UNIVERSIDADE FEDERAL DE SÃO CARLOS
CENTRO DE CIÊNCIAS BIOLÓGICAS E DA SAÚDE
PROGRAMA DE PÓS-GRADUAÇÃO EM ECOLOGIA E RECURSOS NATURAIS

EFEITOS ESPAÇO TEMPORAIS DA POLUIÇÃO PONTUAL E NÃO PONTUAL EM UMA BACIA HIDROGRÁFICA SUBTROPICAL: ECOHIDROLOGIA COMO FERRAMENTA DE CONTROLE

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Pedro Gatti Junior

Tese apresentada ao Programa de Pós-Graduação em Ecologia e Recursos Naturais, para obtenção do título de doutor em Ciências com ênfase em Ecologia e Recursos Naturais.

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RESUMO

Contaminantes são introduzidos em ecossistemas aquáticos, a partir de fontes pontuais e difusas e geralmente são depositados nos sedimentos de lagos e reservatórios. A entrada de poluentes difusos no ambiente é de difícil controle e identificação, enquanto que o controle de fontes pontuais é mais eficiente, pois são facilmente identificados. No entanto, as frequentes descargas de efluentes, mesmo passando por tratamento, podem mudar a dinâmica de entrada de elementos e substâncias em uma região. O objetivo deste estudo foi avaliar a influência espaço-temporal de fontes de poluição pontual e não pontual nas características das águas superficiais e do sedimento de um reservatório (Lobo/Broa, SP) em uma bacia hidrográfica com estações climáticas bem definidas. Além disso, conceitos e tentativas de restauração em diferentes ecossistemas foram revisados com o objetivo de entender quais são os principais controladores da regulação abiótica-biótica entre bacias hidrográficas e ecossistemas aquáticos, com base nos princípios da Ecohidrologia. Para este propósito, as concentrações de Cd, Cr, Fe, Ni, Zn, Pb, Al, Cu, Mn, Hg, As, Se, fósforo total, nitrogênio total e íons na água e no sedimento foram examinadas. Além disso, os níveis de metais (Al, Fe, Mn, Cu, Zn, Hg e As) no perfil do sedimento de pontos amostrais sob influência de diferentes impactos foram avaliados. Este estudo mostrou que as fontes pontuais de poluição promovem uma alta carga de contaminantes nos sedimentos, independentemente da estação. Além disso, as fontes de poluição pontual parecem ser espacialmente e temporalmente as principais causa da composição química de sedimentos do reservatório por causa da frequente liberação de efluentes. Esse estudo também indica que, apesar de várias diferenças biogeográficas, a hidrologia parece ser o principal fator que controla a produção primária, secundária e a sustentabilidade em rios e lagos (reservatórios). Em conclusão, a hidrologia nos trópicos parece diminuir os efeitos esperados de uma temperatura mais elevada. Portanto, para aumentar a resiliência nas águas doces tropicais ações integradas de acordo com as fases hidrológicas são altamente recomendadas.

Palavras-Chave: poluição pontual, poluição não pontual, perfil de sedimentação, latitude, ecohidrologia

ABSTRACT

Contaminants are introduced into aquatic ecosystems, both from point and diffuse sources and usually are deposited in the sediments of lakes and reservoirs. The input of diffuse pollutants in the environment is of difficult control and identification, while the control of point sources is more efficient because they are easily identified. However, the frequent discharges of effluents, althought undergoing treatment, may change the input of elements and substances in a given region. The aim of this study was to assess the spatial-temporal influence of point and non-point source pollution on the characteristics of surface water and sediment in a watershed with well-marked seasons. In addition, concepts and attempts at ecosystems restoration in different regions were reviewed in order to understand the main drivers of abiotic-biotic regulation among watersheds and aquatic ecosystems, based on the principles of Ecohydrology. For this purpose, the concentrations of Cd, Cr, Fe, Ni, Zn, Pb, Al, Cu, Mn, Hg, As, Se, total phosphorus, total nitrogen and ions in water and sediment were examined. Furthermore, levels of metals (Al, Fe, Mn, Cu, Zn, Hg and As) in the sediment profile of stations under of the influence of different impact were evaluated. This study showed that the point source pollution promote a high load of contaminants in sediment, regardless of the season. Furthermore, the point pollution sources seem to be spatially and temporally the main cause of reservoir sediment chemical composition due its frequent effluent release. This study also indicates that, despite several biogeographical differences, hydrology seems to be the main factor that controls the primary and secondary production and sustainability in rivers and lakes (reservoirs). In conclusion, the hydrology in the tropics seems to decrease the expected effects of a higher temperature. Therefore, to increase resilience in tropical freshwaters integrated actions according to hydrological stages are highly recommended.

Keywords: point source pollution, non-point pollution, sedimentation profile, latitude, ecohydrology

Sumário

1. Introdução geral

A água, o solo e a cobertura vegetal são componentes fundamentais da paisagem e determinam a produtividade da terra. O desflorestamento em larga escala, a urbanização e o desenvolvimento da infraestrutura resultante do rápido crescimento da população humana, e as suas aspirações, têm gerado grandes impactos sobre diversos ecossistemas, incluindo os aquáticos (Zalewski, 1992, 1995). Sabe-se que os ecossistemas variam ao longo de gradientes geográficos de clima, latitude, altitude e isolamento (Harper 2009). Pode-se dizer que um ecossistema está sujeito a diferentes graus de perturbações naturais de sua região (ex. regime de chuvas, fogo, marés). Portanto, a níveis locais e regionais existem várias formas de perturbações ambientais que afetam a biodiversidade de uma região. Porém, muitas vezes, os impactos antrópicos vão além da capacidade de suporte do meio ambiente. Este é o resultado de efeitos sinérgicos cumulativos de processos globais (alterações climáticas) e regionais (por exemplo, chuvas ácidas), com vários impactos locais (poluição, extração excessiva de água).

A poluição pode ser definida como a entrada, direta ou indiretamente, de substâncias ou de energia no meio, causada pela ação humana, resultando em efeitos nocivos aos seres vivos (Sciortino et al. 1999). Assim, podemos classificar a poluição como de fonte pontual e de fonte não pontual (difusa). A segunda geralmente resulta do escoamento superficial no solo, precipitação, deposição atmosférica, drenagem, infiltração ou modificações hidrológicas. Os poluentes de fontes difusas são um grande problema ambiental, pois a identificação de sua fonte e o controle de sua entrada no ambiente são difíceis. Enquanto que, qualquer fonte única e identificável de poluição (como saída de efluente por um cano ou chaminé) é classificada como fonte pontual. Assim, o controle de contaminantes emitidos por fontes pontuais é mais eficiente, pois eles são mais facilmente identificados. No entanto, a poluição pontual é frequentemente descarregada nos corpos de água e em alguns casos o tratamento desses efluentes não é totalmente eficaz, liberando contaminantes para corpos hídricos (Lester 1983).

As perturbações diárias podem causar alterações em um ecossistema que foi moldado evolutivamente por perturbações sazonais (Margalef 1968, Poff 1992). Por exemplo, a descarga contínua de efluentes pode causar alterações espaços-temporais na rede trófica de uma bacia hidrográfica em que chuvas sazonais predominam (ou seja, entrada de material alóctone por escoamento superficial em um período definido no ano). Assim, este fenômeno estacional pode perder a significância em consequência das entradas frequentes de materiais alóctones por fontes pontuais de poluição (Poff 1992). Diante dessa realidade, buscando aumentar a resiliência dos ecossistemas, através da melhoria da eficiência de diversos processos em lugares-chave, surgiram novas abordagens transdisciplinares. A Engenharia Ecológica e a Ecohidrologia são assim, alternativas para os problemas, promovendo uma gestão integrada com o propósito de harmonizar as necessidades da sociedade com o potencial da biosfera (Mitsch 1996, Zalewski 2000).

Considerando a problemática colocada, o propósito desse estudo foi avaliar o efeito das diferentes fontes de poluição na bacia hidrográfica do Lobo-Broa (São Paulo, Brasil), além de entender quais são os principais controladores da regulação abiótica-biótica (Zalewski and Naiman 1985) entre regiões e ecossistemas, com base nos princípios da Ecohidrologia. Para tal, no primeiro capítulo, anteciparam-se possíveis diferenças na dupla regulação abiótica - biótica em águas interiores brasileiras em comparação a outras regiões e como as alterações antrópicas podem afetar as funções do ecossistema. No segundo capitulo, foram avaliados os níveis de vários elementos na água e no sedimento ao longo dos tributários e do reservatório para verificar as diferenças entre as duas fontes de poluição em diferentes estações do ano. No terceiro e último capítulo, avaliaram-se os efeitos temporais e espaciais de fontes pontuais e difusas de poluição e sua combinação na deposição dos sedimentos.

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2. Capítulo 1 - The role of Ecohydrology as controlling factor in neotropical regions.

4.1 Abstract

The unevenly distributed population in Brazil and in many developing countries pose challenges in the management and conservation of natural resources. The pressure of human expansion, either in concentration of inhabitants in megacities or on expansion of agricultural frontiers in potentially arable land, combined with pollution and amplification of the stochastic character of climatic processes has brought several changes in the environment, including in the water resources. In the last decades, the uses of ecosystem properties to restore aquatic ecosystems were frequent and divergent results were achieved among different regions. Nevertheless, harmonization of ecosystem potential with societal needs, towards the enhancement of ecosystem resilience, seems to be the most palpable alternative at present to achieve sustainable development. The purpose for this paper is anticipate how the use of ecosystem properties to enhance ecosystem resilience might differ in Brazil (tropical and sub-tropical climate). Therefore, a revision of established and newer concepts on freshwater ecosystem and attempts on restauration and biomanipulation among different regions and climates was performed. The output of this study indicate that despite several biogeographical differences (eg climate, geomorphology) hydrology seem to be the main factor that controls the primary and secondary production in rivers and lakes (reservoirs). The unpredictability hydrology in the tropics appears to decrease the expected effects of higher temperature. Therefore, to enhance resilience in tropical freshwaters integrated actions in accordance with hydrological stages are highly recommended.

4.2 Introduction

Latin America and the Caribbean Islands have 57 percent of the world's primary forests**,** however, South America still has the largest decline in forest area, being the conversion of forest land to agriculture and urbanization the main deforestation driver (FAO 2011)**.** Within the region, Brazil has 13% of the global forest area and the largest extent of tropical forest. It also possesses nearly 13% of the available fresh water on the planet (FAO 2011, ANA 2014). However, Brazil faces great regional differences both in social indicators and in natural resources. For instance, the South and Southeast regions have higher social indicators than the North and Northeast (WBG 2015). On the other hand, the Amazon River Basin contains about 80% of the Brazil superficial waters, but just 5% of its population. In Eastern Atlantic Hydrographic Region, where nearly 8% of the population lives in the capitals Salvador and Aracaju, has less than 0.4% of river waters (ANA 2014).

Despite gains in reducing poverty and deforestation of sensitive biomes over the last years, the country still faces challenges in combining the benefits of agricultural growth, environmental protection and sustainable development (WBG 2015).

In accordance with the Brazilian Panel of Climate Change, the global warming is already having significant effects in Brazil, increasing the frequency of alteration of rainfall and temperature patterns, extreme weather events such as droughts, floods, cold and heat waves (PBMC 2013). For example, in March 2004, Brazil experienced the first hurricane (Catarina) ever observed in the South Atlantic. Moreover, in the last 50 years, heavy rains in the south and southeast of Brazil have become more frequent (PBMC 2013). Accordingly, the main factors that contribute to increased vulnerability are: population pressure; disordered urban sprawl; poverty and rural migration; low investment in infrastructure and services; and problems related to governance with intersectoral coordination (PBMC 2013).

Another example is the recent and worst drought that struck São Paulo State in 80 years, affecting more than 12.3 million habitants (Escobar 2015). Such problem is recurrent in Brazil and is aggravated by the lack of understanding by the Brazilian scientific community and decision makers (Metzger et al. 2010).

In face of these pressures, a transdisciplinary approach emerged in order to enhance resilience of the ecosystems by improving efficiency of several processes in key sites. Thus, Ecological Engineering and Ecohydrology are new solving problems sciences that promote an integrative management tool to harmonize societal needs with biosphere potential (Mitsch 1996, Zalewski 2000). Most common actions to enhance ecosystems resilience front disturbances are: food web manipulation (e.g. top-down and bottom up control); hydrologic control; wetlands; denitrification barriers; and biogeochemical barriers are often are used for ecosystem restauration, mostly in temperate waters (Carpenter et al. 1987, Lake et al. 2007). In Brazil (and neotropics) – besides some punctual initiatives (Scasso et al. 2001, Lazzaro and Starling 2005) - little is known about biotic responses to hydrologic modifications (Pringle et al. 2000) and restauration of streams and lakes. Therefore, the purpose for this revision is anticipate possible differences in abiotic – biotic dual regulation on Brazilian freshwaters and how anthropogenic alterations can affect its ecosystem functions. Thus, the objective of this study is provide a review of established and new concepts and successful actions in other regions and theorize how it can fits to Brazil (tropical and sub-tropical climate).

4.3 Background

A wide range of climatic, geological, geomorphological and hydrological patterns shaped ecological interactions over time. Accordingly with ecohydrology principles (Zalewski 2000, Zalewski and Wagner-Lotkowska 2004), water and temperature are the main driving forces that shaped terrestrial and freshwater ecosystems dynamics. Thus, the hierarchy of controlling factors is: abiotic factors dominate the hydrology, however, when both are stable and predictable, biotic interactions takes places on controlling process.

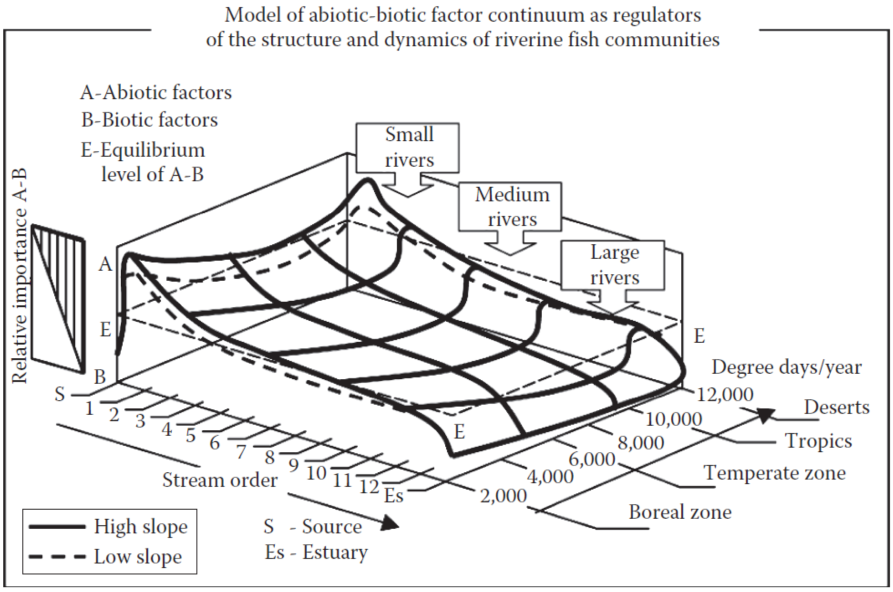

Fig 1. The model of the hierarchy of regulatory factors along the gradients of the stream order, thermal conditions, and slope. Thermal features of a river are presented from the point of view of fish physiological performance by degree-day per year, which is the sum of average daily temperatures. (From Zalewski, M. and R.J. Naiman., The regulation of riverine fish community by a continuum of abiotic-biotic factors, In Habitat Modification and Freshwater Fisheries, ed., J.S. Alabaster, pp. 3-9, Butterworths Scientific Ltd, London, U.K., 1985.)

Being temperature a catalyst for many processes, these processes might be more intense or significant in low latitudes. For instance, the ratio of decomposition are higher in higher temperatures, thus, nutrient cycling and organic matter recycling might be faster (Davidson and Janssens 2006).

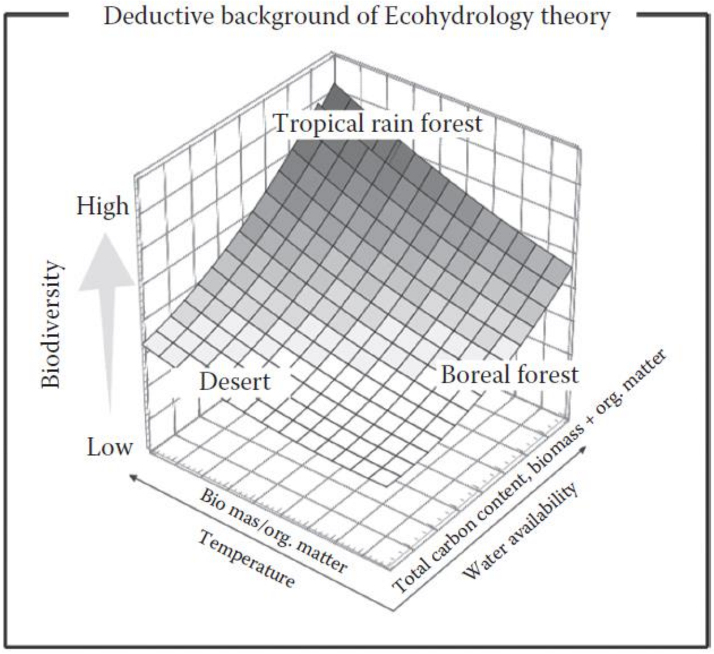

Fig. 2 The amount of water determines the amount of carbon accumulated in the ecosystem, while temperature determines the carbon allocation between biomass and soil organic matter. (From Zalewski, M., Braz. J. Biol., 70 (3 Suppl.), 689, 2010).

Therefore, knowing these significant processes is possible to make the most of their functions and then develop strategies to enhance resilience against a specific stressor. In the following we will discuss some possible differences between temperate and tropical climates in freshwater ecosystems. Because of the significant differences between lotic and lentic systems we separate the discussion into these two topics.

4.4 Rivers and streams

In Brazil, rivers can flow through landscapes as varied as evergreen rain forests (Amazon and the Atlantic rain forests), (semi)deciduous forests, savannah (cerrado), Araucaria forests, grasslands (campos) or semi-arid regions (caatinga). These wide biogeographic patterns (shift of climate, geology and geomorphology) will usually alter directly or indirectly some limiting factors for biotic communities. For example, channel orientation (east-west channels receiving much more light than north-south) and shading by riparian vegetation can affect light regime of a river (Davies et al. 2008). Morevoer, heterogeneity of habitat structure may play an important role in the maintenance of a diverse fish and invertebrate fauna in rivers. Ecotone determines habitat structures, access to light, and temperature, moreover, it regulates the nutrients and pollutants input (Agostinho and Zalewski 1995, Bis et al. 2000, Willis et al. 2005). On the other hand, regarding stream restorations there is no evidence that physical habitat heterogeneity is the primary factor controlling stream invertebrate diversity (Palmer et al. 2010). Shadding heterogeneity appears to be more effective on controlling biodiversity than only reconfiguring channels to enhance structural complexity (meanders, boulders, wood, etc.).

However, some patterns appear to be more clear in tropics. Tropical streams have higher mean temperature, higher insolation, more intense rainfall and thermally stable waters (Ward 1985, Lewis Jr 2008). Consequently, the direct effects of temperature in such higher metabolic potential and lower oxygen saturation in water are expected. Moreover, the tropics harbor a higher biodiversity than their temperate equivalents (Gaston 2000). Other expected differences are not clear in literature such as energy source, food-web structure, productivity, organic-matter processing and nutrient dynamics, and response to disturbance (Boulton et al. 2008).

Research in freshwater ecosystem has been guided by some ecological concepts, such as the river continuum concept (RCC) (Vannote et al. 1980), flood pulses concept (Junk et al. 1989) and riverine productivity model (Thorp and Delong 1994). Although these concepts fits with several cases (Bott et al. 1985, Heiler et al. 1995, Boedeltje et al. 2004), in some they do apply not (Tomanova et al. 2007, Jiang et al. 2011). This gap gives rise to new theories and concepts. The river wave concept summarizes and unifies previous rivers ecosystems concepts such as riverine productivity model, river continuum concept and flood pulses concept (Humphries et al. 2014). The river wave concept proposes that the hydrological disturbance proceeds over time behave like a series of waves. At the troughs of waves, which corresponds to low flow, local autochthonous and allochthonous inputs predominate; on the ascending or descending limbs of waves, which corresponds to rising or descending flood pulses respectively, upstream allochthonous inputs and longitudinal transport of material and energy predominate; and at crests, which correspond to bankfull floods, allochthonous inputs of material and energy and autochthonous production from the floodplain increase (Fig 3)(Humphries et al. 2014).

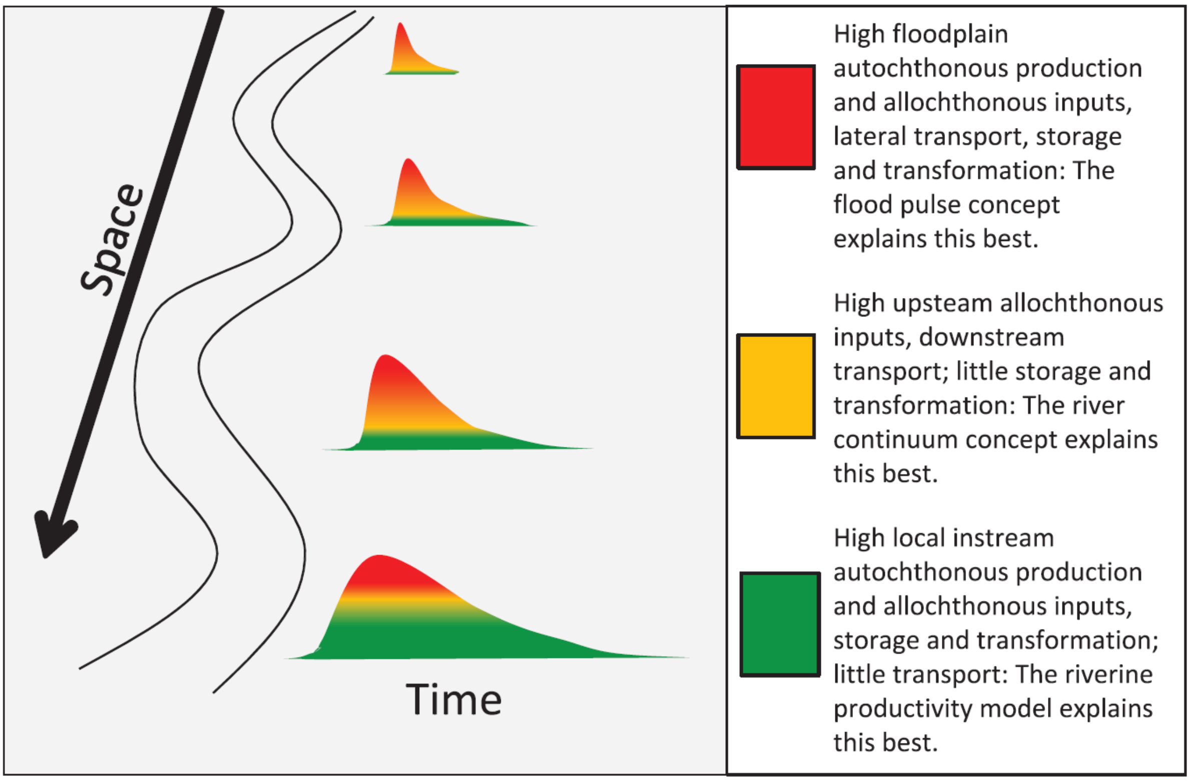

Fig 3. Hypothetical examples of the spatio-temporal variation of river waves and the relative importance of series of waves to autochthonous production, allochthonous inputs, transport, storage, and transformation of material and energy (From Humphries, P., H. Keckeis, and B. Finlayson. 2014. The River Wave Concept: Integrating River Ecosystem Models. BioScience.)

This concept may be the missing link between discrepancies found in the literature, for instance: for source of energy and food web composition. Some studies suggests that autochthonous production is the main source of energy in low order streams in tropics, instead of allochthonous input (litter) common in temperate streams (March and Pringle 2003, Brito et al. 2006, Lau et al. 2009). The possible explanations are higher insolation and temperature the low quality of the litter. Tropical leaves are more diverse, can be less palatable and nutritious; have higher levels of toxic and hard breakable compounds; and take more time to decompose (Loranger et al. 2002, Graça and Cressa 2010). These characteristics may be due adaption to intense herbivory in terrestrial landscape in tropics (Coley 1983) and it may affect the composition of shredders in tropical streams (Bastian et al. 2007). Some studies suggest that litter decomposition in tropics may be driven by microbial activity rather than insect shredders in tropics. Other, suggest that litter breakdown are similar with temperate counterpart, but are driven by omnivorous macroconsumers, such shrimps and crabs (Greathouse and Pringle 2006, Jardine 2014). However, shredder diversity may depend on elevation, water and riparian vegetation along altitudinal characteristics (Yule et al. 2009). Its large body size (higher biomass and less abundance) in tropics allow high-feeding efficiencies, including tough leaves, of these species, and large the body size might enable them to tolerate a wide variety of toxic secondary compounds (Yule et al. 2009, Tonin et al. 2014). Moreover, many species in tropics have omnivorous habits, are smaller in size, have a shorter life cycle and spawn (Paugy 2002, Sarma et al. 2005). Thus, trophic replacement in food web is supposed to occur more often.

Furthermore, our review indicates that hydrology plays a primary factor that characterizes the ecological processes of a river or stream. Hydrology (e.g. high-low floods) causes changes in water transparency, nutrient concentrations and residence time and it may causes misleading interpretation or even masks some effects such temperature or solar irradiation. For example, a study performed in 5 rivers (3 temperate and 2 tropical rivers) with a range of: hydrological regimes; turbidity levels; and nutrient concentrations, found that algal production is usually higher during periods of low discharge in all 5 rivers. The authors concluded that probably the absence of flood pulses and higher levels of nutrients improve conditions (higher water transparency) for primary production (Roach et al. 2014). The authors also found that the gross primary production varied seasonally, but it was faster during the months with highest temperature and greatest solar radiation.

In a study in the lower Mississippi river (along the main channel, a secondary channel, and two backwater lakes) showed that at higher river stages (high flows), hydrologic connected backwater lakes (shorter retention time) showed high turbidity and dissolved nutrient concentrations and low phytoplankton biomass and production, resembling the main river channel (Pongruktham and Ochs 2015). At low river stages (longer retention time) the authors found an increase in phytoplankton and a decline in dissolved nutrients due to decrease in backwater turbulence and turbidity. Moreover, a nutrient depletion and subsequently nutrient limitation state was found. The author hypothesized that autochthonous phytoplankton production is the primary route for energy flux to consumers in seasonally disconnected backwaters. Therefore, hydrologic periods seem to control the energetic dynamics.

However, despite speciation occurs due to shifts in climactic, geological and geomorphological patterns, some species traces may remain similar. In a study among temperate, Mediterranean semi-arid and subtropical rivers, Gallardo et al. (2014) found greater similarity among climatically different river floodplains in biological traits than in macroinvertebrate taxonomic composition. The authors also found positive relation between taxon and trait richness and peaked at sites of intermediate hydrological connectivity. Therefore, independently of taxa composition of a given region, traits analogies or convergence are expected as a function of hydrologic disturbances. For example, shredders and scrapers would be more abundant in connected channels, and predators and deposit feeders at isolated sites (Gallardo et al. 2014).

Both River Wave Concept (e.g. the position on the wave) and trait similarities provide important tools for Ecohydrology. Applying these tools for a specific stressor it is possible to predict in which hydrological stage it will be more harmful and then plan strategies to enhance ecosystem resilience. For example, regions with higher hydraulic retention time appear to behave as a biogeochemical transformation patches which remove/use nutrients for biological production (Pongruktham and Ochs 2015). It is similar at the trough of a river wave (i.e. low flow) and then instream management such as introduction of macrophytes, biogeochemical barriers or sedimentation chambers should be used. For ascending or descending flood pulse (i.e. ascending or descending limbs), where more longitudinal transport of material takes place, construction/restauration of ecotones to reduce diffuse pollution may be more efficient (Izydorczyk et al. 2013) and for high river stage (waves crest) restauration of floodplains and improvement of exchanges between the main channel and the floodplain should be considered.

4.5 Lakes and Reservoirs

Brazil has several small floodplain lakes throughout the Amazon River basin and in Pantanal and most of Brazil's large lakes are created by dammed rivers to produce hydroelectric power or to water supply. Tropical lakes have higher minimum annual irradiance and water temperature compared to temperate lakes (Lewis Jr 1996). Besides light regulation of photosynthesis, it is also is influenced by temperature and nutrients supply, then, primary production depends of other factors for maximum efficiency (Kimmel and Groeger 1984, Carpenter et al. 1985). Hydrology plays a key role in lakes/reservoirs dynamics, especially on controlling the primary production (O'Reilly 2006).

Tropical lakes and reservoirs also experiences frequent shifts in water level, nutrients levels and water transparency related periodic water mixing and flushing dynamic during the high-low flow (Hubble and Harper 2002, Loverde-Oliveira et al. 2009). Nevertheless, the behavior of some shallow tropical lakes is governed by different mechanisms (hydrological dynamics and water level) than those described by alternative stable states theory of shallow lakes (Scheffer and van Nes 2007, Loverde-Oliveira et al. 2009).

Some studies suggest that water residence time in reservoir is the main factor controlling phytoplankton biomass (Rangel et al. 2012, Silva et al. 2014a).

Differences in biological interactions appear to be more evident in lakes maybe due the less complexity and higher hydrological retention tim,. Tropical lakes tend to be more sensitive to the input of nutrients (Lewis 2000) and often have greater risk of long-lasting algal blooms and dense floating plant communities (Jeppesen et al. 2007). Some studies suggest that nitrogen limitation is more common in tropical lakes than in temperate lakes (Downing et al. 1999, Lewis Jr 2002), whereas others suggest that both nitrogen and phosphorus are equivalent as limiting factors (Elser et al. 2007). Higher efficiency in recycling nutrients is expected by higher temperature, more dynamic pattern of stratification and water mixing (Kilham and Kilham 1990, Lewis Jr 1996, Woods et al. 2003, Gudasz et al. 2010).

Plankton (phyto and zoo) has similar composition between temperate and tropical lakes (Lewis 1990, Fernando 1994, Sarma et al. 2005). However, the tropics appear to be more efficient in producing phytoplankton biomass (Kalff and Watson 1986, Attayde and Hansson 2001). On the other hand, zooplankton is smaller in size, which hinders grazing pressure on phytoplankton. Thus, zooplankton control over phytoplankton is weaker than in temperate lakes (Jeppesen et al. 2007, Arcifa et al. 2015). Omnivorous and planktivorous fish (e.g. Tilapia) and invertebrates (e.g. *Chaoborus*) suppress zooplankton community and favor phytoplankton grow, depressing water quality by increasing nutrients and turbidity (Pinto-Coelho et al. 2008, Menezes et al. 2010, Silva et al. 2014b).

Unlike in temperate lakes, macrophytes provides refuges to small fish instead of zooplankton, which avoid these plants in presence of predators, remaining without refuge in the pelagic column (Meerhoff et al. 2006, Iglesias et al. 2007). As in rivers, tropical lakes have several fast-recovering species (multivoltine, shorter life cycle and spawn), maybe due to high temperatures, the daily fluctuations in physical and chemical conditions or sudden environmental changes. It also has higher energy demand per unit biomass (Fernando 1994). Moreover, besides the greater biodiversity of fish, piscivores fish are generally small and thus not efficient in control grassers' pressure.

Because the examples cited above, biomanipulation is not expected to be effective in the tropics. Maintenance of a trophic cascade by piscivores introduction (top-down control) may be more difficult due to the trophic structure in tropical lakes. The relative small size of piscivores and the potential trophic replacement by omnivorous may not favor long-lasting zooplankton grow (Scasso et al. 2001, Jeppesen et al. 2007, Li et al. 2014). Moreover, the introduction of two exotic piscivorous fishes in lakes of the Middle Rio Doce (Brazil), caused a decrease in fish species richness, following by increased of *Chaoborus* populations which replaced the planktivorous fish as major consumers of herbivorous zooplankton (Pinto-Coelho et al. 2008). In other study, the appearance of another invertebrate predator (besides *Chaoborus)* resulted in a higher predation pressure on the smaller zooplankton species, leading to their virtual extinction in the limnetic zone. However, after 12 years, the zooplankton community structure was dominated by medium-size, *r* strategist and competitively superior species. Nevertheless, this relative higher sizer of zooplankton showed no evidence of controlling phytoplankton biomass (Arcifa et al. 2015).

Biomanipulation may reduce the nutrient release from the sediment in tropical lakes, but the dominance of small fish species and the improved growth conditions for cyanobacteria suggest that the effect will not be long-lasting, but see Gao et al. (2014) and Rao et al. (2015). Therefore, reduction of nutrient input in lakes still seems the best alternative for tropics but see Fulton et al. (2015), however, more research and clearly the scientific basis for nutrient threshold levels are needed.

4.6 Final Remarks

It seems reasonably clear that biotic strategy in the tropics led a greater number of species to be: omnivorous, small in size and to have faster life cycle and a greater number of spawns. This can be both: a function of non-predictable hydrology and lower temperature variations in the tropics. For rivers and streams, it is much more difficult to identify patterns between latitudes. Different levels of hydrological regimes, turbidity, energy source, nutrient concentrations and other biogeochemical filters seem to mask ecological processes.

Nevertheless, the ratio of decomposition, nutrient cycle dynamics, organic matter processing could be higher in tropics. Thus, managements to enhance ecosystem absorbing capacity against human impact should be more effective, if optimum conditions for the process are attained.

The river wave concept seems to be a resource to understand rivers across latitudes, allowing the prediction of the energetic dynamics of a river. Species trait characteristics can be a path to follow and to identify behavioral similarities between different regions and latitudes. The river wave concept can be a powerful tool in understanding the abiotic and biotic behavior in rivers at different hydrologic stages, for evaluation and prediction of impacts or for modelling future scenarios and to restore rivers.

Latitudinal (temperate and tropical) differences in biotic responses to abotic factors seem to be more visible in lakes than rivers in tropical temperate and tropical lakes. Phytoplankton biomass appear to be resilient (e.g. to top-down control) in the tropics and mainly controlled by hydrology and phosphorus concentrations. Another fact is that niche overlap decreases the efficiency of top-down control by zooplankton. Therefore, the best strategy to improve the environmental state still is to reduce the external nutrient load (Jeppesen et al. 2007). Apparently, freshwaters in the tropics are very sensitive to nutrients inputs, rapidly changing their physical and biological characteristics. However, more than that, hydrology (rainfall and flow regime, residence time, connection, internal loading) seems to be the mainly factor that drive freshwater responses in all latitudes. As Brazil has several floodplains or dammed river lakes (i.e. rivers connected with lakes and reservoirs), integrated actions in accordance with hydrological stages to enhance resilience in tropical freshwaters are highly recommended. Efforts should be directed first to hydrological alterations, followed by a control of stressors individually or in combination. Thus, it is important to determine in what hydrological stage the stressor may cause further disruption. For example: impact - agricultural runoff; stressor - nitrogen; input period - ascending and descending flows; disturbance period – low water stage; actions - denitrification barriers, ecotones restauration, in-stream biogeochemical patches. Balancing such actions might diminish the frequency of algal blooms that occurs in low water stages and input of suspended solids or nutrients during high stages. Much more is needed to be studied in the tropics and particularly in Brazil; for example, the increasing number of dams is a threat to endemic species and faunal migratory behavior, in addition to changes in floodplain process (Pringle et al. 2000). In a recent paper, Tundisi et al (2014) discussed the need to improve the use of ecohydrological principles to control reservoir operations (including the construction stages). By controlling the limnological factors (lower retention time, ecological downstream water flux – ecological linkage) and other structural measures the improvement and control of the integrity of the ecosystem can be achieved with less impact and better operational performances. Therefore, interventions must be made to prevent / improve / correct a current problem, however, it is necessary to consider the evolutionary time frames and manage actions that interfere the least possible with the evolutionary course of the ecosystem.

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3. Capítulo 2 - The effect of point and non-point source pollution in a watershed with well-marked seasons

2.1. Abstract

Recent years have seen a growing concern with suspended solids released or transported via local anthropogenic activities (i.e. point and non-point pollution source) to rivers and lakes. However, these impacts often occur simultaneously in a watershed, with input of a wide range of contaminants, hindering the evaluation of these impacts individually and combined. The objective of this chapter was to evaluate the influence of point and non-point sources of pollution in suraface, pore water and in sediment characteristics of a watershed with well-marked seasons. For this purpose, the concentrations of Cd, Cr, Fe, Ni, Zn, Pb, Al, Cu, Mn, Hg, As, Se, total phosphorus (TP), total nitrogen (TN) and ions in sediments and water were examined. Moreover, the concentrations of these elements in the fine fraction (<63 µm) of sediment were also evaluated. This paper shows that point pollution sources promote a high load of contaminants in sediments regardless the season. In addition, point sources input seem to be the main cause of reservoir sediment composition. Nevertheless, the levels of elements in the sediment varied periodically, according to the season and sources of pollution. Furthermore, hydrogeochemical characteristics of the reservoir, such as silt and clay, concentration of Al, Fe and Mn favor the retention of particular elements which have propensity to establish bounds or exchanges.

Keywords: point source pollution, non-point source pollution, sediment retention, metals, phosphorus, cations.

2.2. Introduction

The reduction of pollutant inputs from point and non-point sources in natural waters are now government's priorities for conservation of water resources word-widely (Palaniappan 2010). Generally, multiple stressors (point and non-point source) occur at the same time in a watershed (Ormerod et al. 2010). Although they are important pollution sources, there is a lack of information about the combined input of these pollution sources in watersheds, except for a few models (Santhi et al. 2001, Di Luzio et al. 2004, McCray et al. 2005). Usually, non-point source is related with seasonal surface runoffs by rainfall, irrigation or snowmelt, whereas, point source pollution come from identifiable inputs of wastes that are continuously discharged via pipes or drains into rivers and lakes. Stormwaters increase the amount of substances that reach the waterbodies but also some of the combined runoff with raw effluents can overflow the capacity of wastewater treatment plants (Lee and Bang 2000). Furthermore, even after passing through wastewater treatment systems, effluents still release heavy metals and organic matter in water bodies (Lester 1983, Imai et al. 2002, Karvelas et al. 2003). In addition, after the discharge, it is difficult to identify the fate of contaminants in the watershed.

Reservoir sediments represent a repository of most contaminants and elements carried by rivers and their content can be an indicator of watershed uses and the diverse impacts of human activities (Pita and Hyne 1975, Mulholland and Elwood 1982). These elements are usually adsorbed onto particle surfaces and settle to the bottom, providing a pool of contaminants that can be released to the overlaying waters through natural or anthropogenic processes, such as redox cycling, pH change, bioturbation or resuspension (Eggleton and Thomas 2004, Hwang et al. 2011). However, point and non-point source pollution have a wide range of contaminant characteristics. For example, municipal wastewater is composed of domestic, industrial and run-off waters from urban areas, while non-point source is usually composed by soil particles, organic matter, heavy metals (from natural source or not) and agrochemicals that adhere to sediment (Lee and Bang 2000). Therefore, well-marked seasonal rainfall period and element retention in sediment in the watershed might be suitable conditions to the adequate evaluation of both impacts.

The purpose of this paper is to assess the effect of point and non-point source pollution in the Lobo (Broa) Reservoir, São Paulo, Brazil. This reservoir was chosen because it has a well-marked dry-rainy seasons and soils characteristics that indicate it has potential to retain elements in its sediments (Chalar and Tundisi 2001). It also has two main rivers that are under influence of different sources of pollution. To answer the question, the extent and distribution of nutrients, heavy metals, ionic composition in sediments and surface water were evaluated. It was also examined if sediment retains elements with interrelationships between sediment grain size and element concentrations. Source, levels of elements and their transport according with seasons, are also discussed.

2.3 Methods

Site description

The study was carried out at Lobo-Broa Reservoir (Fig. 1), a freshwater reservoir located in the central region of São Paulo State, South-Eastern Brazil. It was constructed in 1936, originally for hydroelectric power generation, although tourism has been its main use in more recent years. Ecological research in the watershed and in the reservoir started in 1971 (Tundisi and Matsumura-Tundisi 2013). The tropical climate (Köppen: Cwa) presents typically dry (May–October) and wet periods (November–April). Annual precipitation is around 1500 mm per year. It is a small polymict reservoir where the two main forcing functions that drive the dynamics of the reservoir are precipitation and wind. For more details see Tundisi and Matsumura-Tundisi (2013). The reservoir has two main affluent, the Itaqueri River and the Lobo Stream, which receive different anthropogenic pressures (Fig. 1). The Itaqueri River receives continuous and point source pollution from wastewater treatment plant (WTP) of Itirapina City and a mining company. Until 2012 the WTP treated only 80% of the total city wastes, whereas Lobo Stream catchment receives pulses of diffuse pollution from agriculture.

Most soils of the Cerrado region are latosols. In general, these soils are deep, well drained and acid; also feature aluminum toxicity, high levels of iron and poor nutrient levels. The natural vegetation is predominantly cerrado (Brazilian savannah), gallery forests along the rivers and *Pinus* sp. and *Eucalyptus* sp. in the reforestation areas. There also are both permanent and occasional agricultural activities in the upstream area of the reservoir.

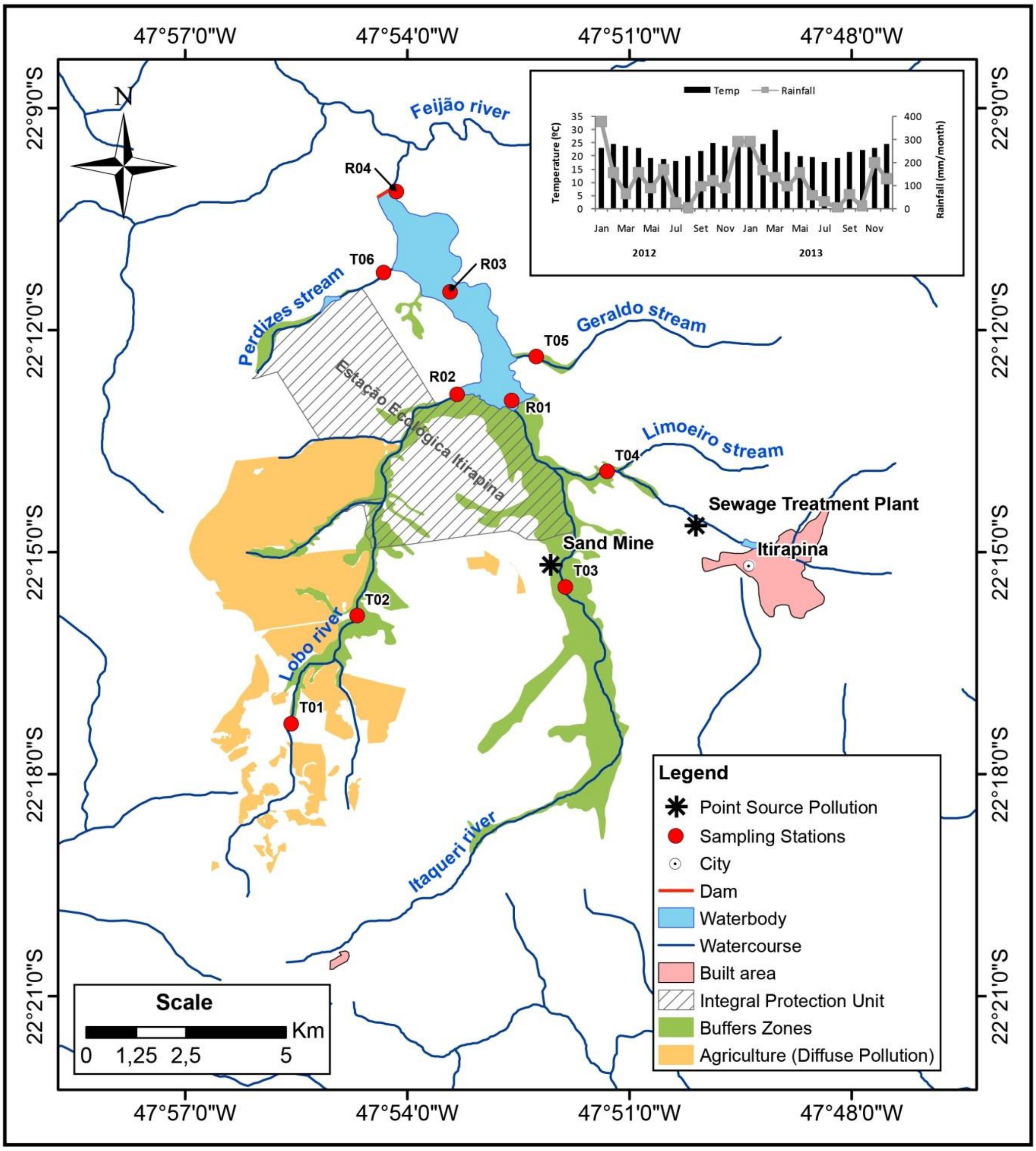

Fig 1. Map with locations of study sites. Six sample stations are located in tributary rivers (T01, T02, T03, T04, T05 and T06) and other four stations are in the reservoir (R01, R02,

R03 and R04). Stations in the Lobo Stream basin are in the left (T01, T02 and R02) and those in the Itaqueri River basin are on the right (T03, T04, and R01).

Sampling methodology and procedures

Samples were collected in August 2012 (dry season) and March 2013 (rainy season) in ten sites of the Lobo-Broa watershed, of which six of the stations are located in rivers and streams and four stations located in the reservoir (Fig 1). The sediment samples were taken using a gravity corer (Uwitec, Mondsee, Austria) with 60 cm long and 6 cm i.d. core liner in the reservoir stations, and a plastic spatula in the tributaries. Water physical and chemical parameters (pH, conductivity, turbidity, dissolved oxygen, temperature, TDS and ORP), were measured with an YSI multiparameter probe (model 6600 V2).

Water and Sediment analyses

The determination of metals (Cd, Cr, Fe, Ni, Zn, Pb, Al, Cu, Mn, Hg, As and Se) in the sediment samples were performed with a Varian, AA240 FS (Fast Sequential) atomic absorption spectrophotometer. An atomizer with an air/acetylene burner was used for determining all the investigated elements. For Cd, Cr, Fe, Ni, Zn, Pb, Al, Cu, Mn 500 mg of sediment samples were digested with a combination of hydrochloric acid and nitric acid. Hg concentration was determined by cold vapour atomic spectrophotometry with the presence of vanadium pentoxide. Arsenic and Se were performed by hydride generation. The organic nitrogen Kjeldahl (TN) in sediment and surface water was determined using the methodology described in SMWW (APHA 2005).

The total phosphorus (TP) in sediment and surface water was determined by spectrophotometry after ignition and digestion according to the methodology described by Andersen (1976).

Percent sand (> 850 – 63 µm), silt (63 - 4 µm) and clay (< 4 µm) were determined by standard sieving and pipette methods.

The sediment pore water was separated by centrifugation at 2500 RPM and the extract was carefully transferred to polyethylene flask. Thus, dissolved ions analyses made for pore water and surface water for fluoride, chloride, nitrite, nitrate, sulfate, sodium, ammonium, potassium, magnesium and calcium were performed by liquid ion-exchange chromatography (DIONEX DX-80 model).

Statistical analysis

It was used a two-way PERMANOVA to estimate the effect of season (rainy or dry season) and type of sample (tributary or reservoir) on physical and chemical features of water and sediment in the watershed. In the case of significant interaction between season and type of sample, a one-way PERMANOVA between all paired combinations of factor levels was applied; a Bonferroni correction was used to correct p values for multiple comparisons. The response variables tested were: percentage of fine grains, chloride, nitrite, nitrate, sulfate, sodium, ammonium, magnesium, potassium, calcium, Fe, Zn, Al, Cu, Mn, TP, and TN for sediments, and PT, sulfate, chloride, sodium, ammonium and potassium for surface water. The same approach was used to estimate the effect of season and type of sample in the catchments individually (Lobo and Itaqueri). Following the PERMANOVAs, a series of Two-Way ANOVAs were performed to find which explanatory variables (season x type, season x pollution source, type x pollution source) would better explain the elements pattern along the watershed. Data were transformed to natural logs (Ln+1) prior to analysis, and only data that showed normal distribution were tested. The covariance between metals, sediment particles size (percentage of <63 µm), TP, TN and ions was examined by means of the Pearson linear correlation coefficient. All analyses were performed in the software PAST v 2.17 (Hammer et al, 2001).

2.4 Results

Along the watershed, the concentration of elements varied according with season and water body type (lotic or lentic system), but also, interaction between then were observed (Table 1). Lobo Stream catchment (T01, T02 and R02) showed an increase in concentration for almost all variables analyzed in the rainy season compared with the dry season. Whereas Itaqueri catchment (T03, T04 and R01) showed higher concentration of almost all variables downstream of the point pollution sources (T04 and R01) regardless of the season (and sometimes higher than downstream station in reservoir). Downstream stations in reservoir (R03 and R04) showed high values in both seasons as stations that was polluted by point sources (T04 and R01) (Table 3 and 4). Thus, significant differences among season and pollution source or type (river or reservoir) and pollution source (point and non-point) were observed when stations T04, R01, R03 and R04 were analyzed as subjected to point sources and T01, T02, R02, T03, T05, T06 as subjected to non-point sources (Table 2). Better explanation were achieved using type x source (Fig 2), especially for sediments samples.

Table 1 - Results from the multivariate permutational analysis (PERMANOVA) of differences in season and type (river or reservoir) in the watershed, in the two main catchments and in the reservoir.

PERMANOVA	Season			Type			Season x type		
	Mean square	**F**	**p**	Mean square	**F**	**p**	Mean square	**F**	**p**
Watershed	85886	3.07	0.041	436105	15.567	0.0002	64197	2.29	0.09
Lobo catchment	13195	10.88	0.047	18961	15.64	0.09	15599	12.87	0.10
Itaqueri catchment	86681	11.70	0.125	2.25E+09	30.41	0.04	23181	0.31	0.16
Reservoir		25.48	0.116						

Table 2 - Results of two-way ANOVA testing associations in elements between river and reservoir and pollution source.

	Two-Way ANOVA		Season x type		Season x source		Type x source	
			F	p	F	p	F	p
SEDIMENT	Thin sediment	Factor A:	0.06	0.81	0.05	0.83	44.29	**5.53E-03**
		Factor B:	29.91	**5.15E-02**	21.97	**0.0002**	38.37	**1.29E-02**
		Interaction:	0.24	0.63	1.16	0.30	17.86	0.001
	Chloride	Factor A:	61.45	**7.21E-07**	36.80	**1.64E-02**	2.32	0.15
		Factor B:	11.88	**0.003318**	3.64	0.07	1.19	0.29
		Interaction:	5.37	0.03	0.26	0.62	0.94	0.35
	Nitrate	Factor A:	1.77	0.20	0.79	0.39	2.83	0.11
		Factor B:	6.65	**0.02**	0.29	0.60	0.28	0.61
		Interaction:	20.69	0.0003	3.12	0.10	1.09	0.31
	Ammonium	Factor A:	0.38	0.55	0.57	0.46	13.05	**0.0023**
		Factor B:	8.57	**0.01**	19.99	**0.0004**	20.40	**0.0004**
		Interaction:	0.0001	1.00	0.66	0.43	7.57	0.01
	Potassium	Factor A:	0.03	0.88	0.04	0.84	6.86	**0.02**
		Factor B:	5.24	**0.04**	18.30	**0.001**	15.21	**0.001**
		Interaction:	2.72	0.12	3.45	0.08	5.26	0.04
	Calcium	Factor A:	3.47	0.08	4.14	0.06	2.47	0.14
		Factor B:	2.97	0.10	6.53	**0.02**	4.54	**0.05**
		Interaction:	2.49	0.13	3.09	0.10	1.60	0.22
	Fe	Factor A:	0.96	0.34	0.92	0.35	38.21	**1.32E-02**
		Factor B:	23.86	**0.0002**	21.53	**0.0003**	35.80	**1.91E-02**
		Interaction:	0.18	0.67	1.05	0.32	18.81	0.001
	Al	Factor A:	3.29	0.09	3.06	0.10	32.51	**3.28E-02**
		Factor B:	27.43	**8.14E-02**	22.14	**0.0002**	28.23	**7.00E-02**
		Interaction:	0.15	0.7056	2.37	0.14	14.15	0.002
	Mn	Factor A:	4.10	0.05997	10.87	**0.005**	27.08	**8.70E-02**
		Factor B:	19.58	**0.0004243**	65.57	**4.74E-04**	34.19	**2.48E-02**
		Interaction:	0.41	0.5329	13.86	0.002	13.66	0.002
WATER	Nitrate (water)	Factor A:	1.44	0.25	0.88	0.36	6.68	**0.02**
		Factor B:	7.51	**0.01**	0.16	0.70	0.23	0.64
		Interaction:	3.73	0.07	0.54	0.47	4.03	0.06
	Ammonium (water)	Factor A:	0.15	0.70	0.12	0.73	2.92	0.11
		Factor B:	2.29	0.15	1.08	0.31	1.65	0.22
		Interaction:	2.63	0.12	0.35	0.56	3.75	0.07
	Potassium (water)	Factor A:	1.12	0.30	1228.00	0.28	0.30	0.59
		Factor B:	0.18	0.67	1.74	0.21	2.58	0.13
		Interaction:	0.12	0.73	0.08	0.79	8.30	0.01
	Chloride (water)	Factor A:	8.60	**0.01**	16.07	**0.001**	0.44	0.52
		Factor B:	0.37	0.55	14.59	**0.002**	9.15	**0.01**
		Interaction:	0.003	0.95	0.01	0.93	6.01	0.03
	Calcium (water)	Factor A:	1.17	0.29	1.15	0.30	0.39	0.54
		Factor B:	0.42	0.53	0.06	0.82	0.05	0.82
		Interaction:	0.64	0.44	0.64	0.43	0.35	0.56

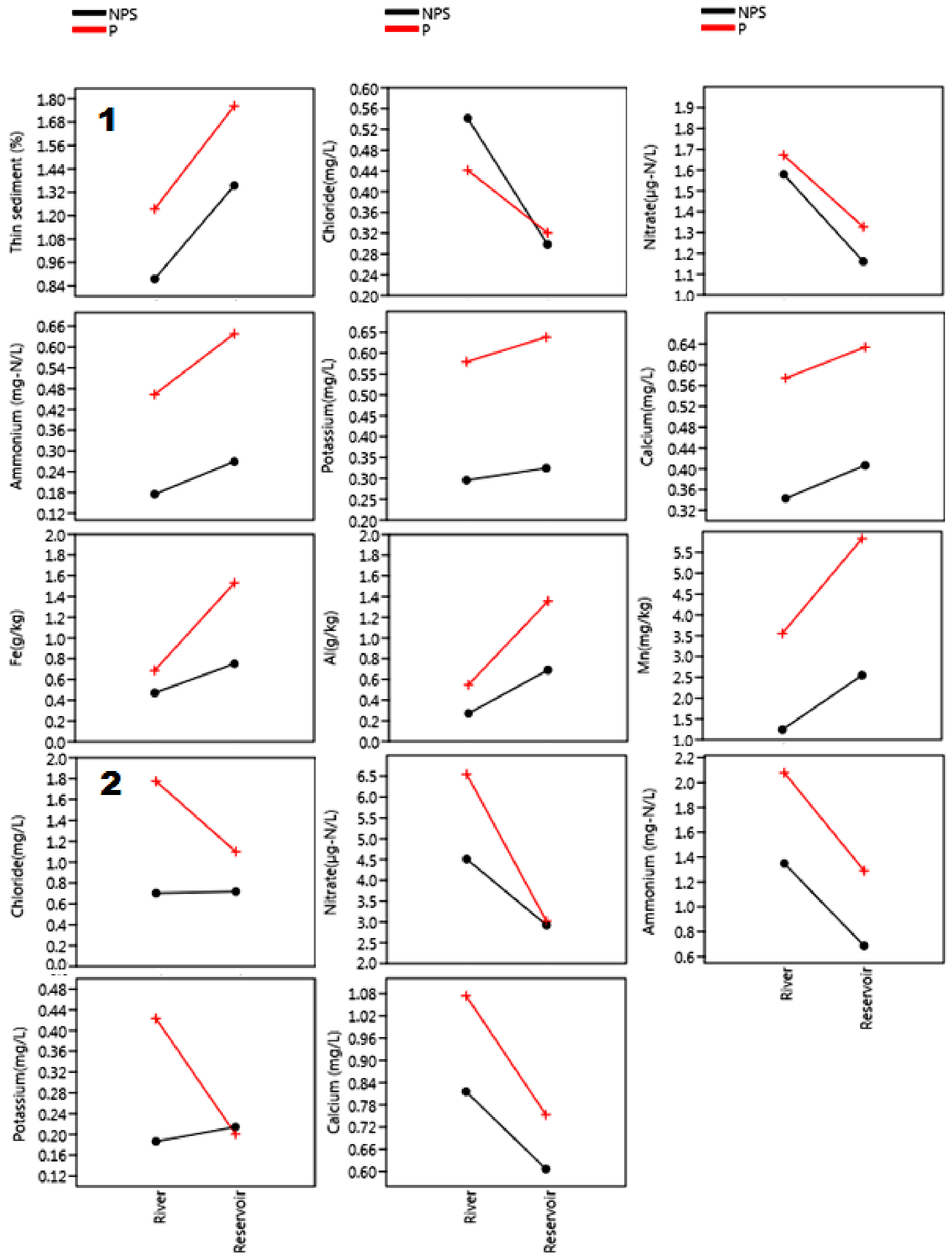

Fig 2 - Interaction plot from Two-Way ANOVA showing the response variable in function of explanatories variables (type x pollution source). In 1, the elements concentration in sediment is shown and, in 2, elements concentration in water samples. NPS = non-point source pollution and PS = point source pollution. Note that percentage of fine grains, cations and metals showed distinct pattern among sediment and water whereas anions (nitrate and chloride) showed similar patterns.

Table 3 - Ionic, nitrogen (TN) and phosphorus (TP) concentrations in the sediment and superface water in dry and rainy seasons at different stations.

ANION, NITROGEN AND PHOSPHORUS CONCENTRATION IN SEDIMENT

	Chloride (mg.L^{-1})		Nitrite (µg-N.L^{-1})		Nitrate (µg-N.L^{-1})		Sulfate (mg-SO4.L^{-1})		TN (mg.L^{-1})		TP (mg.L^{-1})	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Dry	Rainy	Dry	Rainy
T01	0.74	11.38	< D.L.	< D.L.	41.33	40.26	0.28	3.83	0.1	2.13	0.02	0.11
T02	2.09	5.32	< D.L.	< D.L.	40.34	50.67	0.25	0.33	0.13	0.13	0.01	0.04
T03	0.74	5.82	< D.L.	< D.L.	20.76	29.3	0.22	0.79	0.18	0.32	0.02	0.02
T04	0.45	4.26	< D.L.	101.64	20.67	100.76	0.31	0.45	0.96	0.58	0.17	0.36
T05	0.4	3.01	1.87	< D.L.	32.53	126.43	0.26	0.12	0.13	0.34	0.01	0.03
T06	0.35	5.84	< D.L.	255.6	18.34	29.73	0.2	0.61	0.2	0.32	0.01	0.02
R01	0.32	3.14	< D.L.	320.61	41.57	12.59	0.39	0.46	4.61	6.62	0.85	1.34
R02	0.82	1.17	< D.L.	125.24	22.73	7.84	0.46	0.77	0.28	5.7	0.01	1.07
R03	0.29	1.43	< D.L.	153.07	28.65	3.46	0.54	0.35	5.24	5.74	0.34	0.73
R04	0.49	2.29	0.37	278.65	193.53	5.13	1.92	0.39	3.88	2.47	0.66	0.78

CATION CONCENTRATION IN SEDIMENT

	Sodium (mg.L^{-1})		Ammonium (mg-N.L^{-1})		Potassium (mg.L^{-1})		Magnesium (mg.L^{-1})		Calcium (mg.L^{-1})	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
T01	3.86	13.16	0.23	0.25	1.14	1.71	1.87	0.08	4.33	0.66
T02	3.24	6.12	0.1	0.15	1.56	0.69	0.46	0.11	1.97	0.49
T03	2.21	5.91	0.01	0.45	0.04	0.96	0.2	0.55	1.03	2.49
T04	5.42	6.25	1.75	2.07	1.86	4.03	0.32	0.67	2.45	3.08
T05	2.08	3.57	< D.L.	0.18	< D.L.	0.58	0.06	0.1	0.75	1
T06	3.46	6.35	2.65	3.57	1.66	3.2	0.28	0.09	0.56	0.78
R01	8.65	4.13	4.59	2.7	6.28	2.71	3.81	1.01	12.83	0.84
R02	3.64	1.94	0.17	1.95	0.74	1.56	0.41	0.88	1.3	1.83
R03	4.94	2.69	3.87	2.86	3.86	1.85	3.39	1.75	8.88	4.18
R04	6.75	3.78	2.53	3.94	5.25	1.89	0.61	1.19	3.51	0.08

ANION, NITROGEN AND PHOSPHORUS CONCENTRATION IN WATER

	Sodium (mg.L^{-1})		Ammonium (mg-N.L^{-1})		Potassium (mg.L^{-1})		Chloride (mg.L^{-1})		TN (mg.L^{-1})		TP (mg.L^{-1})	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Dry	Rainy	Dry	Rainy
T01	2.36	2.4	36.11	32.01	1.04	0.58	1.18	0.8	0.92	0.2	50.77	48.91
T02	0.84	1.79	14.14	36.18	0.57	0.72	0.55	1.63	0.41	0.3	42.2	36.6
T03	0.71	2.44	3.28	20.41	0.75	1.03	0.5	3.17	0.31	0.41	31	60.41
T04	2.97	7.63	41.41	338.65	1.12	2.31	2.57	8.75	0.31	0.71	91.6	210.65
T05	0.3	1.56	7.32	28.99	0.04	0.45	0.12	1.95	0.2	0.2	24.1	24.19
T06	0.5	1.25	61.62	30.62	0.15	0.37	0.67	1.02	0.2	0.2	20.33	26.77
R01	2.46	2.48	5.81	12.99	0.96	0.84	1.68	2.31	0.51	0.61	69.2	55.7
R02	0.5	1.92	4.55	3.25	0.56	0.72	0.32	2.19	0.82	0.51	30.23	36.1
R03	1.78	1.62	40.91	3.25	0.35	0.47	1.75	3.5	0.51	0.41	42.77	33.45
R04	2.39	1.52	109.85	28.53	0.37	0.63	0.84	2.61	3.78	0.51	48.47	34.73

Table 4 - Metal concentration in sediment in dry and rainy seasons at different stations.

	Cd ($mg.kg^{-1}$)		Fe ($g.kg^{-1}$)		Ni ($mg.kg^{-1}$)		Zn ($mg.kg^{-1}$)		Al ($g.kg^{-1}$)	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
T01	< D.L.	< D.L.	1.81	4.62	< D.L.	< D.L.	< D.L.	5.08	0	2.58
T02	< D.L.	< D.L.	1.21	1.76	< D.L.	< D.L.	< D.L.	1.04	0	0.85
T03	< D.L.	< D.L.	0	1.86	< D.L.	< D.L.	< D.L.	1.32	0	1.36
T04	< D.L.	< D.L.	5.43	2.68	< D.L.	< D.L.	< D.L.	2.56	3.47	1.79
T05	< D.L.	< D.L.	3.18	2.77	< D.L.	< D.L.	< D.L.	0.66	2.26	2.16
T06	< D.L.	< D.L.	2.18	2.65	< D.L.	< D.L.	< D.L.	1.61	0	2.12
R01	< D.L.	< D.L.	18.95	12.12	< D.L.	15.08	29.16	64.44	13.74	14.51
R02	< D.L.	2.87	0.87	15.99	< D.L.	17.25	< D.L.	111.9	0	23.09
R03	< D.L.	< D.L.	30.44	28.37	< D.L.	10.75	< D.L.	23.5	17.16	15.19
R04	< D.L.	4.41	58.27	105.31	< D.L.	25.17	23.54	50.3	37.52	52.07
	Cu ($mg.kg^{-1}$)		Mn ($mg.kg^{-1}$)		As ($mg.kg^{-1}$)		Se ($mg.kg^{-1}$)		Hg ($mg.kg^{-1}$)	
T01	< D.L.	< D.L.	< D.L.	42.2	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	0.05
T02	< D.L.	< D.L.	< D.L.	7	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
T03	< D.L.	< D.L.	< D.L.	10.71	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
T04	< D.L.	< D.L.	55.4	20.65	0.05	< D.L.	< D.L.	< D.L.	< D.L.	< D.L.
T05	< D.L.	< D.L.	< D.L.	12.57	0.05	0.03	< D.L.	< D.L.	< D.L.	< D.L.
T06	< D.L.	< D.L.	< D.L.	3.43	0.12	0.09	< D.L.	< D.L.	< D.L.	< D.L.
R01	< D.L.	32.65	609.8	172.44	0.19	0.07	0.08	0.05	< D.L.	0.22
R02	< D.L.	39.81	< D.L.	162.54	< D.L.	0.11	< D.L.	0.1	< D.L.	0.46
R03	< D.L.	26.2	421.2	360.77	0.3	0.18	0.24	0.2	0.26	0.4
R04	< D.L.	44.35	304	318.05	0.34	0.2	0.08	< D.L.	0.2	0.25

Levels of percentage of fine grains, cations and metals, were always higher content in the reservoir and at stations under influence of point source pollution. The reservoir showed higher percentage of silt and clay (< 63 µm) (over 30%) and streams and rivers showed 90% of large grain, except the site R01 and R02 that showed 10.84% in rainy and 6.64% in dry seasons respectively (Fig 3). Stream and rivers presented values lower than 7% of fine grains, excepting the site T04 that showed 13.94% in the dry season. Increments of fine grains were observed in rainy season for stations influenced mainly for diffuse sources (Lobo Stream catchment, T03 and T06) and in dam (R04). Total carbon in sediments ranged from 0.113 to 0.0234 $mg.g^{-1}$ in the tributaries and 45.47 to 137.2 mg/g in reservoir in rainy season samples.

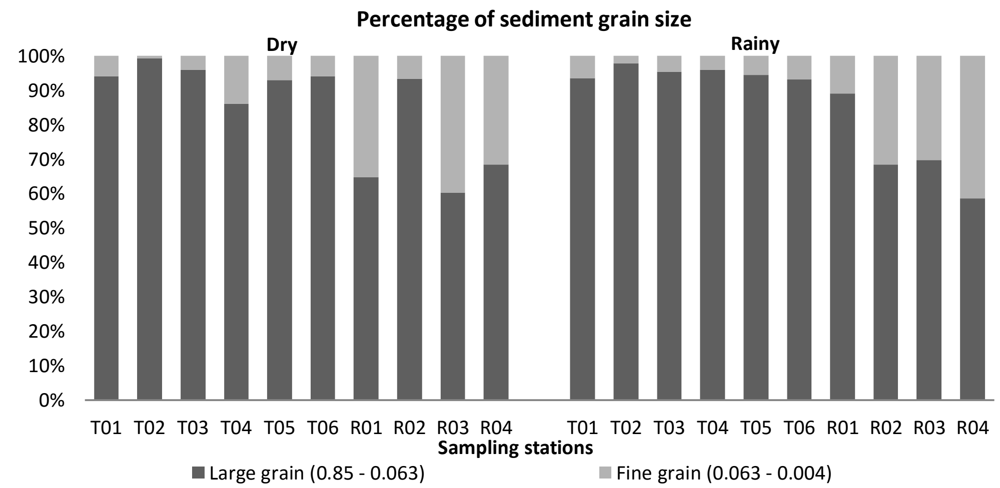

Fig 3 - Percentage of sediment grain size in dry and rainy seasons at different stations.

Stations downstream to the point source pollution releases (stations T04, R01, R03 and R04) showed higher levels of PT, TN, ammonium, potassium, magnesium, Fe, Al, Mn and As in sediment. The river sediments downstream of the WTP (T04) showed higher concentrations of Al, Fe, Mn, TN and TP than Lobo Stream mouth in the reservoir (R02) in dry season (Table 3 and 4). Nevertheless, Fe, Al and Mn were present in all stations samples. Presence of Cd, Ni, Cu, and Se were observed in reservoir stations,

Lower values of temperature, pH and redox potential were observed in the dry season (Table 5). With the exception the station R04 (near the dam), the water showed a high degree of oxygenation, positive redox potential and pH slightly acid. Therefore, suitable conditions to elements retention in the reservoir were observed.

Table 5 - Bottom water parameters in dry and rainy seasons at different stations.

		Temp (°C)	Cond (uS.cm^{-1})	TDS (mg.L^{-1})	pH	ORP (mV)	Turb (NTU)	OD (mg.L^{-1})
T01	Dry	17.7	4	30	6.7	168.1	13.4	8.2
	Rainy	24.6	69	45	7.1	241.4	12.3	5.7
T02	Dry	18.7	9	10	6.3	142.3	7.6	8.3
	Rainy	22.8	26	17	7.1	277.9	8.8	7.2
T03	Dry	17.2	16	10	6.7	176.4	11.5	8.3
	Rainy	22.6	24	16	7.2	216.2	16.6	6.5
T04	Dry	18.1	31	20	6.1	172.4	5.7	5.9
	Rainy	24.2	48	32	6.7	269.1	7.1	3.8
T05	Dry	17.8	9	10	6.2	161.6	6.3	7.8
	Rainy	22.5	10	7	7.2	304.1	7.4	6.9
T06	Dry	19.1	6	0	5.7	208	6.5	7.1
	Rainy	27.4	7	4	6.4	195	7.9	6.2
R01	Dry	16.5	26	17	6.2	199	9.5	8
	Rainy	31.3	17	11	7.4	196	9.8	7.8
R02	Dry	16.8	9	6	5.8	221	9.2	8
	Rainy	31.1	17	10	7.4	181.5	8.2	7.6
R03	Dry	19.7	13	9	7.4	191	17.5	9.1
	Rainy	26.6	19	12	7.1	273	11.4	5.3
R04	Dry	18.1	21	13	6.6	109	9.5	1.9
	Rainy	24.8	36	24	6.6	228	78.9	0.6

Correlations were observed among distribution of particles size, TP, TN, sediment pore water and metals in dry and rainy seasons in sediment (Table 6). All variables were correlated with fine sediment (<63 µm). Regarding the metals relationships with fine grains, Zn had the lowest correlation coefficient (0.48), As and Se above 0.60, and Fe, Al, Mn, Fe above 0.80. The major metals found in sediment (Al, Fe and Mn) showed strong correlations with other metals, TP, TN, ammonium and potassium (above 0.60), the exceptions was Al:potassium and Al:Se.

Table 6 - Correlation matrix between variables in dry and rainy season in sediment samples.

	Thin sediment (%)	Ammonium (µg-N.L^{-1})	Potassium (mg.L^{-1})	Magnesium (mg.L^{-1})	Calcium (mg.L^{-1})	Fe (mg.kg^{-1})	Zn (mg.kg^{-1})	Al (mg.kg^{-1})	Mn (mg.kg^{-1})	As (mg.kg^{-1})	Se (mg.kg^{-1})	Hg (mg.kg^{-1})	TP (mg.g^{-1})	TN (mg.g^{-1})
Thin sediment (%)		0.002	0.008	0.001	0.049	2.97E-02	0.03	2.29E-01	6.03E-02	0.001086	5.53E-01	0.000312	8.40E-02	8.41E-02
Ammonium (µg-N.L^{-1})	**0.64**		2.5E-02	0.004	0.29	0.0004	0.01	0.003	0.0001	7.53E-01	0.01	0.02	0.0036	0.0003
Potassium (mg.L^{-1})	**0.58**	**0.85**		0.01	0.08	0.002	0.02	0.01	0.0005	0.005	0.02	0.11	0.01	0.002
Magnesium (mg.L^{-1})	**0.66**	**0.61**	**0.55**		0.001	0.04	0.13	0.08	0.005	0.06	0.002	0.04	0.003	0.02
Calcium (mg.L^{-1})	**0.45**	0.25	0.4	**0.67**		0.39	0.93	0.57	0.11	0.49	0.01	0.71	0.25	0.24
Fe (mg.kg^{-1})	**0.84**	**0.72**	**0.65**	**0.47**	0.2		0.004	9.19E-08	1.78E-03	4.04E-02	0.001	0.0001	8.40E-02	1.27E-01
Zn (mg.kg^{-1})	**0.48**	**0.57**	**0.5**	0.35	-0.02	**0.62**		0.001	0.001	0.07	0.03	0.005	1.49E-01	0.0002
Al (mg.kg^{-1})	**0.8**	**0.63**	**0.56**	0.4	0.13	**0.96**	**0.69**		3.18E-03	7.64E-01	0.001	2.46E-01	1.90E-02	4.27E-02
Mn (mg.kg^{-1})	**0.83**	**0.76**	**0.71**	**0.6**	0.36	**0.89**	**0.68**	**0.88**		0.001	0.0001	0.001	2.65E-03	3.02E-04
As (mg.kg^{-1})	**0.68**	**0.77**	**0.61**	0.43	0.16	**0.84**	0.41	**0.77**	**0.69**		0.001	0.01	0.02	0.002
Se (mg.kg^{-1})	**0.78**	**0.56**	**0.51**	**0.65**	**0.55**	**0.68**	**0.48**	**0.68**	**0.75**	**0.69**		0.0002	0.001	5.47E-01
Hg (mg.k^{g-1})	**0.72**	**0.5**	0.37	**0.47**	0.09	**0.75**	**0.6**	**0.8**	**0.7**	**0.6**	**0.74**		0.001	4.07E-02
TP (mg.g^{-1})	**0.77**	**0.62**	**0.59**	**0.62**	0.27	**0.77**	**0.81**	**0.8**	**0.88**	**0.5**	**0.67**	**0.7**		8.58E-03
TN (mg.g^{-1})	**0.82**	**0.72**	**0.64**	**0.52**	0.27	**0.81**	**0.73**	**0.84**	**0.91**	**0.64**	**0.78**	**0.79**	**0.86**	

2.5 Discussion

Point and non point pollution and its effect in reservoir

The effect of point and non-point source pollution can be observed by the variation of nutrients, metals and some cations concentration in the sediment along of hydrologic gradient of the watershed. As expected, Lobo Stream catchment (non-point source influence) showed higher concentration of elements in the rainy season probably due effects of runoff (Carpenter et al. 1998, Kato et al. 2009). Although less pronounced Itaqueri River catchment (because point source influence) was also under the influence of runoff and showed higher values for some elements in the rainy season. However, due the point sources pollution, the continuous effluent releases promote a high load of nutrients or other pollutants regardless of the season (Jirka and Weitbrecht 2005, Brooks et al. 2006). This is corroborated by the station upstream to the point sources (T03) that showed similar behavior as rivers and streams that are not impacted by point sources discharges (Lobo Stream catchment and streams T05 and T06).

Downstream stations R03 and R04 showed the same patterns in dry season of the stations directly affected by point sources (R01 and T04), suggesting that point sources inputs are the main source of local sediment composition in dry season. This is supported by the similar pattern between variables (Fig 2) when stations R03 and R04 were analyzed as influenced by point source pollution without the seasonal effect. Of course the reservoir also has influence of recreational activities and land occupation. Point sources pollution as main source of local sediment contamination were observed in rivers, lakes and estuaries (Owens et al. 2001, Ruiz-Fernández et al. 2002, Pardos et al. 2004).

Seasonality and pollution source

In this study, the continuous input of pollutants from point sources overrides the seasonal effects downstream the releases. Seasonality patterns in concentration of elements for water and sediments are better observed in rivers and streams than in the reservoir (Table 3 and

4), maybe due to the discussed continuous load of contaminants. Other factors may also have caused this pattern, such as differences in buffer zone integrity, and variation in nutrient transport pattern (Roth et al. 1996, Jobbágy and Jackson 2001, Stieglitz et al. 2003, Hickey 2004). Nevertheless, the high concentration of Al, Fe and TP in reservoirs and the increase of fine grain (and also TP for rivers) in stations under predominance of non-point sources pollution in rainy season indicates weathering and surface runoff (due to multiple land use). For instance, stations along Lobo Stream showed high increment of fine grains confirming the susceptibility of this river to agricultural runoff. Furthermore, Chalar and Tundisi (2001) showed correlation between total aluminum concentration and rainfall, indicating the allochthonous origin of Al in the Lobo/Broa reservoir.

Generally the grain size decreases in the direction of the transport (Mothersill 1969, Self 1977). Liu et al. (2013) and Zhao et al. (2013) also reported higher concentration of bio-available phosphorus and metals, respectively, in reservoir compared with tributaries. Meus dados

This is particularly important because the fertilization is done during or after planting in the rainy season, so the runoff can lead to a drastic sudden increase in levels nutrients (Berka et al. 2001, Kim et al. 2006). In Rivers, sediment plays a major role in the transport of phosphorus. Stone and English (1993) suggest that the combined export of fine-grained sediment from tributary rivers into Lake Erie may represent a large potential nutrient source for biotic uptake.

Source of elements and transport patterns

Three transport patterns to the reservoir can be identified according to the concentration of some elements in the sediment following hydrologic gradient (Fig 4).

First (A) is the cumulative increase of elements concentration from rivers and streams to the reservoir in the rainy season, while, in dry season, there is a decrease of elements concentration donwstream from the point source pollution. This can be observed for Ammonium, Calcium, Magnesium, Potassium, Mn, and TP. This result shows how the pollution sources differ in pollutant apport between seasons (Singh et al. 2005). The decrease of the concentration of these elements along the reservoir gradient in dry season, may be related to sedimentation, biotic uptake or water autodepuration (Foster and Lees 1999, Bernot et al. 2006), since these elements come from a single upstream source.

The second transport pattern (B) is found in the increase of metals (Fe, Al and As) from rivers and streams to the reservoir in both seasons. This result is probably related with watershed geochemistry and the drainage of these metals by river and streams and its trapping due the dam (Brune 1953). Similarities among soil-sediment such as grain size and low nutrients content in rivers sediments and high levels of Al and Fe (especially in the reservoir) are in accordance with (PRADO 1995, Leite 2014) that characterized the soil as having a high content of iron and aluminum, as well as a low base saturation. Therefore, weathering and surface runoff indicated that allochthonous source of energy are relevant in the watershed and correlation among elements with grain size, Fe and Al and will be discussed in the next topic below.

The third pattern observed (C) is the apparent source of Hg, Se, Cu, Cd, Ni and Zn from point and especially non-point sources in the rainy season (Buffleben et al. 2002). Here, it is difficult to define which metals are pollution or natural input from runoff from surrounding areas. Still, changes in land use, deforestation or exposed soils will increase the historical amount of suspended solids that reach water bodies.

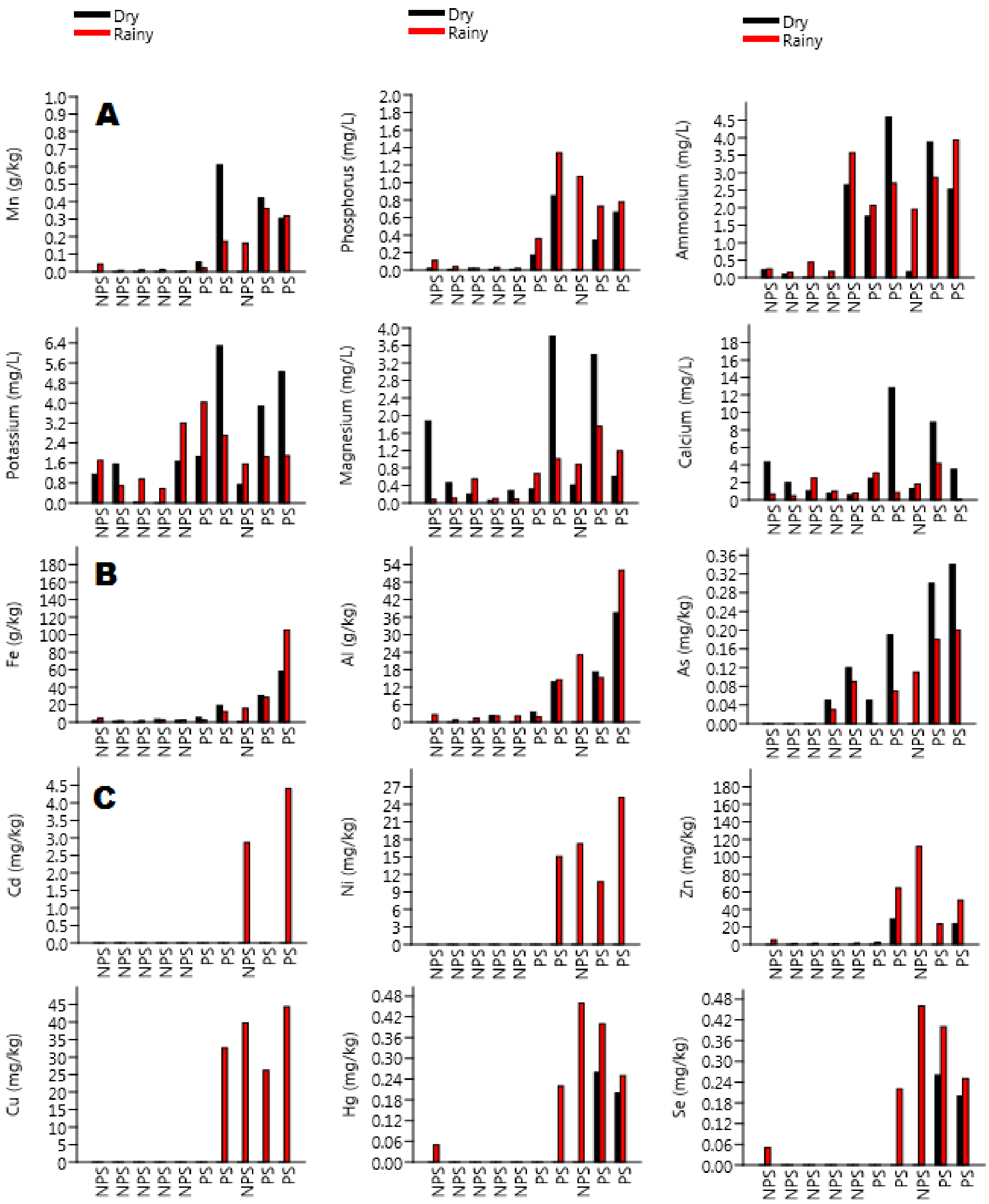

Fig 4 – Elements concentration in sediment along the watershed in function of pollution sources (NPS – non-point source, PS – point sources), from left to right, T01, T02, T03, T05, T06, T04, R01, R02, R03 and R04. In A, increase of elements concentration from rivers and streams to the reservoir in the rainy season and decrease downstream from the point source pollution in the dry season. B increase of elements concentration from rivers and streams to the reservoir in both seasons. C increase of elements concentration from point and non-point sources in the rainy season

Retention of elements

The watershed has favorable conditions for retaining elements in the sediment (Table 5). Fine grains (silt and clay) and the major metals found in sediment (Al, Fe and Mn) showed strong positive correlation and with other elements, thus, its variation co-varies the concentration of the other elements. Smaller particles (<63 µm) have the capacity to retain elements due to physical (e.g. grain size, surface area, surface charge) and chemical (e.g. composition, cation exchange capacity) characteristics (Horowitz and Elrick 1987). This effect is attributed to co-precipitation, adsorption and complexion of metals on particle surfaces. Several studies concerning processes of metal accumulation in sediments indicates that significantly higher metal concentrations occur in finer size fractions (Thorne and Nickless 1981, Tessier et al. 1982, Forstner 1989, Moore et al. 1989, Stone and Droppo 1996, Lin et al. 2002, Walling et al. 2003, Zhu et al. 2006, Roy et al. 2013). Thus the fine particles in the Lobo-Broa reservoir represent an important way of accumulating nutrients and pollutants in the system.

The strong correlation of the major metals (e.g., Al – 0.80, Fe – 0.84 and Mn – 0.83) with fine grains suggests that they also play an important role on sediment transport and retention. In this sediment size fraction, increased concentrations of Fe, Al and Mn most likely represent oxides and hydroxides which have scavenger functions. Therefore, the high correlation (above 0.60) of Al, Fe, and Mn with Zn, As, Se, Hg and TP should be a function of Fe, Mn and Al oxides. For example, in the The Hudson River Estuary Fe showed co-variances with Hg and Pb in superficial water (Sañudo-Wilhelmy and Gill 1999), suggesting that similar transport patterns of Pb and Hg from the watershed by continental runoff into the river is also provided by co-variances with Fe concentration which was the major soil constituent. Moreover, hydrous oxides of Al, Fe and Mn on particulate surfaces, under oxidizing conditions, are significant for concentrating of other metals (Whitney 1975, Tessier et al. 1982, Horowitz and Elrick 1987, Moore et al. 1989, Stone and Droppo 1996, Liu et al. 2006, He et al. 2012) and phosphorus (Stone and English 1993, Chalar and Tundisi 2001, Liu et al. 2013) in aquatic systems. Daskalakis and O'Connor (1995) verified that at least 50% of the concentration variations for the elements As, Cr, Cu, Ni, Pb, Sn, and Zn can be accounted for by co-variation with Fe or Al. Therefore, in the case of the Lobo-Broa reservoir, variations of Fe and Al also indicate the covariance of other elements.

In shallow lakes as Lobo-Broa reservoir, the whole water column is usually well mixed and oxidized with positive redox potential, which precipitates Al, Fe and Mn in oxides and hydroxides in the sediments. Organic matter, Al, Fe and Mn oxides bind to metals and P, retaining these elements in the sediment of the reservoir. Whereas pH and redox values remain in favorable conditions, these elements also will stay sorbed in sediments. PT correlation with these major metals also indicates surface runoff in the watershed or sediment post mobility in the reservoir. This is in accordance with Chalar and Tundisi (2001) who registered in Lobo/Broa reservoir dominance of Al bound P in sediment settling flux, in the other hand, where in the sediment bed was found a dominance of organic-humic bound P. The authors suggested the effect of bottom release of inorganic P (coming from allocthonous Mn, Fe and Al bound P) to the water column, by wind resuspension and then re-settling associated with organic matter.

Furthermore, the organic matter is an important constituent because the grains are often coated by organic substrates which adsorb pollutants (Horowitz and Elrick 1987). Organic matter probably adhere on small size fractions and can bind phosphorus superficially. For example, the station R01 showed high concentration of TP and TN in summer (Table 3) in spite of less fine grain content (Fig 3), however, this station showed higher total carbon percentage (13.72%) compared with the other stations.

Opposite trends were observed for cations (ammonium, potassium, calcium) among sediment and water in rivers and reservoirs (Fig 2). This trends also may be due to the retention of these cations in sediments. The reason is due fine grain composed by colloidal clays, humic substances and iron and aluminum oxides have generally electrically negatively charged surfaces, which attract mainly with cations (Ronquim 2010). The absence of significance and correlation of anions (Table 2), and similar interactions trends of chloride and nitrate in sediment pore water and surface water (Fig 2) supports that anions have lower exchanges capacities in the watershed.

2.6 Conclusion

In the present paper the effect of point and non-point source pollution was investigated on the concentration of various elements and substances in order to understand the combined effect of these sources along the Lobo-Broa reservoir. Our results showed that in the catchment under non-point source pollution influence, the levels of elements varied according with the dry-wet season. On the other hand, in the catchment under the point source pollution influence the continuous effluents releases promoted a high load of elements in both season. Thus, the downstream stations under both impacts influence showed similar behavior as point sources pollution catchment (high levels of elements regardless of the season). Therefore, we concluded that the continuous point sources input seems to be the main driver of reservoir sediment composition due its frequent inputs. This is supported by the high levels of elements in the dry season and the non-apparent effect in the reservoir during the rainy season despite higher levels of elements in the catchment under non-point sources influence.

The reservoir has at least three sediment delivery tendencies, however its difficult to identify natural and antropic processes. In summary, species of elements and their levels vary according with pollution source and seasonality, and this is probably related to the hidrogeochemical characteristic of the watershed. For example, elements bound with fine grains and the major metals in soils and sediment (Al, Fe and Mn) may play an important role in instream or in allochthonous matter transport. In the same way, elements that have no propensity to establish bounds or exchanges - in this case, anions - will not have significant interactions in the watershed. Thus, allochthonous energy may be an important process in the ecological dynamics of the watershed in the rainy period. However, this seasonal phenomenon – that must have shaped the biological communities over time – may be losing it significance in consequence of the year-round inputs from point source pollution.

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4. Capítulo 3 - Spatio-temporal effects of point and non-point source pollution in a sub-tropical reservoir

3.1 Abstract

Contaminants are introduced into aquatic ecosystems from both point and diffuse sources and usually are deposited in lakes sediments. Often, contaminations by these two sources merge in the environment, becoming difficult to identify the sources and fate of contaminants in the watershed. Moreover, the combined effect of these sources on sediment profile is not well understood. The purpose of this study was to understand temporal and spatial effects of inputs of point and non-point sources of pollution and its combined effect on sediment deposition. For achieve the goals, sediment cores were collected in the output (mouth) of two tributaries rivers under different impacts - point and non-point source of pollution – and downstream in the reservoir. Sediment profiles were analyzed each 1 cm for Fe, Al, Mn, Cu, Zn, Hg and As and generalized additive models (GAM) were used to predict the combined effect of both impacts. Our results showed that the sediment profile of point and non-point pollution catchments has distinct pattern of metal distribution. Each metal similarly oscillated along sediment profile in the catchment affected by non-point source pollution, whereas, levels of Fe, Mn and Al increased in upper sediment layer for point source pollution. Downstream stations showed more similar distribution shapes with point source pollution catchment. Moreover, prediction with both catchments combined showed an increase tendency of Fe and Mn levels as point sources catchment and downstream stations. We concluded that point sources influence all reservoir due to continuous discharge of contaminants while non-point sources contribute with periodic concentration peaks in sediment profile.

3.2 Introduction

Diffuse pollutants are a major environmental problem worldwide (USEPA 2002, EEA 2015), while the control of point sources is more efficient because they are more easily identified. However, since the point source pollutants are often continuously discharged into water bodies, effluent treatment is often not fully effective, and heavy metals and organic matter are released to waterbodies (Lester 1983, Imai et al. 2002, Karvelas et al. 2003). Thus, the concentration of pollutants released into rivers and then deposited on reservoirs may progressively increase over time if the pressures also increase (Ruiz-Fernández et al. 2002, Vörösmarty et al. 2003, Brooks et al. 2006). Non-point source pollution originates from multiple sources (runoff from rainwater, snowmelt, irrigation, atmospheric deposition) over an area and eventually will reach water bodies (Duda 1993). Althought the release of contaminants is often continuous on point sources, this kind of contamination is more periodic or seasonal for non-point sources, depending mainly on climatic events (e.g. rainfall regime) (Young et al. 1989, Fujioka 2001). The input of these types of contaminants often occurs at the same period and merges in the environment, hampering the identification of the fate of contaminants sources in the watershed (Albek 2003, Ormerod et al. 2010). Moreover, biological and chemical interactions contribute to pollutant transport and distribution (Bryan and Langston 1992, Eggleton and Thomas 2004, Hwang et al. 2011). Based on these temporal patterns of input and accumulation of heavy metals we can also generate models for other elements, and create strategies to mitigate the adverse effects of these sources of contamination(Zalewski 2000, Mitsch et al. 2001). Furthermore, the combined effect of these sources on sediment profile is poorly understood.

Sediment profiles can record past anthropogenic pressures on the watershed and give information about previous impacts. Accordingly, metals can be suitable indicators of environmental pollution (Hakanson 1980), and although their natural background levels and presence in types of both impacts, metals can give valuable information about the temporal frequency of sediment deposition and their combined pattern resulting from both impacts (Vink et al. 1999)

The objective of this study was assess temporal and spatial effects of point and non-point sources of pollution on sediment deposition. For this purpose, we sampled the sediment profile at the mouth of two tributaries from a reservoir subject to point and diffuse sources of pollution associated with different anthropogenic impacts. Moreover, we used Generalized Additive Models (GAM) to model the individual and combined effect of both types of pollution on the sediment profile.

3.3 Methods

The study was carried out at Lobo-Broa Reservoir, a small polymictic reservoir in São Paulo State, Brazil (Fig 1). The tropical climate exhibits well-marked dry (May–October) and rainy periods (November–April), and the mean annual precipitation is around 1500 mm. The reservoir has two main tributaries, the Itaqueri River and the Lobo Stream, which receive different anthropogenic pressures (Fig. 1). The Itaqueri River receives mainly point source pollution from a Wastewater Treatment Plant (WTP) located on the surrounding city (Itirapina, 15.524 hab), which until 2012 treated only 80% of the total city sewage, and from a sand mining company. In contrast, the Lobo Stream receives diffuse pollution from agriculture.

Sampling methodology Sediment analyses and procedures

Sediment cores were collected in four sites of the Lobo-Broa reservoir in March 2013 (see Fig. 1) using a 60 cm gravity corer (Uwitec, Mondsee, Austria). The sediment was sliced each 1 cm and each station obtained the following length: Itaqueri 23 cm; Lobo 19 cm; MID, 22 cm; DAM, 23 cm. The level of metals in the sediment samples were made on a Varian Model

AA240 FS (Fast Sequential) atomic absorption. An atomizer with an air/acetylene burner was used for determining all the investigated elements. For Fe, Ni, Zn, Al, Cu and Mn Levels, 500 mg samples were digested with a combination hydrochloric acid and nitric acid. Hg levels were obtained by cold vapour atomic absorption with the presence of vanadium pentoxide and As quantification was made by hydride generation. The quantification was based on calibration curves of standard solutions of metals, determined several times during the analysis.

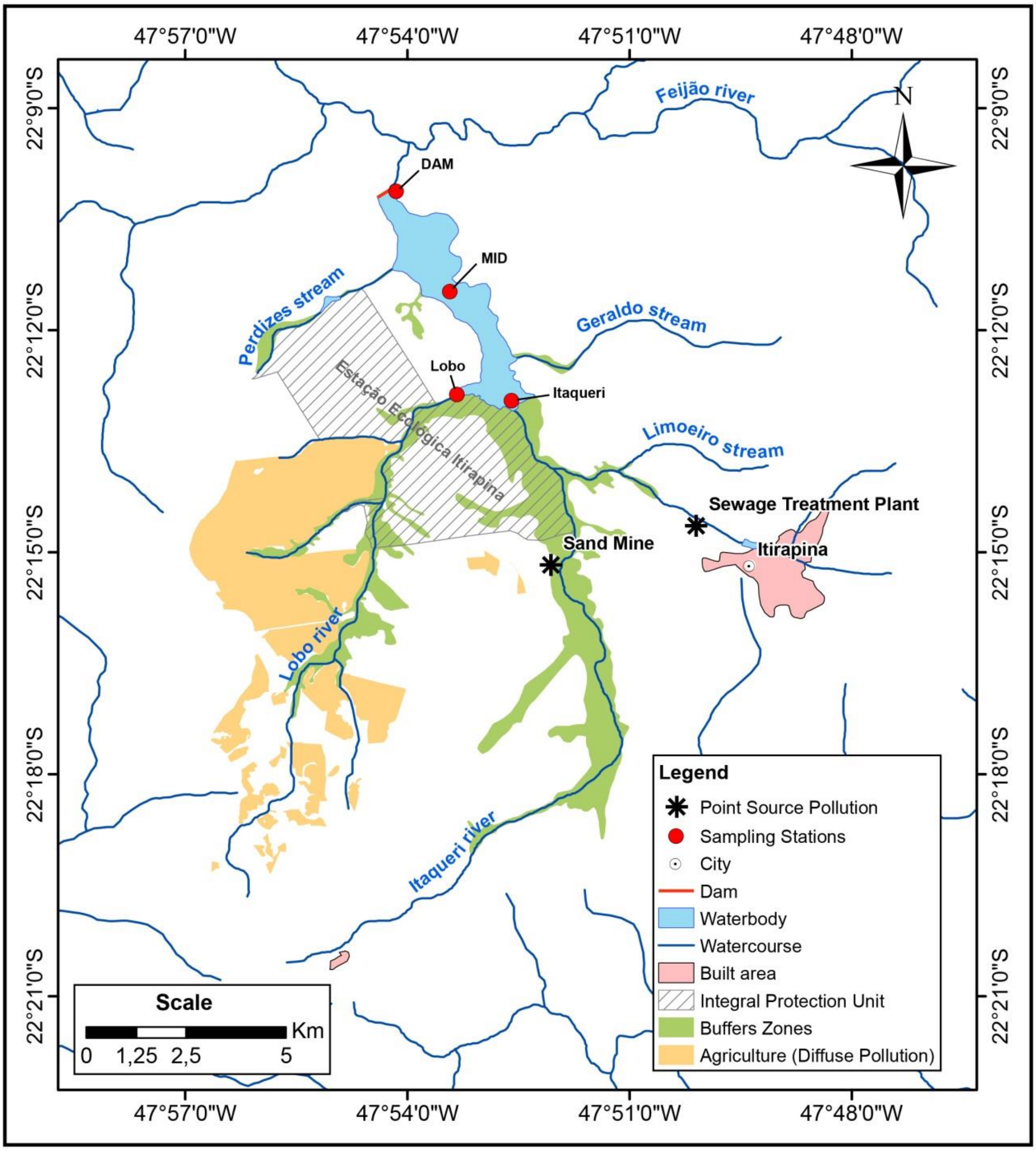

Fig 1. Map with approximate locations of study sites. Lobo Stream undergoes mainly agricultural impacts. Itaqueri River undergoes impacts mainly of effluent from a wastewater treatment plant (WTP) and sand mine.

Statistical analysis

We used Generalized Additive Models (GAM) to estimate the effect of depth on the level showed by each metal in the sediment of our sampling sites. Response variable consisted on the values obtained for each metal across the sediment profile, and the explanatory variable the corresponding depth. Effects of depth on the metal levels were estimated by non-parametric smoothing with the R package mgcv; smoothers were based on a penalized regression spline approach with cross-validation, and the final smooth terms were built from a k=-1 dimension basis (Wood 2011). We performed a GAM to each metal based on both catchments with different pollution source together (Itaqueri and Lobo) and for each point separately (Itaqueri, Lobo, MID, DAM). We used this approach for two reasons: first, to verify if both sources combined are responsible for the downstream sediment profile characteristics; and second, to avoid the calculation of unrealistic metals/depth smooth curves by GAM models based on stations with large differences in metal level. The covariance among the metals was examined by means of the Pearson linear correlation coefficient. We performed all analysis in the R statistical environment (R.Development.Core.Team 2014).

3.4 Results

According to the smoothing curves generated from GAM models the mouth of both rivers (Itaqueri and Lobo Stream) showed different patterns of metals concentration in the sediment profile. The non-point source catchment (Lobo Stream station) showed similar distribution shapes for all metals along sediment profile. The distribution was unimodal peaking at sediment depth around 14 cm for Fe, Al, Mn, Cu and As, at 10 cm for Hg and Zn, and from 8 to 3 cm for all elements showed either lower concentration or were absent (Fig 2). In contrast, in the point source catchment (Itaqueri mouth) the levels of Mn and Fe tended to increase continuously with depth, while Al, Zn and Cu increased from 10 to 1 cm and Hg showed waveform oscillation along the sediment profile (Fig 3). No Arsenic was detected in samples from the Itaqueri River.

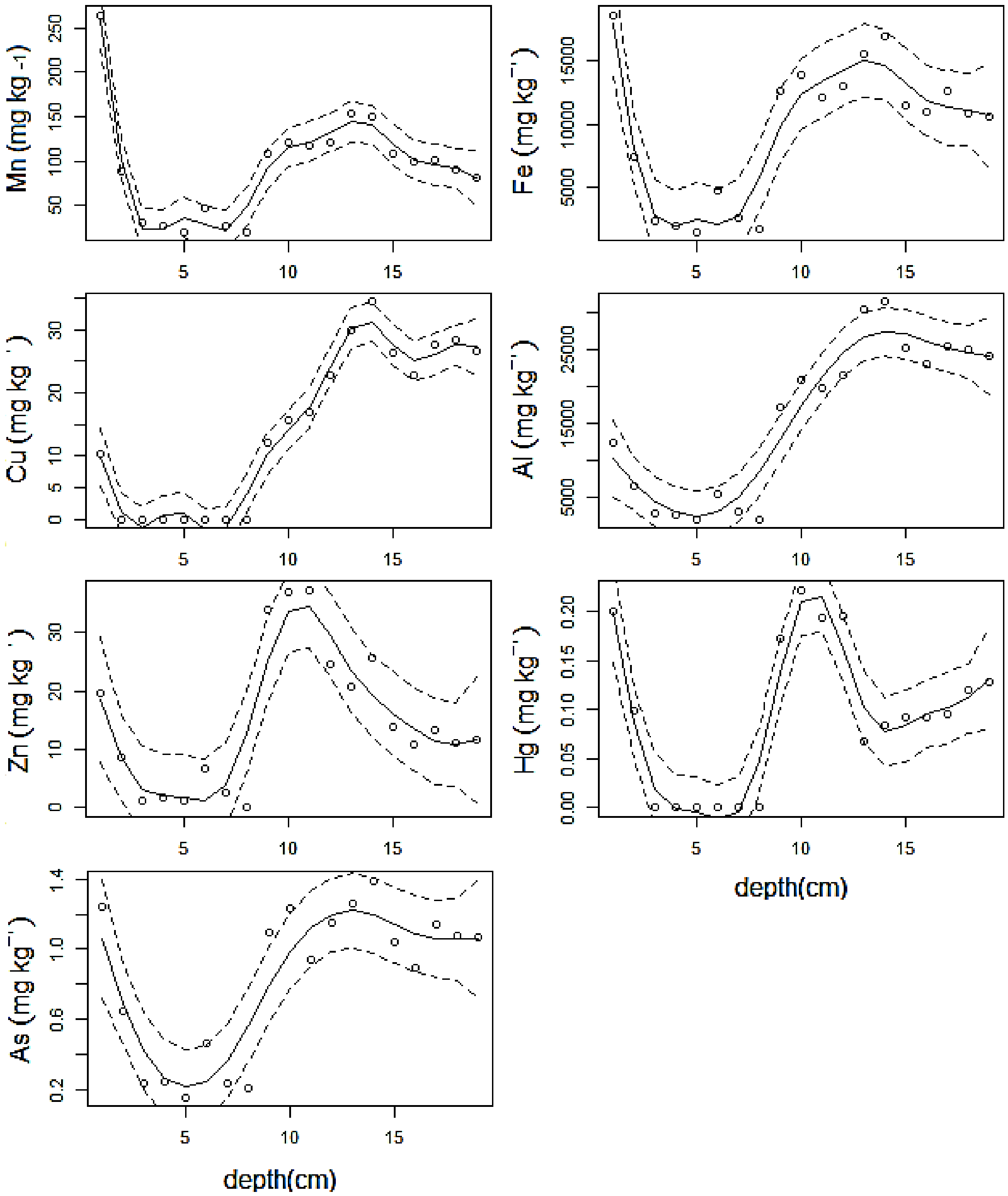

Fig 2. Smoothing curves based on Generalized Additive Models predicting the response of seven metals to the depth in the sediment profile, in a catchment mainly affected by non-point sources pollution (Lobo Stream mouth). Model predictions and confidence intervals are represented by solid and dashed lines, respectively. R-sq.(adj): Mn - 0.923; Fe - 0.839; Cu – 0.965; Al - 0.904; Zn – 0.763; Hg – 0.879; As – 0.772.

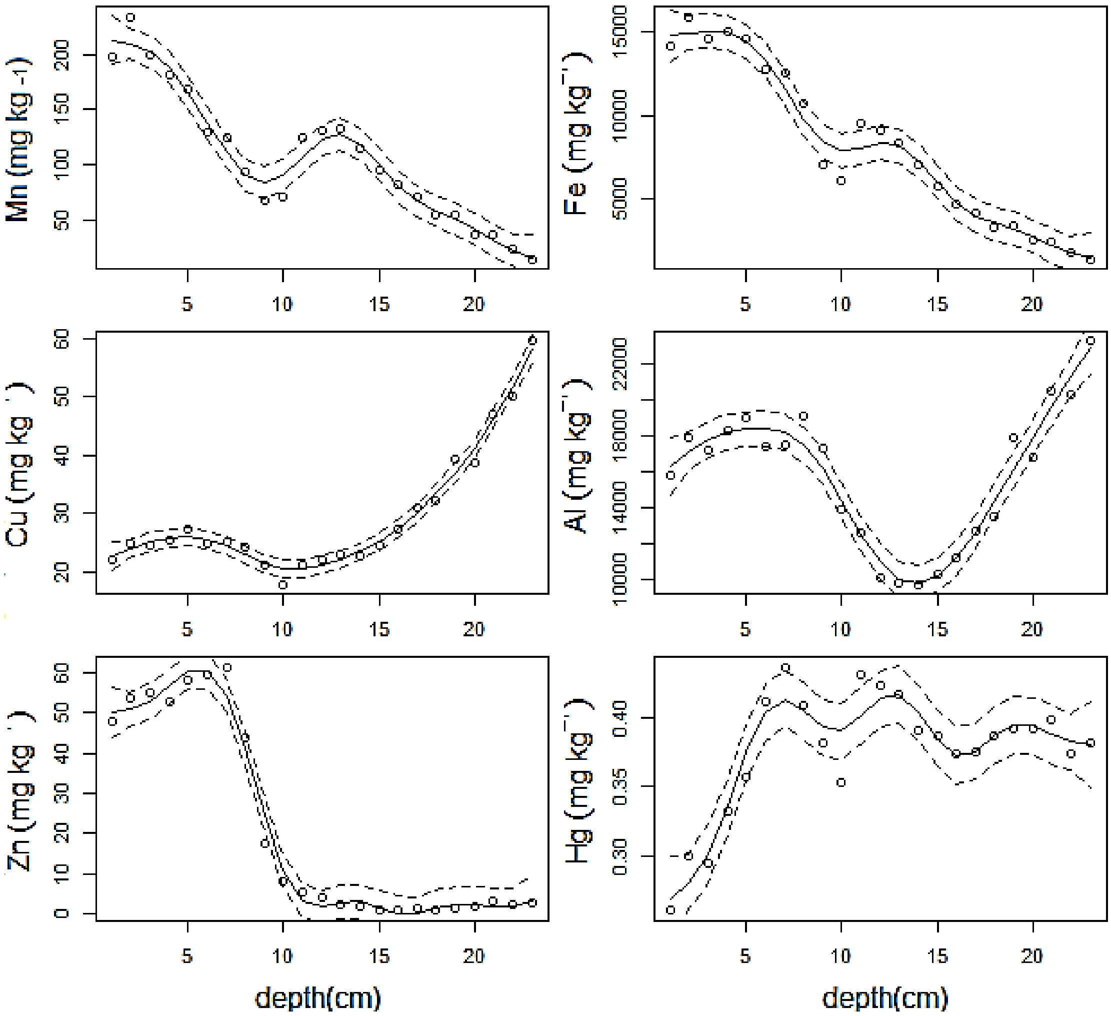

Fig 3. GAM models showing the distribution of metals with depth in the catchment mainly affected by point sources pollution (Itaqueri River mouth).Solid lines show the prediction made by the model and confidence intervals are shown by dashed lines. R-sq.(adj): Mn - 0.957; Fe - 0.966; Cu – 0.98; Al - 0.939; Zn – 0.98; Hg – 0.845.

In the downstream station of both sources, in the middle of the reservoir (MID), the concentration of Fe, Al, Zn and Mn in the sediment also increased from 22 to 1, whereas the Cu showed the same response from 15 to 1 cm. Hg concentration oscillated waveform from 15 to 1 cm. Here, Fe, Mn, Zn, Cu and Hg showed similar distribution shapes to that point source catchment (Fig 4).

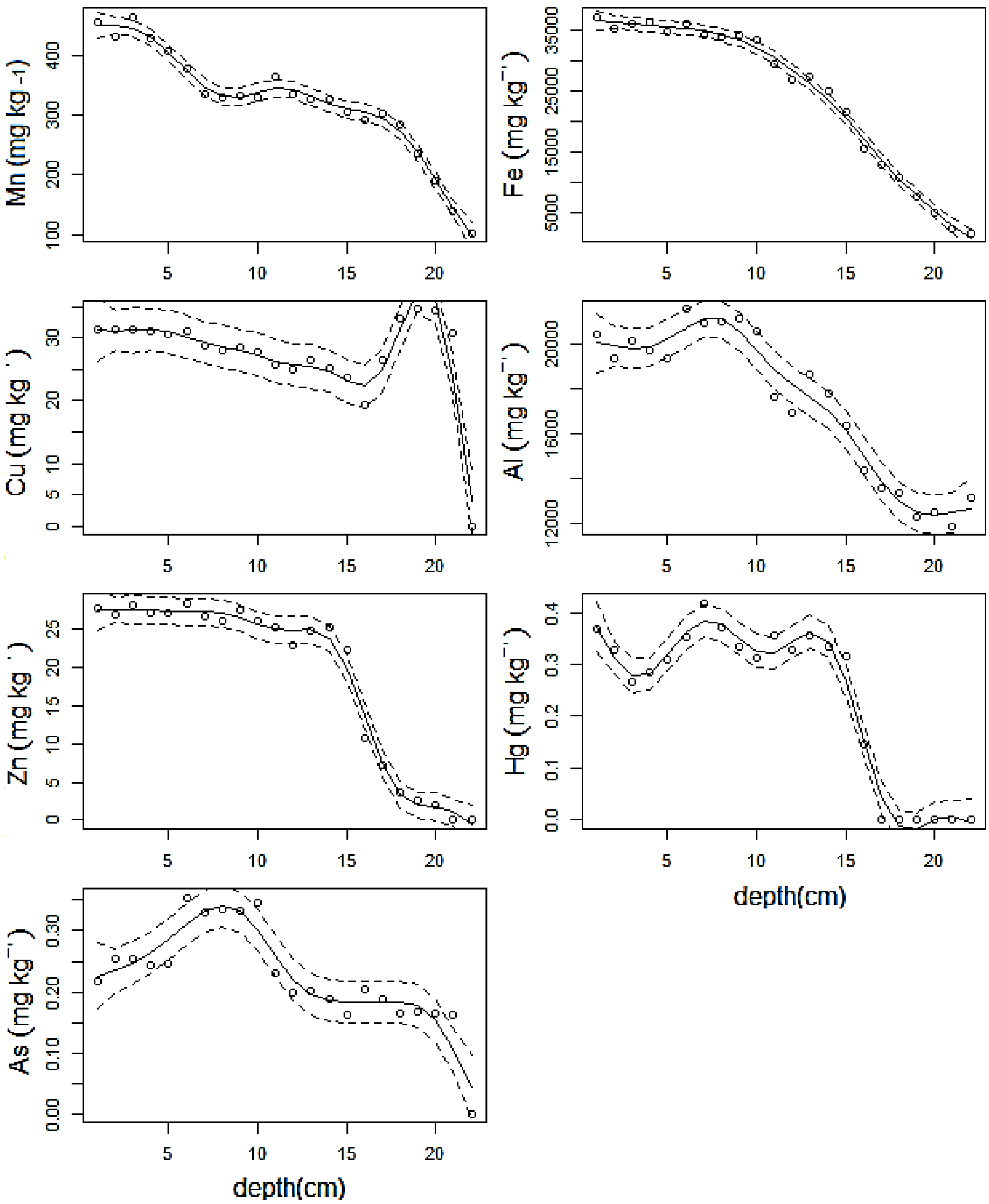

Fig 4.GAM models showing the distribution of metals with depth in the middle of the reservoir (MID).Solid lines show the prediction made by the model and confidence intervals are shown by dashed lines. R-sq.(adj): Mn - 0.983; Fe - 0.992; Cu – 0.854; Al - 0.946; Zn – 0.982; Hg – 0.973; As - 0.855.

In the DAM station, the only metals that showed a distinctive pattern along the sediment profile was Mn, which tended to increase linearly, and As, whose distribution oscillated waveform. Concentration of Al, Fe, Zn, Cu and Hg oscillated up and down each centimeter, making it difficult to establish a standard (pattern). Nevertheless, the DAM station showed the highest levels of Fe, Al, Zn and Cu (Fig 5).

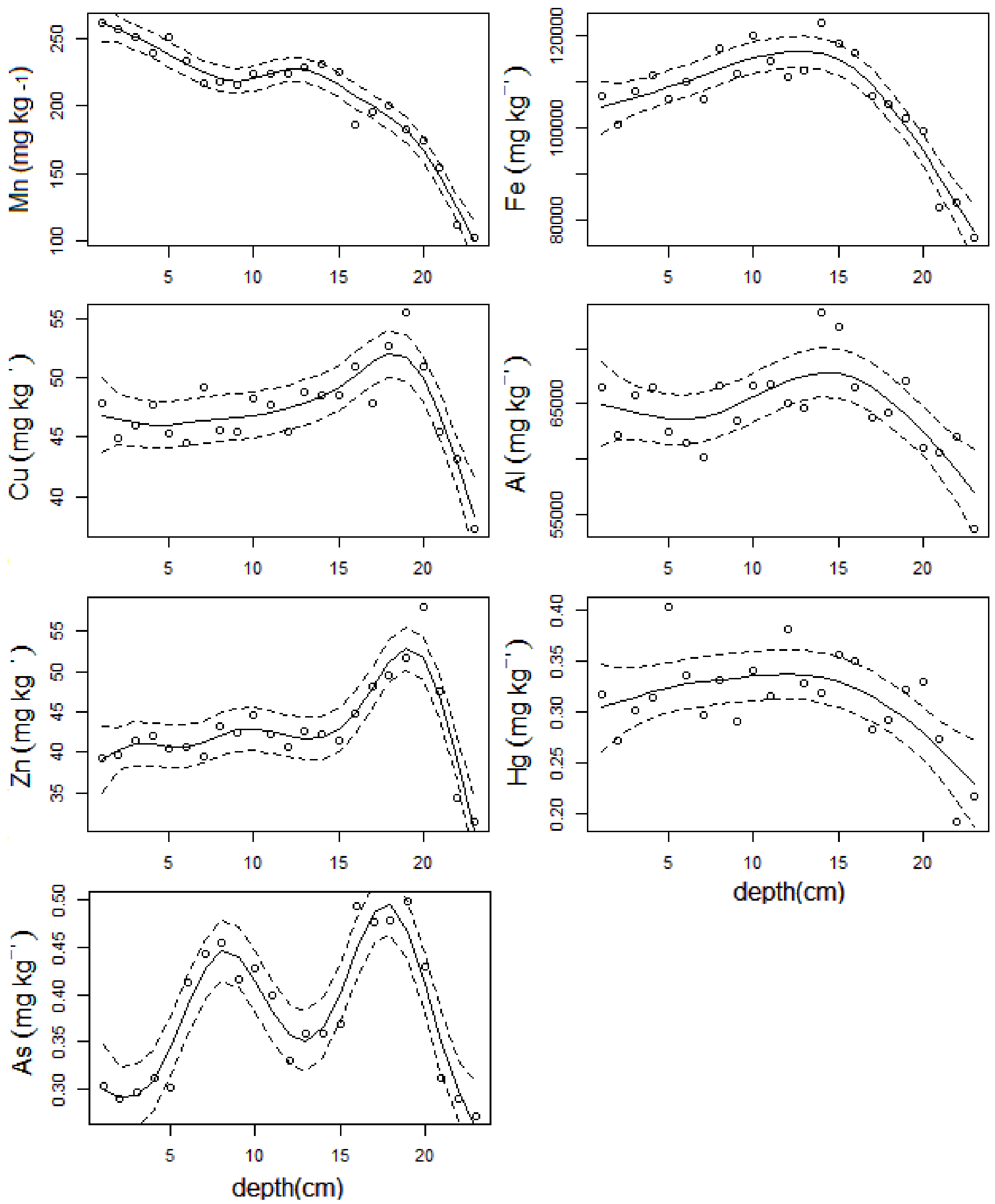

Fig 5.GAM models showing the distribution of metals with depth near the dam of the reservoir (DAM).Solid lines show the prediction made by the model and confidence intervals are shown by dashed lines. R-sq.(adj): Mn - 0.955; Fe - 0.876; Cu – 0.713; Al - 0.515; Zn – 0.814; Hg – 0.447; As - 0.862.

The concentration of metal across the sediment profile showed distinctive peaks in upstream stations Lobo and Itaqueri and downstream stations MID and DAM. The concentration of Mn peaked at 13 cm both in the Lobo and Itaqueri stations, whereas it peaked at17 and 11 cm in the MID station ; and at14 in the DAM. Cu; In Lobo, 14, in Itaqueri, rising from 9 to 5; MID, 20, 19 and rising from 15 to 1, and in DAM, 19.For Zn Lobo 11, 10 and 9; Itaqueri 9, 8 and 7; MID, 15, 14, 13 and constant; DAM, 20 and constant from 15 to 1.Despite that other peaks can be observed for other metals is difficult to identify whether these peaks were temporally correlated.

Predictions of the response of metal levels to sediment depth obtained from GAM models combining data from Lobo and Itaqueri stations showed mixed results, depending on the element considered (Fig 6). They showed a trend of increasing concentrations of Mn (R2 = 0.448) and Fe (R2 = 0.242) from 20 to 1 cm depth. This response for Mn is similar to that obtained in stations MID and DAM, whereas results for Fe are more similar to station DAM than MID. In contrast, this model combining both Itaqueri and Lobo catchments does not well explain variation of Al, Zn, Cu, Hg and As throughout the sediment profile. The Al was the single major metal, whose concentration did not show a continuous increase throughout the sediment profile of Itaqueri station. Prediction for Zn concentration in the sediment profile was the less similar to that observed in other points; despite increase with sediment depth, it does not adequately reflect the distribution for Zn in stations MID and DAM, which tends to become constant from 15 to 1. Beside a high R2 (0.60), response of Cu according to this model also differed from those obtained for the MID and DAM stations, since Cu was not detected in the sediment of Lobo station from 8 to 2 cm depth. Prediction for As were waveform as station MID and As was not detected in Itaqueri station. In DAM station, despite the up and down oscillation the model did not predict waveform smooth curves. Although Hg showed waveforms oscillations in Itaqueri and MID station, the prediction showed a descending line due to low and high concentration of Hg in Lobo and Itaqueri station samples, respectively.

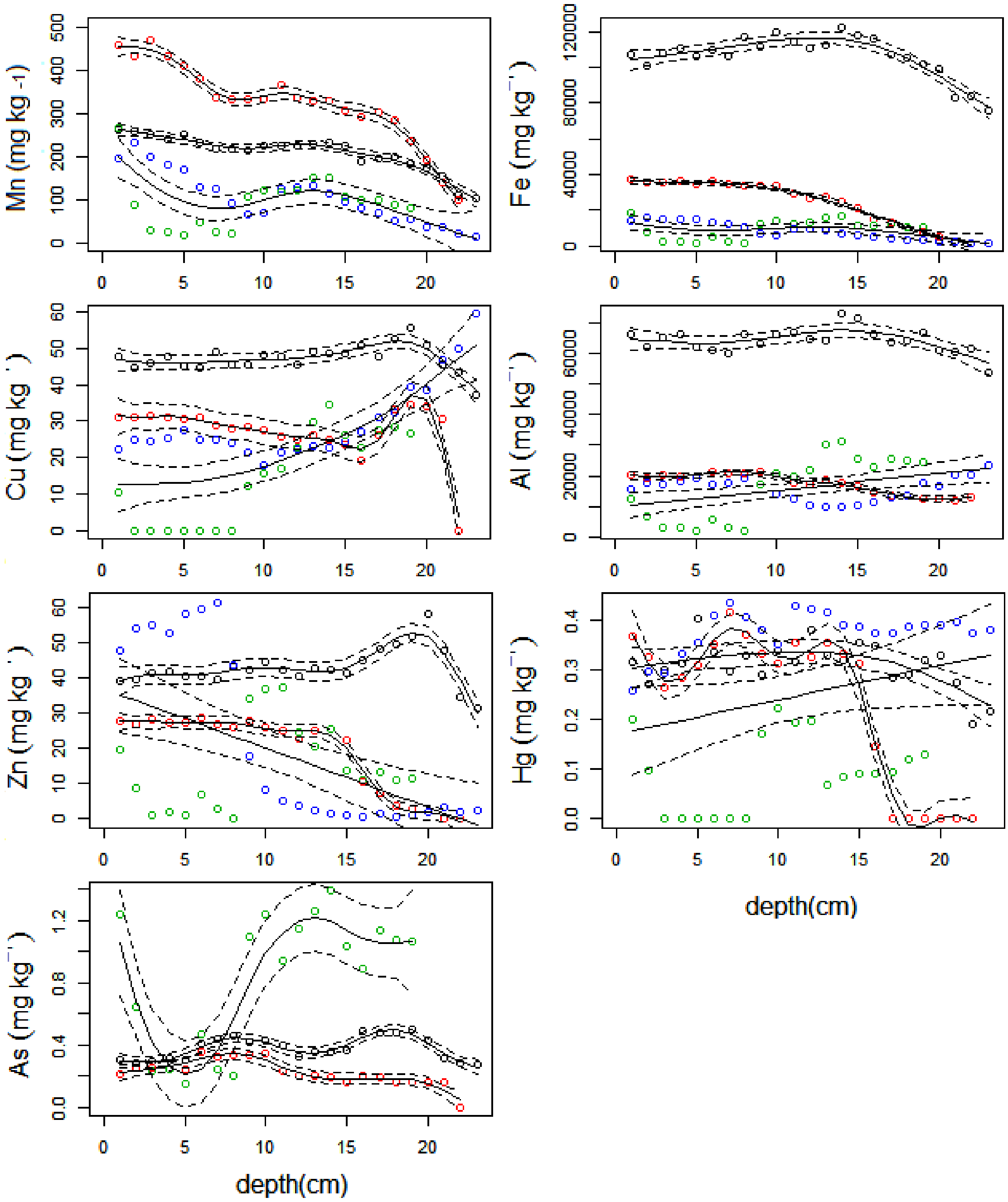

Fig 6. Graphs showing smoothing lines based on Generalized Additive Models predicting the response of seven metals to the depth in the sediment profile, combining data from Lobo (green circles) and Itaqueri(blue circles) rivers mouth. Model prediction of downstream station MID (red circles) and DAM (black circles) were also plotted in the graph. Solid lines show the prediction made by the model and confidence intervals are shown by dashed lines. R-sq.(adj): Mn - 0.448; Fe - 0.242; Cu – 0.604; Al - 0.184; Zn – 0.251; Hg – 0.056.

Our results suggest that the point source pollution catchment were more similar to downstream stations MID and DAM than to non-point catchment. For instance, in addition to

Fe and Mn, Itaqueri, MID and DAM stations showed similar distribution of Al (from 12 to 1 cm), Cu (from 15 to 1) and Hg (from 16 to 1) across the sediment depth profile. Furthermore, similarities between point source pollution catchment and downstream stations can be observed in the smooth curve obtained from GAM models based on both catchments (Fig 6, blue circles), despite of the low variance explanation provided by these models.

In general, Pearson coefficients indicated high linear correlation among the metals analyzed, excepting Hg, either based on data from the individuals catchments or from the whole reservoir. Nevertheless, stronger correlations were observed for Al, Fe and Mn in non-point source catchment compared with point source catchment (Table 1).

3.5 Discussion

Effect of point and diffuse sources of pollution on sediment deposition.

Point and non-point sources of pollution had different effects on sediment deposition. Constant discharges by point sources pollution seem increase levels of Fe, Mn, Al and Cu in the more superficial sediment layers in the Itaqueri catchment . In contrast, all metals showed similar deposition patterns in the Lobo Stream, suggesting that the deposition of metals in the sediment of this catchment was more constant over time.

We believe that this is a consistent result, assuming that the surface runoff is not selective and considering that these small catchments have similar soil characteristics and are subject to similar rainfall regime (well-marked dry-rainy seasons) .The levels of metals in sediment vary seasonally due high-low flows and climate forces plays an import role on sedimentation (Anderson 1996 Jain et al. 2005, Zhao et al. 2012). For instance, sediment deposition may be affected by flood events, atmospheric deposition and surface runoff (Baumann et al. 1984, Audry et al. 2004). Moreover, similar temporal pattern of metals concentration in sediment occurred in most of the cores from Buzzards Bay, EUA (Shine et al. 1995) and from two estuaries in eastern England (Wright and Mason 1999).

In contrast with these similar distribution shapes of Lobo, Itaqueri River showed progressive enrichment in upper sediment layer as consequence of point source pollution. Generally, continuous discharge of point source pollution occur regardless of diffuse inputs (e.g. flood events, atmospheric deposition and surface runoff) induce by climate seasonality. This trend was observed in dated sediment cores in Mersey Estuary (UK), where the increase of metal levels corresponded to the beginning of industrialization (M. Fox et al. 1999), and in a small bay in Lake Geneva (Switzerland) before the improvement of a local sewage treatment station (Loizeau et al. 2004). Similarly, the presence of non-residual metals fraction in the top sediment layer indicated anthropogenic inputs from the recent industrial development in Pearl River delta, China (Li et al. 2001). Therefore, the continuous point sources inputs and its eventually deposition seems to modify the natural deposition patterns of the Lobo-Broa Reservoir.

Effects of combined inputs.

Point sources seem contribute with most of contamination in the Lobo-Broa reservoir, both spatially and temporally. Stations MID and DAM also showed an increase with depth for Fe, Mn, and Al. Despite that Fe, Al and Mn occur naturally in the soil (CETESB 2001) they are often continuously discharged into rivers by anthropogenic activities, so the concentration of these elements may increase independent of natural processes. It is assumed that Fe and Al has reached a steady state and is not being accumulated by natural processes (Martin and Meybeck 1979). Thus, geochemical imbalances, for example increase in metals level over time, may be attributed to anthropogenic sources. Moreover, the ratio of conservative elements (Fe, Al, Si, etc.) can be used to determine the relative mobility of different metals (e.g. metal/Fe and/or metal/Al) (Daskalakis and O'Connor 1995, Jain et al. 2005).

In Mandovi estuary, India, enrichment of Fe and Mn in sediment are also related with mining activities in the upstream areas from the estuary (Alagarsamy 2006).

Point source pollution as main impact in reservoir is supported here by GAM models for Mn and Fe response to sediment depth, which predicted similar ascending smooth curves with MID and DAM. Even though predictions for Al, Zn and Cu differ from results obtained for MID and DAM, is possible observe similar distribution trends among Itaqueri, MID and DAM station. We believe that these differences in the model prediction between stations are related to intrinsic differences in both metal concentration and pattern of deposition. Furthermore, both stations showed similar peaks of metal concentration in the sediment, suggesting that the whole watershed has a similar rainfall regime, as already explained (Baumann et al. 1984, Reed 1989). However, the present study was not focused on obtaining accurate time series of sediment deposition, also because, the historical climatic events of the watershed is not well reported.

PADROES DE ACUMULACAO

Nevertheless, point source as main impact is in agreement with the observations stated in previous studies in; Lake Geneva, Switzerland (Loizeau et al. 2004, Pardos et al. 2004); in Mandovi estuary, west coast of India(Alagarsamy 2006); in four major estuaries in Sydney, Australia (Birch et al. 1996); and in Lot River, France, even after end of smelting activities (Audry et al. 2004). Furthermore, diffuse sources in the Georges River/Botany Bay estuary in Sydney, Australia, increased metals level approximately four times compared to background values, which were rised in up to 50 times by point sources (Birch et al. 1996).

Transport pattern and contribution of diffuse sources.

In this study, Al, Fe and Mn are natural soil constituents and occurred in both pollution sources. Thus, similar source or transport patterns are probable due the high linear correlation (above 0.64) between these major metals and others in the watershed (Yu et al. 2001). In general, these associations occur because of bounds and complexation by fine grains (silt and clay), organic/sulfide complexation and oxides/hydroxides (such Fe-Mn oxides)(Whitney 1975, Roy et al. 2013). The metals in non-point source catchments showed both stronger correlations and more similar response to sediment depth than the point source pollution catchment, highlighting that most metals (excepting Hg) from this catchment come from same source. On the other hand, weaker or negative correlations between levels CONTENTS of Al, Cu and Hg in the point source catchment indicate variations in effluents composition over time or contribution from diffuse sources (Casey 1975, Whitney 1975, Chipasa 2003). Nevertheless, despite the weak correlation of Al with Fe and Mn, the distribution of Al along sediment profile was similar to that showed by Cu and Zn.

Contrariwise, if metals were originated from different sources, their behavior during the transport and deposition are expected to vary. On the other hand, the absence of correlation of Hg with the major metals also supports that it is not controlled by a single factor, but a combination of factors (Jain et al. 2005). Since Hg exhibited a particular deposition pattern, a possible source is the runoff of roads, or even atmospheric deposition.

Table 1. Correlation matrix between metals in the Lobo Stream catchment, Itaqueri River catchment and in the whole reservoir.

Lobo							
	Al	Fe	As	Cu	Hg	Mn	Zn
Al		0.00039	3.66E-01	3.03E-07	0.06465	0.00081	0.00204
Fe	0.72982		8.50E-07	0.00153	0.00075	1.17E-10	3.97E-03
As	0.80175	0.95965		0.00013	0.00173	1.27E-04	8.65E-02
Cu	0.96433	0.67467	0.76643		0.08331	0.00292	0.00457
Hg	0.43212	0.70476	0.66912	0.40751		0.00069	5.66E-01
Mn	0.70175	0.98596	0.92632	0.64409	0.70833		2.35E-04
Zn	0.6614	0.88772	0.83509	0.6207	0.7903	0.89474	

Itaqueri							
	Al	Fe	Cu	Hg	Mn	Zn	
Al		0.9358	0.00563	0.37839	0.28422	0.04775	
Fe	-0.0178		0.0095	0.35155	4.86E-07	1.21E-01	
Cu	0.5583	-0.5287		0.80893	0.00889	0.16663	
Hg	-0.1927	-0.2036	-0.0534		0.3057	0.66353	
Mn	-0.2332	0.93676	-0.5326	-0.2233			0.0017658
Zn	0.417	0.77866	-0.2984	-0.0959	0.61561		

Whole reservoir							
	Al	Fe	As	Cu	Hg	Mn	Zn
Al		1.21E-13	7.93E-05	4.96E-15	0.24673	0.00132	7.17E-10
Fe	0.76092		9.93E-09	5.26E-04	0.17618	8.03E-08	4.34E-06
As	0.5706	0.67239		0.05643	2.57E-01	0.07629	0.0032
Cu	0.7666	0.54371	0.20531		0.02083	0.00706	0.0001
Hg	0.12551	-0.1464	-0.4349	0.24749		0.47844	0.10423
Mn	0.33887	0.65184	0.19106	0.28686	0.07699		1.01E-01
Zn	0.67545	0.60767	0.31264	0.4049	0.17537	0.45392	

As and Hg showed waveforms deposition trends along the sediment profile for all stations. However, the higher concentration of As in Lobo catchment (compared with downstream station MID and DAM), indicates that temporal loads of As originate mainly from Lobo Stream. Both As and Hg may come mainly from diffuse sources due to its distribution pattern, although these source may differ between As and Hg. As was correlated with the major metals (Al, Fe, Mn), suggesting that these metals shared similar source and origin.

Indeed, it is hard to define the source of elements because they can come from both point and non-point source (Shine et al. 1995, Jain et al. 2005). For example, in a study in Pearl River Estuary, the authors suggests multiples possible sources for metal contamination in the sediment: wastewater discharges for Cu, Zn and Cd; agricultural runoff for Cu and Cd; atmospheric inputs for Pb; and runoff from mining/smelting activities for Cd (Liu et al. 2011). In Manwan Reservoir, enrichment of Cd and Zn in reservoir sediment were probably due to input of fertilizers and pesticides, domestic sewage, and industrial wastes (Zhao et al. 2013). Nevertheless, clear differences were observed among the sediment profile of these pollution sources and similarities among point sources pollution catchment and downstream stations.

The DAM Station showed an up and down concentration pattern for every metal from 15cm depth, and it suggest the seasonal high-low flow dynamics of the watershed, since the dam trap sediments from upstream areas (Brune 1953). It also explains the higher concentration of Al, Fe and Cu in DAM and Mn in MID station. In addition, it is important to note that recreational activities and post depositional mobility of metals (Zwolsman et al. 1993, Shine et al. 1995) may also contribute to these values, although they were not considered in this study.

3.6 Conclusion

In the present study we investigated the temporal and spatial effects of point and diffuse sources of pollution on sediment deposition along Lobo-Broa Reservoir. We also used GAM analysis to predict the combined inputs of these sources at the sediment profile in the reservoir. We noted clear differences in point and non-point sources of pollution deposition patterns and it may be related to with its inputs frequency. Thus, the point source pollution catchment showed higher level of metals in upper sediment layers, whereas, for non-point pollution, levels of metals varied widely over time, but both sources showed a similar distribution along the sediment profile. Nevertheless, our models encourages that point source pollution are both spatially and temporally the main source of sediment pollution in the Lobo-Broa reservoir due its similarities with point source catchment and downstream stations. Finally, similar smooth curves and strong correlation among metals suggest mutual sources and transport patterns in catchment, and in this study, positive covariance in non-point source pollution catchment were stronger than point source catchment. On the other hand, the absence correlation of Hg indicates that it comes from a different source and the most likely source is atmospheric deposition.

As differences between point and non-point source were well marked and point source was the main responsible for net sediment characteristic, secondary management for point sources (besides effluent treatment) are indicated. Accordingly, actions such as the establishment of “settling ponds” after effluent treatment, aiming decrease the effect of continuous release of elements in water bodies, may contribute with the maintenance of the biotic community. Usually, biotic communities are evolutionary adapted to nutrients input dynamics (periodic inputs), which depends of high-low river flow. Changing this pattern probably will have adverse effect in biotic communities, especially in well market climates (Vannote et al. 1980, Junk et al. 1989, Humphries et al. 2014).

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5. CONCLUSÕES FINAIS

O presente trabalho investigou o efeito da poluição pontual e não pontual nos níveis de vários elementos para compreender o efeito combinado dessas fontes ao longo do reservatório do Lobo-Broa. Nossos resultados mostraram que a bacia hidrográfica tem influência de poluição pontual e não pontual. No entanto, a poluição pontual e lançamentos contínuos promovem uma alta carga de elementos espacialmente e temporalmente no reservatório. Portanto, concluímos que as fontes pontuais parecem ser o principal controlador da composição de sedimentos do reservatório devido a frequência de despejo. Em resumo, os tipos de elementos e seus níveis tendem a variar de acordo com a fonte de poluição e sazonalidade, e sua retenção e persistência no sedimento está relacionada com a característica hidrogeoquímica da bacia. Como a bacia tem estações climáticas bem definidas, a entrada sazonal de material alóctone deve ser um fator importante na dinâmica ecológica no período chuvoso. No entanto, este fenómeno sazonal - que deve ter moldado as comunidades biológicas ao longo do tempo - pode perder a significância em consequência da entrada de matéria durante todo o ano por parte das fontes pontuais de poluição. Aparentemente, as águas doces no Brasil são muito sensíveis às entradas de nutrientes, mudando rapidamente as suas características físicas e biológicas. Como o Brasil tem vários rios represados, ações integradas, de acordo com as fases hidrológicas para aumentar a resiliência dos ecossistemas aquáticos são altamente recomendadas.

Os esforços devem ser direcionados primeiro para alterações hidrológicas (por exemplo, descarga contínua de poluição pontual), seguido de uma medida controle um estressor específico ou a combinação que causa alterações no ambiente. Determinar em que fase hidrológica (por exemplo, seca) o estressor pode causar mais perturbações. Equilibrar essas ações pode diminuir a frequência de florações de algas, que ocorrem em fases de baixa água, e de sólidos em suspensão ou entrada de nutrientes durante os estágios elevados. Todas as intervenções devem ser feitas para prevenir/melhorar/ corrigir um problema atual, no entanto, é extremamente necessário considerar a historia evolutiva do local e gerenciar ações que interfira o mínimo possível no curso evolutivo.