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Impact of copper sulfate application at an urban Brazilian reservoir: A geostatistical and ecotoxicological approach

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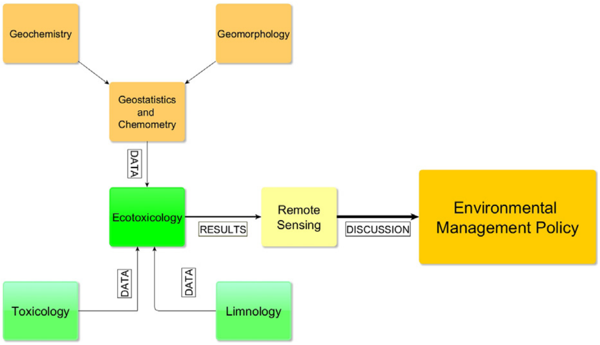
HIGHLIGHTS

- An evaluation of a surficial sediment ecotoxicity of a reservoir is proposed.
- Analysis is based on sediment chemical analysis; geoprocessing; geostatistics; SQGs.
- Impacts of the reservoir's management policy is undertaken.
- Data shows the effect of the reservoir's management policy over its ecotoxicity.

GRAPHICAL ABSTRACT



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ABSTRACT

A landscape ecotoxicology approach was used to assess the spatial distribution of copper in the recent bottom sediment (surficial sediment) of a Brazilian subtropical reservoir (the Guarapiranga reservoir) and its potential ecotoxicological impacts on the reservoir ecosystem and the local society. We discuss the policies and procedures that have been employed for the management of this reservoir over the past four decades. Spatial heterogeneity in the reservoir was evaluated by means of sampling design and statistical analysis based on kriging spatial interpolation. The sediment copper concentrations have been converted into qualitative categories in order to interpret the reservoir quality and the impacts of management policies. This conversion followed the Canadian Water Framework Directive (WFD) ecotoxicological concentration levels approach, employing sediment quality guidelines (SQGs). The SQG values were applied as the copper concentration thresholds for quantitative-qualitative conversion of data for the surficial sediment of the Guarapiranga. The SQGs used were as follows: a) interim sediment quality guideline (ISQG), b) probable effect level (PEL), and c) regional reference value (RRV). The quantitative results showed that the spatial distribution of copper in the recent bottom sediment reflected the reservoir's management policy and the copper application protocol, and that the copper concentrations varied considerably, ranging from virtually-zero to in excess of 3 $\mathrm{g_{copper}/kg_{ds}}$. The qualitative results demonstrated that the recent bottom sediment was predominantly in a bad or very bad condition, and could therefore have impacts on the local society and the ecosystem. It could be concluded that the management policy for this reservoir was mainly determined by the desire to minimize short-term costs, disregarding long-term socioeconomic and environmental consequences.

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1. Introduction

The eutrophication of water sources is a serious problem in many regions worldwide, requiring the urgent attention of researchers and environmental managers (Margalef et al., 1976; Vallentyne, 1978; UNEP-IETC, 2001; Pelley, 2016; Qin et al., 2013; Azevedo et al., 2015; Beghelli et al., 2015; Vidović et al., 2015). Caused by excessive concentrations of nitrogen and phosphorus in the aquatic ecosystem, eutrophication can result in public health issues and ecological alterations including massive blooms of phytoplankton and cyanobacteria (Rast et al., 1989; Correll, 1998; Jiang et al., 2010).

Cyanobacteria are a major socioeconomic problem due to the release of toxins and taste-and-odor compounds into lakes, reservoirs, and rivers, leading to significant economic and public health issues, especially where water bodies are used for drinking water supply, recreational purposes, and/or cultural and socioeconomic services (Graham et al., 2008). Due to the significant impacts of harmful algal and bacterial blooms (including cyanobacteria, thermotolerant coliforms, and other pathogenic bacteria), these phenomena require the adoption of direct control or mitigation measures (Thornton et al., 1996; Raloff, 2002; Beaulieu et al., 2005).

The occurrence of cyanobacterial blooms constrains the recreational use and socioeconomic potential of many water bodies in countries of all continents across the globe (Codd et al., 2005). These last authors denoted that several countries over the world have or still are suffering from the eutrophication: a) in South Africa, the eutrophication has severe impacts on health, society, and the economy; b) Netherlands and Norway have experienced increasing loss of recreational water use during the summer months, due to eutrophication; c) in Europe and Oceania there have been other temporary closures of water bodies for recreational activities, with consequent losses in terms of amenity and the local economy, despite the monitoring of cyanobacteria populations and cyanotoxins, and the implementation of recreational safety guidelines and procedures.

In order to control and/or mitigate water resources eutrophication, several countries have produced limnological guidelines, management protocols, and environmental quality reports, which vary in terms of the type of action, the environmental issues assessed, and the management procedures adopted (Macdonald et al., 2000). A few countries (such as Brazil) have implemented water management policies based on microcystin concentrations in the water body (Codd et al., 2005; Brasil, 2011).

In some countries (especially the developed ones), the use of copper sulfate ($CuSO_4 \cdot 5H_2O$) as an algicide was abolished a long time ago (Codd et al., 2005). However, in Brazil, it is still one of the commonest methods used to control cyanobacteria. In the case of the Guarapiranga reservoir in São Paulo state, massive amounts of copper sulfate have been used since 1979 (Mancuso, 1987), with the reservoir sometimes receiving 350 tons of copper sulfate in only one year (CETESB, 2009). Nonetheless, there has been no evidence of improvement in the water quality of this reservoir (CETESB, 2013).

The use of copper sulfate to prevent algal growth and "clean" the water body has led to several intoxications of livestock due to the release of cyanobacterial toxins through membrane cell rupture (Yoo et al., 1995). A case of severe intoxication of humans has also been reported after treatment of water used for human consumption with copper sulfate (Byth, 1980; Bourke et al., 1983). Elsewhere, a massive fish kill of >6 tons occurred after treatment of an algal bloom with copper sulfate in Kezar Lake, New Hampshire, USA (Sawyer et al., 1968). In Nova Scotian lakes, there have been observed effective local fish, plankton and bottom fauna kill due to copper sulfate application (Smith, 1939).

According to SMITH (1939), copper sulfate is toxic to diatoms, dinoflagellates, chlorophytes, and cyanobacteria. Copper sulfate inhibits photosynthesis and cell division, hinders nitrogen and phosphorus uptake, reduces the photosynthetic pigments in the cells, affects plasma membrane permeability, deceases cell motility, alters the distributions of proteins, lipids, and fatty acids within the cells, and even results in membrane cell rupture (Wehr and Sheath, 2003).

Copper sulfate application is considered a risky water management method compared to other alternatives, once: a) it causes membrane cell rupture, and specifically for the case of cyanobacteria, it enhances the cyanotoxines release into the water (EPA, 2014, 2016); b) it is potentially toxic to humans both in ion (Cu^{2+}) and full molecule states ($CuSO_4$) (Holtzman et al., 1966; Singh and Singh, 1968; Krieger, 2001; Saravu et al., 2007; Sinkovic et al., 2008). Direct contact and exposure to copper sulfate in the air can lead to skin thickness increase and green coloration of the skin, teeth, and hair. In the respiratory system, chronic exposure leads to nasal inflammation, septum perforation, and ulceration. Copper may cause hepatotoxicity, and loss of fertility has been observed in laboratory animals (Pedrozo, 2003). In adults, emetic copper sulfate dosages range from 0.25 to 0.5 g (as Cu). Intake of water or food containing 25 $mg_{(Cu)}$/L has been reported to cause acute gastroenteritis, while a dose of 250 $mg_{(Cu)}$/kg/day can lead to hepatic necrosis in higher animals (Barceloux, 1999). Repeated oral doses of copper sulfate were found to affect the liver, stomach, and kidneys in rats (Bartram et al., 1999).

Fortunately, copper sulfate tends to precipitate in limnological environments, becoming fixed in the sediment (John and Leventhal, 1995; Smith, 2007; Nordstrom et al., 1999; Beghelli et al., 2015; CETESB, 2012, 2013, 2015). Nevertheless, even low levels of copper sulfate or ionic copper can be lethal to fish and microorganisms, which are highly sensitive to the metal, with mortality of microorganisms at levels typically around 1.0 mg/L, while trout, carp, catfish, and ornamental goldfish present mortality at copper concentrations of around 0.5 mg/L (CETESB, 2003). Nonetheless, reports as Korosi and Smol (2012) denote that copper sulfate not only alters the aquatic food webs, but it also imposes a resilience to the system, inhibiting the ecosystem to recover to its previews state prior to the algicide applications.

Several factors affect the toxicity of dissolved copper in water. Copper toxicity decreases with increasing water hardness, due to the competition between calcium and copper for absorption sites on biological surfaces (WHO, 1998). Under certain conditions of pH and carbonate concentration, most of the aqueous copper Cu (II) becomes complexed, reducing its reactivity (WHO, 1998; Barceloux, 1999). Only a small portion of the copper remains in the aqueous state, while another portion is adsorbed by suspended particles or is complexed by carbonates and hydroxides. In aqueous environments such as reservoirs and lakes, the largest portion of the copper remains attached to organic compounds including humic and fulvic acids (Pedrozo, 2003), which can hinder the evaluation of potential ecotoxicological effects.

Despite the ecotoxicological and human health implications of copper sulfate, it offers an easy and relatively inexpensive technique for water body management, producing a rapid environmental response (Padovesi-Fonseca and Philomeno, 2004; Kansole and Lin, 2017). Nevertheless, the use of copper sulfate is not the only option for water quality management (Beaulieu et al., 2005; Huh and Ahn, 2017). Other effective methods for the control of algae and cyanobacteria include the use of hydrogen peroxide, which is associated with fewer long-term ecotoxicological impacts (Matthijs et al., 2012; Bauzá et al., 2014; Lürling et al., 2014).

The São Paulo State agency responsible for basic sanitation (SABESP) has used hydrogen peroxide for algal control, obtaining strong and positive environmental responses (Caleffi, 2000; CETESB, 2008; SABESP, 2011b). Many other possible techniques avoid the use of algicides: flushing, destratification, hypolimnetic aeration, epilimnetic mixing, metalimnetic mixing, and layer aeration are just some of these other options available (Straškraba and Tundisi, 1999).

One specific type of eutrophication prevention method for water bodies is full sewage collection and treatment (Hassler, 1969; Golterman et al., 1983). Since the sewage is fully treated, passing through tertiary and in some cases quaternary processes, the residual phosphorus and nitrogen level is minimal, compared to *in natura*

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