{2-}}}{K_{eq_CaCO_3}} - 1 \quad P_2 = k_{Fe_3(PO_4)_2} \frac{C_{Fe^{2+}}^3 C_{PO_4^{3-}}^2}{K_{eq_Fe_3(PO_4)_2}} - 1 \quad P_3 = k_{FeS} \frac{C_{Fe^{2+}} C_{S^{2-}}}{K_{eq_FeS}} - 1$	
Acid/Base Equilibrium	
$AB_1 = k_{H_2O} \left(1 - \frac{C_{H^+} C_{HO^-}}{K_w} \right)$	$AB_6 = k_{H_2PO_4} \left(C_{H_2PO_4} - \frac{C_{H^+} C_{HPO_4^{2-}}}{K_w} \right)$
$AB_2 \Rightarrow C_{CO_2} = C_{H_2CO_3}$	$AB_7 = k_{HPO_4} \left(C_{HPO_4} - \frac{C_{H^+} C_{PO_4^{3-}}}{K_{HPO_4}} \right)$
$AB_3 = k_{H_2CO_3} \left(C_{H_2CO_3} - \frac{C_{H^+} C_{HCO_3^-}}{K_{H_2CO_3}} \right)$	$AB_8 = k_{H_2S} \left(C_{H_2S} - \frac{C_{H^+} C_{HS^-}}{K_{HS}} \right)$
$AB_4 = k_{HCO_3^-} \left(C_{HCO_3^-} - \frac{C_{H^+} C_{HCO_3^-}}{K_{HCO_3^-}} \right)$	$AB_9 = k_{HS} \left(C_{HS} - \frac{C_{H^+} C_{HS^-}}{K_{HS}} \right)$
$AB_5 = k_{NH_4^+} \left(C_{NH_4^+} - \frac{C_{H^+} C_{NH_3}}{K_{NH_3}} \right)$	
Adsorption/Desorption	
$AD_1 = k_{ad_Fe} \frac{K_{ad_Fe} C_{max_Fe} C_{PO_4}}{1 + K_{ad_Fe} C_{PO_4}}$	$AD_2 = k_{ad_Al} \frac{K_{ad_Al} C_{max_Al} C_{PO_4}}{1 + K_{ad_Al} C_{PO_4}}$

6.2.4 The Modeling Platform

The modeling platform AQUASIM created by Reichert (Reichert 1994, Reichert 1995a, 1995b) was used in to apply the model conception. AQUASIM is a one-dimensional modeling platform (resolving the depth of the sediments) for calculation of particulate and dissolved

substances concentration, based on molecular diffusion, reaction, deposition and bioturbation. The governing differential equations fixed in the software are as follow:

Equation 6.1:

$$\frac{\partial(\theta S_i)}{\partial t} = \frac{\partial}{\partial z} \left(\theta D_{S_i} \frac{\partial S_i}{\partial z} \right) + r_{S_i}$$

Equation 6.2:

$$\frac{\partial X_i}{\partial t} = - \frac{\partial(v_{sed} X_i)}{\partial z} + \frac{\partial}{\partial z} \left(D_{B,X_i} \frac{\partial X_i}{\partial z} \right) + r_{X_i}$$

where θ is the porosity of the sediment, t is time, z is the depth within the sediment (zero at the sediments surface and positive values downward), D_{S_i} is the molecular diffusion coefficient of dissolved substance i , S_i is the concentration of dissolved substance i in the pore water (mass/pore water volume), r_{S_i} is the reaction rate of dissolved substance i (mass/total sediment volume and time), X_i is the concentration of particulate substance i in the sediment (mass/total sediment volume), v_{sed} is the sediment solid phase velocity movement relative to the sediment surface, D_{B,X_i} is the effective diffusion coefficient of particulate substance i and r_{X_i} is the reaction rate of particulate substance i (mass/sediment volume and time). The AQUASIM kernel equations are fully explained by Dittrich *et al.* (2009).

6.2.5 Calibration and Scenarios formulation

Base Scenario – Calibration

This is the reference scenario representing all the processes of the conceptual model (Figure 14), with constant concentration of oxygen at the SWI of 8 mg/L (no variation through the 365 days of modeling). The objective of this scenario is to have a base line to compare with scenarios where O_2 concentration changes.

The calibrated parameters were O_2 concentration, TFe, TAl, P adsorbed by FeOOH (P_{FeOOH}) and P adsorbed by AlOOH (P_{AlOOH}). TFe and TAl were calculated by the model as expressed in Equation 6.3 and 6.4. P_{FeOOH} and P_{AlOOH} were calculated as expressed in Equation 6.5 and 6.6.

The P adsorption to Fe and Al minerals is expected to happen in the surface of those minerals. Thus, not all the mass of the minerals will be used in adsorption process. To calculate the Fe and Al mass fraction used in the adsorption process, the adsorption rate was restricted as defined in Equation 6.7 and 6.8. The parameters λ_{Fe} and λ_{Al} in these equations were defined in order to adjust the modeled results to the experimental data. These parameters represent the fraction of Fe and Al mass used in adsorption comparing with the total mass of Fe and Al present in FeOOH and AlOOH.

Scenario 1 - Oxygen depletion at the sediment-water interface

In this scenario, a shift in O₂ concentration from 8 mg/L to 0 mg/L is made, beginning at day 195 to 255 (2 month) at SWI. This represents an anoxic period in the hypolimnion of the lake. In addition, an input of organic matter is made during the anoxic period representing the settling of dead algae from the epilimnion to hypolimnion.

Scenario 2 - Assessment of the effect of suppressing the hydrogen sulfide reaction with Fe(II) (inhibition of FeS production).

The scenario 2 has the same characteristics as scenario 1 but with the FeS production process suppressed to understand how this reaction can affect P mobility and availability.

Scenario 3 - Determination of optimal AlOOH:FeOOH ratio for P retention

With the objective of determining the AlOOH:FeOOH ratio at which P adsorption is maximum, several modeling runs were executed with increasing AlOOH initial and settling concentrations for each run. This made possible to evaluate the phosphate final concentration for AlOOH:FeOOH molar ratios from 0.23 to 12.54, after 365 days of simulation, at 5 mm depth. The AlOOH:FeOOH molar ratios were tested for the condition expressed in scenario 1 and 2. This scenario will deliver insight of the AlOOH:FeOOH ratio that presents a maximum retention capacity for each scenario.

6.3 Results and discussion

6.3.1 Calibration

The model was calibrated for concentration of O_2 , TFe, TAl, P_{FeOOH} , and P_{AlOOH} minerals. The results revealed that the model fitted the experimental data rigorously. The results are depicted in Figure 6.3 to Figure 6.5.

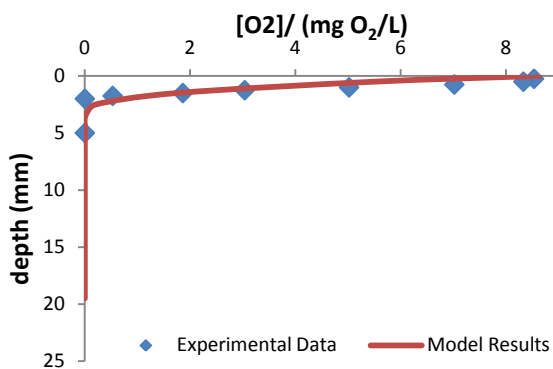


Figure 6.3. Concentration of O_2 as function of sediment depth for experimental data and model results.

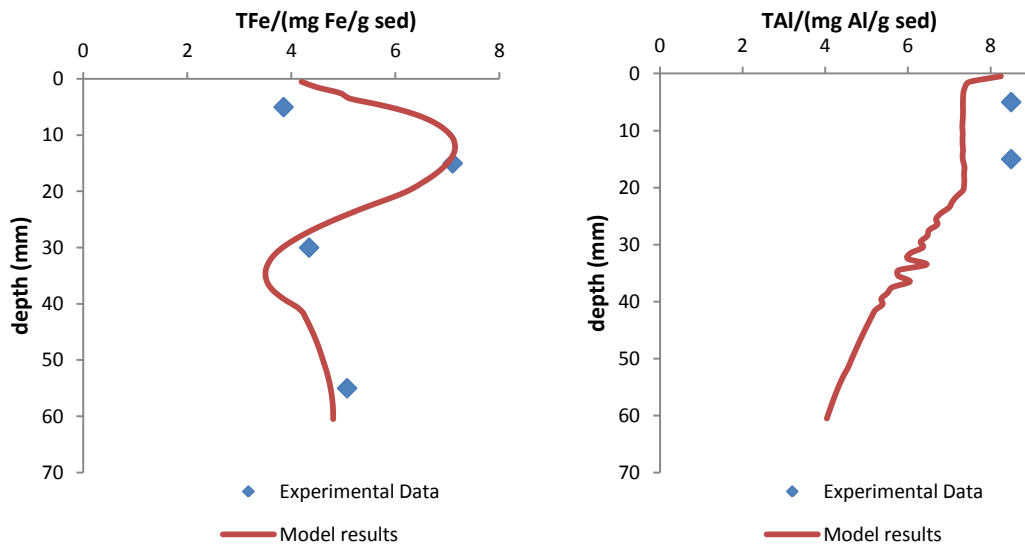


Figure 6.4. Total concentration of Fe per sediment mass (Figure on the left) and total Al per sediment mass (Figure on the right) both in function of sediment depth.

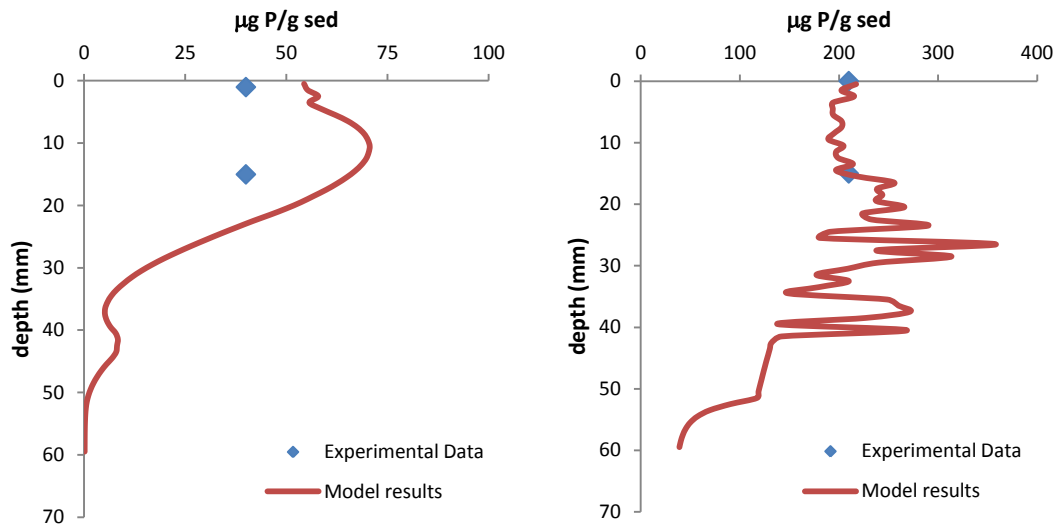


Figure 6.5. P bounded to FeOOH per sediment mass (left) and P bounded to AlOOH per sediment mass (right).

The calibration results for P_{FeOOH} and P_{AlOOH} showed that the mass of Fe bounded to P is only 1.5 % (Equation 6.7: $\lambda_{\text{Fe}} = 0.015$) of the total mass of Fe present in the FeOOH available. Curiously, the same result was found for AlOOH; as only 1.5 % of the Al present in AlOOH mass was used to retain P, according to Equation 6.8 ($\lambda_{\text{Al}} = 0.015$).

These results can be explained by the fact that AlOOH and FeOOH minerals are not very porous materials and the area available for adsorption is low. Thus, only the molecules of the surface of these minerals will adsorb P, which represents a small amount of mineral mass compared with the total mineral mass available.

This leads to a very important conclusion: raising the concentration of Al or Fe minerals in sediments to enhance the P retention is not dependent on the quantity of metallic mineral; it is dependent on the available area of adsorption. Thus, if remediation techniques that includes settling of Al or Fe minerals in lakes or reservoirs should take into account the size of the particles rather than the mass of it.

Equation 6.3:

$$TFe = \frac{X_{FeOOH} \times \frac{M_{Fe}}{M_{FeOOH}} + X_{FeOOH-P} \times \frac{M_{Fe}}{M_{FeOOH-P}} + X_{Fe_3(P_4)_2} \times \frac{3 \times M_{Fe}}{M_{Fe_3(P_4)_2}} + X_{FeS} \times \frac{M_{Fe}}{M_{FeS}} + C_{Fe_2} + X_{M_{Fe}} \times \theta}{X_{sed}}$$

Equation 6.4:

$$TAl = \frac{X_{AlOOH} \times \frac{M_{Al}}{M_{AlOOH}} + X_{AlOOH-P} \times \frac{M_{Al}}{M_{AlOOH-P}}}{X_{sed}}$$

Equation 6.5:

$$P_{FeOOH} = \frac{X_{FeOOH-P} \times M_P}{X_{sed} \times M_{FeOOH-P}}$$

Equation 6.6:

$$P_{AlOOH} = \frac{X_{AlOOH-P} \times M_P}{X_{sed} \times M_{AlOOH-P}}$$

Equation 6.7:

$$\text{if } \lambda_{Fe} \times \left(X_{FeOOH} \times \frac{M_{Fe}}{M_{FeOOH}} \right) > \left(X_{FeOOH-P} \times \frac{M_{Fe}}{M_{FeOOH-P}} \right) \text{ then } AD_1 \text{ else } AD_1 = 0$$

Equation 6.8:

$$\text{if } \lambda_{Al} \times \left(X_{AlOOH} \times \frac{M_{Al}}{M_{AlOOH}} \right) > \left(X_{AlOOH-P} \times \frac{M_{Al}}{M_{AlOOH-P}} \right) \text{ then } AD_2 \text{ else } AD_2 = 0$$

6.3.2 Predictive scenario results

Scenario 1

This scenario is focused on the effect of a shift in O₂ concentration, representing an anoxic period in the hypolimnion (between 195 to 255 days of simulation).

The phosphate concentration in the pore water increases in time due to organic matter mineralization. According to the model, the OM mineralization rate reaches its maximum value during the oxic period, and has higher values in the first 3 mm of sediment. Under that depth, where oxygen is no longer available, the OM is mineralized under anaerobic conditions at lower rates compared with the aerobic metabolism. This rate difference is a result of the lower efficiency of the anaerobic metabolism but also because there is higher OM availability at the SWI (oxic layer) due to deposition. When the SWI turns anoxic, all the reactions of mineralization of OM are under anaerobic rates including at the SWI. Consequently, according to the model results, phosphate production as a result of OM degradation is five times lower. In addition, Fe(III) from FeOOH is reduced to Fe(II) which will react with phosphate precipitating as Fe₃(PO₄)₂ (vivianite), as demonstrated in Figure 6.7 (left), removing dissolved phosphate from the pore water.

The Figure 6.6 shows the decrease in phosphate concentration when the sediments turn completely anoxic (time = 190 d). What is interesting is that FeOOH-P complex is dissolved and phosphate is released (Figure 6.8 - right), as expected (Einsele, W., 1936; Mortimer, C., H., 1941 and 1942) represented in Figure 5.3 (BD fraction). Thus, one should expect a rising concentration of phosphate instead of the decrease predicted by the model (Figure 6.6). We can conclude that phosphate contribution from OM mineralization and dissolution of FeOOH-P complex during the anoxic period is lower than the phosphate produced from OM mineralization during the oxic period ($[P_{OM} + P_{FeOOH-P}]_{anoxic} < [P_{OM}]_{oxic}$)*.

The model included an increased OM deposition during the anoxic period simulating the algae settling after a bloom occurrence. Thus, when oxygen concentration rises (265 d) an extra

* P_{OM} means P from OM mineralization and P_{FeOOH-P} means P from FeOOH-P complex dissolution.

amount of OM is available in the upper sediment layer resulting in an increased OM mineralization and consequently rising phosphate concentration. Despite the phosphate concentration drop during the anoxic period, as shown in Figure 6.6, when sediments are exposed to an aerobic-anoxic cycle, the phosphate concentration in the succeeding aerobic phase will be higher than if the sediments were always exposed to oxygen, for the same time of simulation. Thus, we can observe a peak of phosphate concentration at the end of the anoxic period, which could explain the behavior of some lakes that have an algae bloom after the anoxic period.

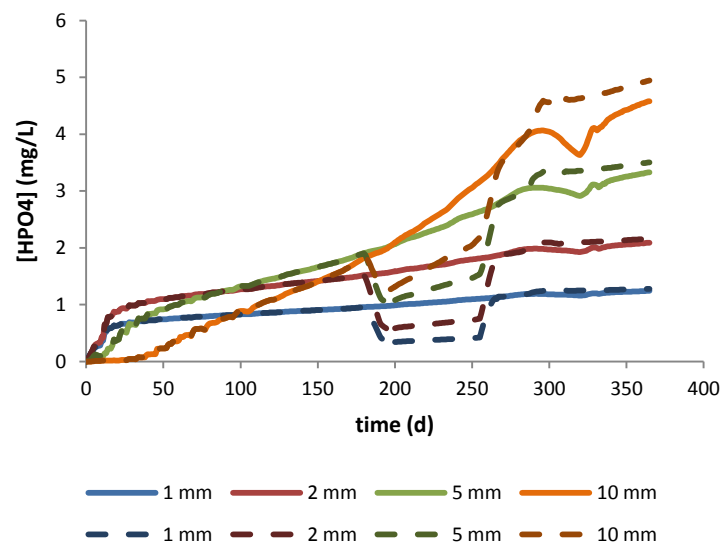


Figure 6.6. Simulation results of phosphate concentration in sediments for the first 10 mm, for the base scenario (line) and scenario 1 (sketched line).

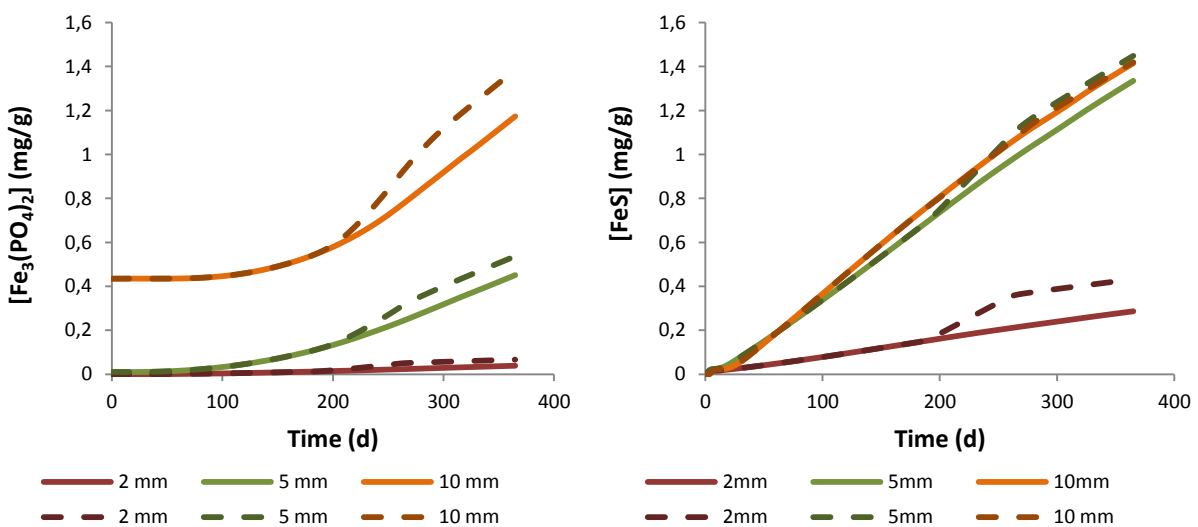


Figure 6.7. Simulations results for vivianite (left graph) and iron sulfide (right graph) concentration in the first 10 mm of sediment. At both graph are represented the base scenario (full line) and scenario 1 (sketched line).

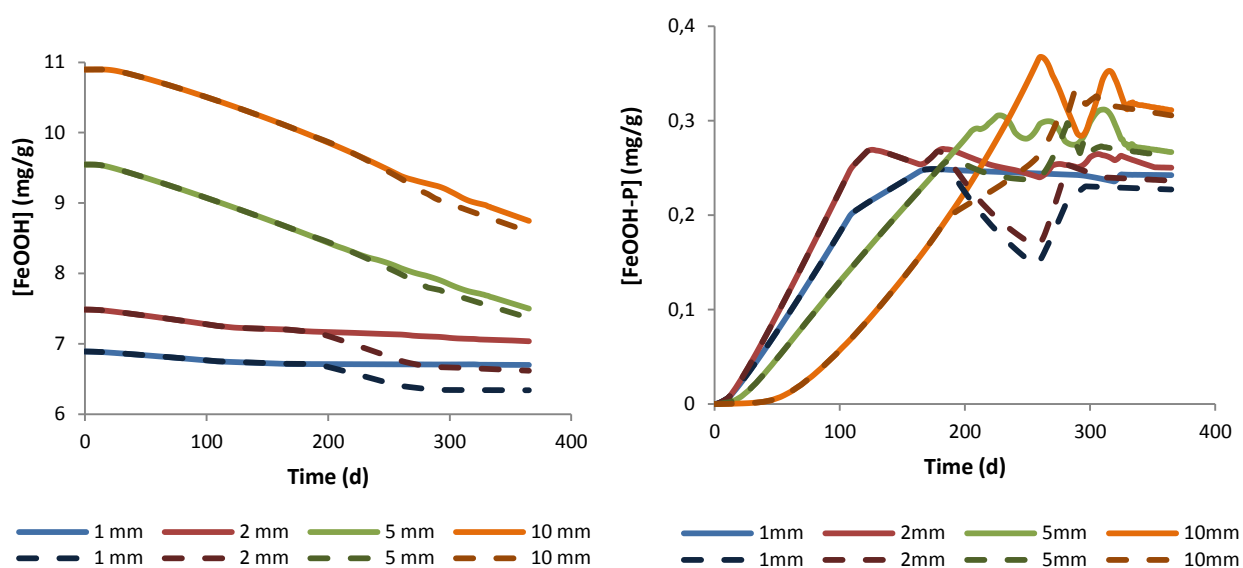


Figure 6.8. Simulations results for iron oxy-hydroxide (left graph) and for iron oxy-hydroxide bound to phosphate (right graph) concentration in the first 10 mm of sediment. At both graph are represented the base scenario (full line) and scenario 1 (sketched line).

Another conclusion from this scenario is that the concentration of AlOOH-P between the base scenario (constant O_2 concentration) and scenario 1 (oxic-anoxic cycles) does not change. This can be explained by the fact that the adsorption rate is relatively fast compared with other diagenetic reactions. Thus, according to this model, AlOOH reaches its maximum adsorption capacity after 57 d (for the first 10 mm), limiting additional phosphate adsorption. Thus, Al mineral play an important role in phosphate retention before its saturation. The adsorption by Al minerals can occur further if these minerals are added to the bottom of the lake (naturally or artificially). In this case, the phosphate adsorption by AlOOH will buffer FeOOH saturation. The results in scenario 1 and 2 (Figure 6.6 to Figure 6.9) were obtained with AlOOH:FeOOH molar ratio of 4.6, but different ratios will give different results. Thus, there must be an optimal AlOOH:FeOOH ratio that maximizes phosphate removal from the pore water. This is explained in more detail in discussion of scenario 3 results.

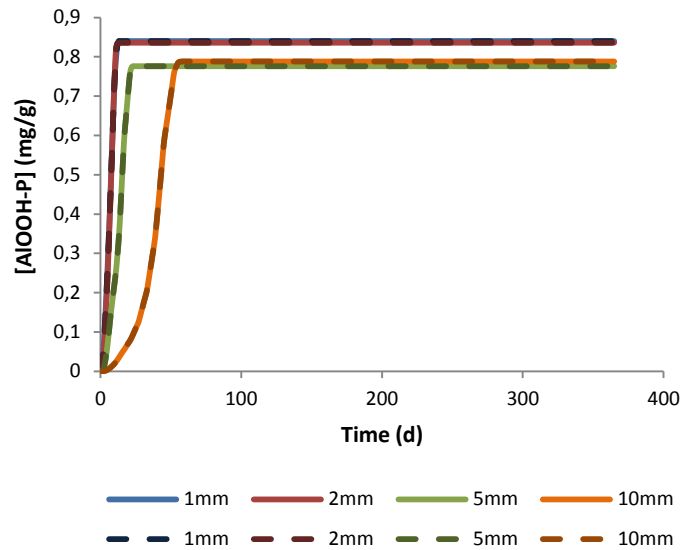


Figure 6.9. Simulations results for concentration of aluminum oxy-hydroxide bound to phosphate in the first 10 mm of sediment. Both base scenario (full line) and scenario 1 (sketched line) are represented.

Scenario 2

This scenario is similar to scenario 1 in all aspects, but with the suppression of FeS production. The scenario 2 has the objective of demonstrating the effect that Fe(II) availability has on P retention (by suppressing FeS precipitation). The results show that phosphate concentration in the pore water (Figure 6.11 – left graph) decreased 43.6 % (at 1 mm depth) to 96.4 % (at 10 mm depth), compared with the scenario 1 (where FeS production occurs).

This can be explained by the fact that, as no Fe(II) is precipitated as FeS, leaving more Fe(II) available to react with HPO_4^{2-} with concomitant formation of $\text{Fe}_3(\text{PO}_4)_2$ (compare vivianite concentration between scenario 1 and 2 in Figure 6.11 – right graph) that removes dissolved P from the pore water.

In addition, during the anoxic period (between day 195 and 255) the P concentration decreases like previously found in scenario 1, for the same reason earlier discussed: OM mineralization is less intense during the anoxic period resulting in less P production. But what is different between scenario 1 and scenario 2 is that when oxygen is re-available (at the end of the anoxic period) the P peak seen in scenario 1 (Figure 6.11 – left graph, full line) does not exist in scenario 2 (Figure 6.11 – left graph, dotted line). This means that, although organic P deposition (from algae settling) increased the organic P in the sediments, during

the anoxic period, the P released from the additional OM mineralization is easily buffered by $\text{Fe}_3(\text{PO}_4)_2$ formation. Thus, as vivianite formation occurs and less phosphate is available, FeOOH and AlOOH minerals will be less saturated raising the P retention capacity. This is demonstrated by the lower concentrations of FeOOH-P and AlOOH-P in scenario 2 compared with scenario 1 (Figure 6.12).

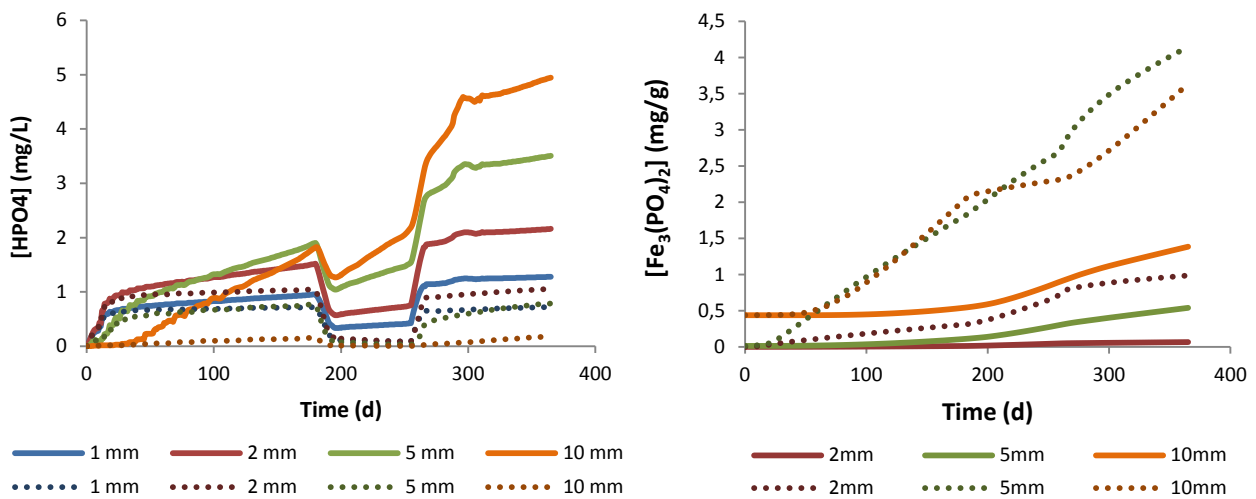


Figure 6.10 – Simulations results for phosphate (left graph) and vivianite (right graph) concentration in the first 10 mm of sediment. At both graph are represented the scenario 1 (full line) and scenario 2 (dotted line).

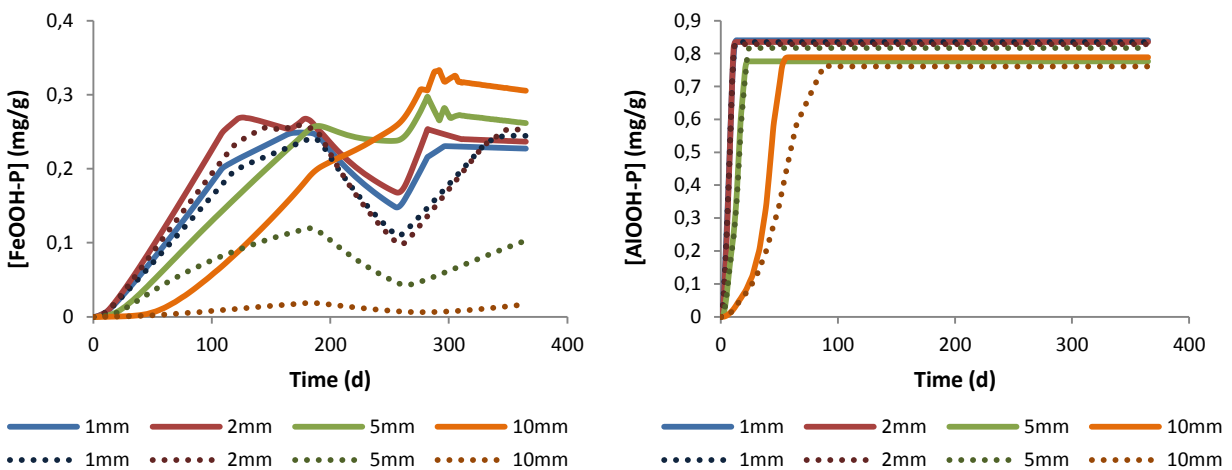


Figure 6.11 - Simulations results for FeOOH-P (left graph) and AlOOH-P (right graph) concentration in the first 10 mm of sediment. At both graph are represented the scenario 1 (full line) and scenario 2 (dotted line).

Scenario 3

To calculate the optimal AlOOH:FeOOH ratio, several simulations with ratios from 0.23 to 12.54 were computed for both scenario 1 and 2. The ratios were set changing initial conditions of AlOOH concentration. One dimensionless variable was defined as the total sorption capacity (Φ) and was calculated as described by Equation 6.9.

Equation 6.9:

$$\Phi = \frac{C_{\max} - C_i}{C_{\max}}$$

where C_{\max} (equal to C_0) represents the concentration of phosphate in the pore water if the adsorption process would not occur; C_i is the phosphate concentration for a certain AlOOH:FeOOH ratio. The variable Φ can be perceived as the total percentage of phosphate retained in the sediments for a certain AlOOH:FeOOH ratio.

The results are presented in Figure 6.12. It is clearly perceptible that P retention is largely influenced by hydrogen sulfide concentration. In one hand, scenario 1 sets the worst retention capacity conditions with total hydrogen sulfide ($\Sigma\text{H}_2\text{S} = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}]$) concentration of 0.010 mmol. In the other hand, in scenario 2, $\Sigma\text{H}_2\text{S} = 0$ and represents the highest retention capacity conditions (the correlation equations obtained are represented in Figure 6.12).

Kopáček *et al.* (2005 and 2007) concluded that sediments with $\text{Al}(\text{OH})_3:\text{Fe}(\text{OH})_3$ ratio* > 3, would prevent P release during hypolimnetic anoxia (due to enhanced retention capacity in sediments). Comparing their finding with our results, for $\Sigma\text{H}_2\text{S} = 0$ (scenario 2), AlOOH:FeOOH ratio of 3.0 would represent a total sorption capacity of 81.0 % ($\Phi = 0.810$ at 365 d of simulation – oxic period), which means that 81.0 % of soluble P in pore water is removed, compared with a scenario where no P adsorption happens by AlOOH (AlOOH:FeOOH ratio = 0). Moreover, as demonstrated before (Figure 6.6 and Figure 6.10 - left), during the anoxic period less P is released from OM mineralization. Thus, less P is

* In the present model, only P adsorption to AlOOH and FeOOH minerals was included, as a result of the available data. However, we understand that different Al and Fe oxides and hydroxides may coexist in the sediment. Nevertheless, we consider that the adsorption mechanism is similar for all these minerals, being all represented as AlOOH and FeOOH to simplify the model. Thus, we will consider that $\text{Al}(\text{OH})_3:\text{Fe}(\text{OH})_3$ ratio is similar to AlOOH:FeOOH ratio.

available and a strong retention capacity ($\Phi = 0.810$) causes a more accentuated phosphate concentration reduction ($[\text{HPO}_4^{2-}] = 40 \mu\text{g/L}$ at 5 mm depth). With such low phosphate concentration in the pore water it is not expected to be observed a significant internal P input, which corroborates Kopáček *et al.* (2005 and 2007) work.

However, total sorption capacity is largely reduced with the presence of $\Sigma\text{H}_2\text{S}$ (Figure 6.12). Following the previous reasoning, sediments with $\text{AlOOH}:\text{FeOOH}$ ratio of 3.0 and $\Sigma\text{H}_2\text{S} = 0.01$ mmol would have a total sorption capacity of 27.0 % ($\Phi = 0.270$). To reach a total sorption capacity of 81.0 %, $\text{AlOOH}:\text{FeOOH}$ ratio should be 58.0. This means that the $\text{AlOOH}:\text{FeOOH}$ ratio that maximizes retention is dependent on the $\Sigma\text{H}_2\text{S}$ concentration.

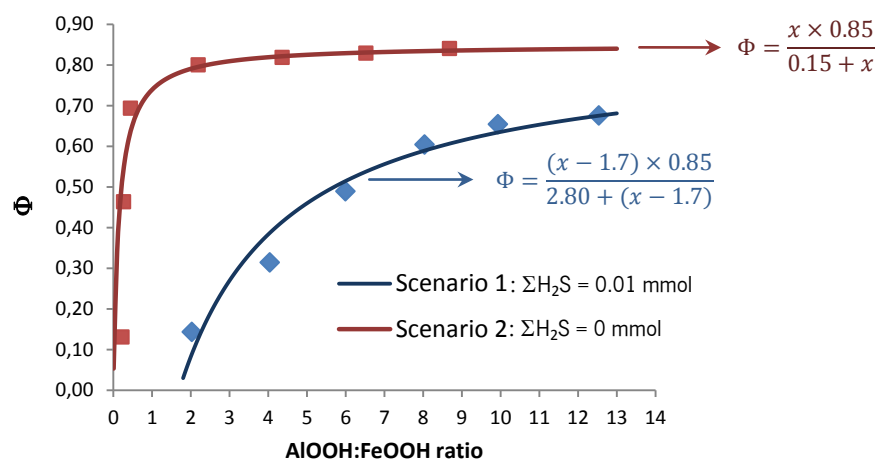


Figure 6.12. Total sorption capacity for scenario 1 and scenario 2: results from the model (marks) and respective correlations (line). In the correlation equation showed in the graph, $x = \text{AlOOH}:\text{FeOOH}$ ratio.

As explained before (scenario 2), this is due to the reaction between Fe(II) and $\Sigma\text{H}_2\text{S}$ which forms FeS that competes with the precipitation reaction between Fe(II) and PO_4^{3-} which forms $\text{Fe}_3(\text{PO}_4)_2$, and removes dissolved phosphate from the pore water (Gächter, R. *et al.* 2003). The less $\text{Fe}_3(\text{PO}_4)_2$ is created, the more dissolved P will be available; and this equilibrium is largely controlled by $\Sigma\text{H}_2\text{S}$ concentration. By consequence, if $\text{Fe}_3(\text{PO}_4)_2$ production is not favored due to high $\Sigma\text{H}_2\text{S}$ concentration, $\text{AlOOH}:\text{FeOOH}$ ratio must be increased (raising AlOOH concentration) to have the same retention capacity of a lake/reservoir with low $\Sigma\text{H}_2\text{S}$ concentration, which in some cases may not be viable.

In a management perspective, this information is extremely useful to understand P release potential and to point effective remediation processes. The approach must be different for each lake/reservoir types. For example, volcanic lakes with fumaroles (Cruz and França, 2006) will have an additional sulfate input that can be reduced to hydrogen sulfide and consequently decrease vivianite concentration with time. Another common approach is to use aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$ – Alum) to induce the P precipitation as aluminum phosphate and as aluminum hydroxide colloid flock that settles in the sediments (John Wehr *et al.*, 2002). This seem to an ambiguous and short-term treatment because P is removed by precipitation with aluminum but an input of sulfate is also made. If sulfate reaches sediments and diffuses to anoxic layers where sulfate reduction happens, $\Sigma\text{H}_2\text{S}$ concentration will increase with concomitant FeS production, decrease in Fe(II) and $\text{Fe}_3(\text{PO}_4)_2$ concentration, lowering P retention that will enhance P flux to the water column with time. Thus, if treatment with alum is administrated, $\Sigma\text{H}_2\text{S}$ concentration in sediments should be monitored to understand if dissolved sulfate crosses the SWI in depth or if it is removed from the water body by effluents before reaching the sediments.

6.5 Conclusion

A mathematical model was conceived with the objective of determining the influence of oxygen variation in mineral composition of the sediments that influence P mobility. According to the results obtained from the model, when the sediments are in anoxic period the phosphate production by OM mineralization decrease comparing with the same system in oxic condition; besides the rising of OM mineralization rates with other last electron acceptors compounds. This is a consequence of the higher efficiency of OM mineralization when oxygen is present. In addition, during anoxic period Fe(II) is produced in major quantities which leads to phosphate removal as it precipitates in the form of $\text{Fe}_3(\text{PO}_4)_2$, reducing dissolve P concentration in the pore water. Furthermore, lakes that experience oxic/anoxic cycles in the hypolimnium and OM settling from dead algae from the epilimnium can exhibit a peak of phosphate release as a result of increased mineralization of OM accumulated after the anoxic period.

However, even with intense phosphate production by OM mineralization, some lake's sediments have the capability of acting as a sink of P rather than as a source of it. This capability is strongly related with the Al and Fe mineral composition but also with the $\Sigma\text{H}_2\text{S}$ concentration. Al and Fe minerals can act as a fast P removing barrier by an adsorption mechanism. But the retention capacity of these minerals is limited by the available contact area for P adsorption. As this is a fast reaction, if there is high phosphate concentration in the pore water, Al and Fe minerals will saturate rapidly.

However, soluble P can also react with Fe(II) in anoxic sediment layer precipitating as vivianite and reducing P availability. In this case, Al and Fe mineral P adsorption can endure with time, specially if there is a natural input of these minerals into the lake (Kopáček, 2001), becoming an important chemical barrier to P release. Nevertheless, the presence $\Sigma\text{H}_2\text{S}$ change this equilibrium as it reacts with Fe(II) to form FeS, decreasing vivianite formation and thus increasing phosphate concentration in pore water. Thus, AlOOH:FeOOH optimal ratio change from system to system and is largely dependent of the $\Sigma\text{H}_2\text{S}$ concentration.

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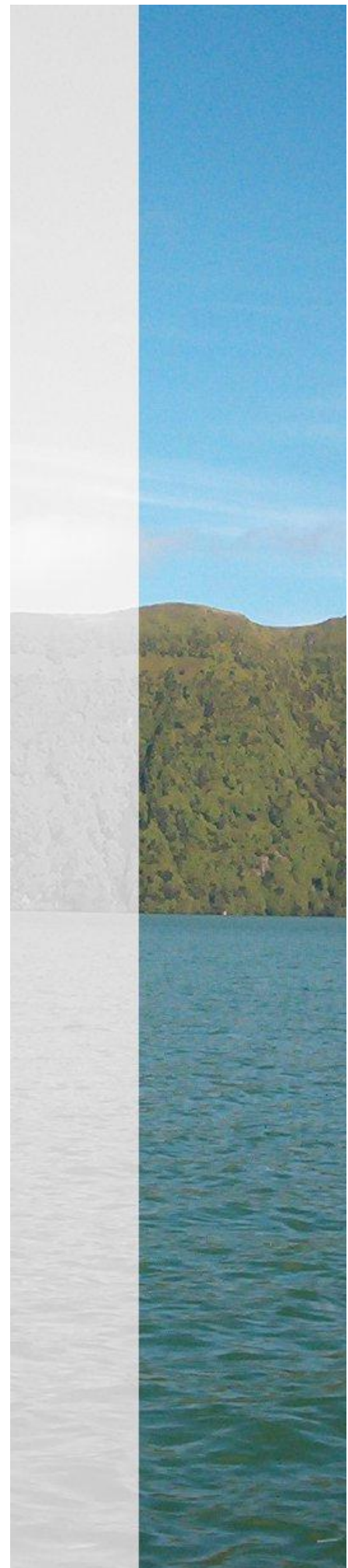
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Chapter 7.

Future Perspectives



Several years of investigation and experience were condensed and expressed in this thesis, setting guidelines to understand P mobility in sediments. This knowledge can now be used to diagnoses the P retention capacity in sediment of a certain lake and to set adequate remediation procedures.

Next, we suggest a framework for retention capacity diagnose and remediation procedures according to the main findings in this research work.

The first analysis required for water quality remediation in lakes/reservoirs is to understand the magnitude of the external input of nutrients, mainly P as the aim is to reduce eutrophication. If external P input endures, algae will continue to grow independently of the internal P input. A possible way of disabling external P input is to build a structure perpendicular to the effluent flow (or longitudinal to river flow at bottom of it) in order to force the water to pass through a system filled with Al and/or Fe (hydr)oxides that would retain P by adsorption.

Considering that P external load is controlled to a minimum, internal load should now be the main concern. The first step is to set the actual reference in terms of P retention capacity (check the saturation of the sediments). This can be made through a P sequential extraction procedure. Total Al, Fe, Ca and Mn should also be measured through digestion of the sediments. If possible, Al and Fe (hydr)oxides minerals concentration should be estimated to set the $\Sigma Al_xO_yH_z$: $\Sigma Fe_xO_yH_z$ ratio^{*}. The presence and concentration of hydrogen sulfide should be assessed to understand if this chemical compound is lowering significantly the P retention capacity. Concentration of hydrogen sulfide can be determined by microsensors (*in situ* or in laboratory).

After setting the reference, remediation measures can be applied. Before any real application, it is strongly recommended the use of mathematical models to predict results and check the viability of the project.

* $\Sigma Al_xO_yH_z$ represents the sum of all Al mineral that have P adsorption capacities, e.g., Al_2O_3 ; $Al(OH)_3$; $AlOOH$. The same is for: $\Sigma Fe_xO_yH_z$ representing all the Fe mineral with P adsorption capacities.

If retention capacity is low, a possible approach for raising P retention capacity in sediments could be settling natural particulate rock material in the bottom of the lake or reservoirs with high concentration of Al and Fe oxides and hydroxides. Large costs can be associated to such mitigation method. Thus, the viability and cost/benefit of such project should be assessed for each case. However, for largely eutrophized lakes or reservoirs with high internal P inputs and small bottom area, this remediation method could be an option.

Another hypothesis for small reservoirs could be pumping water from the reservoir through several reactors filled with Al and Fe oxides and back to the reservoir. The P is retained in the reactor and the re-introduced “clean water” will have a dilution effect on the reservoir diminishing P availability for algae growth. The viability of this project is highly dependent on the water body volume. Thus, in deep lake with large surface areas this might not be possible to concretize. However, in smaller systems, like shallow lakes or small artificial reservoirs this could be an optimal solution.

However, if natural input of sulfate to the water body exists, the recovery process could be much slower. A possible solution could be to find a non-toxic chemical that would prevent the formation of FeS in the sediments, leaving Fe(II) available to precipitate with dissolved P. This is a solution that still requires more investigation.

In addition to the results presented in this thesis, other factors like microbial community in sediments, temperature variation, light intensity and retention time have a strong effect of P availability in the water body. Thus the study of this complex system should always be supported with mathematical modeling

As future work, research on the inactivation of FeS production, dimensioning an efficient P adsorption reactor and the development of a diagenetic module for 3D modeling are possible options aiming the mitigation of lakes and reservoirs eutrophication.