Science of the Total Environment 639 (2018) 588–595

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Trace organic chemical pollutants from the lake waters of San Pablo City, Philippines by targeted and non-targeted analysis

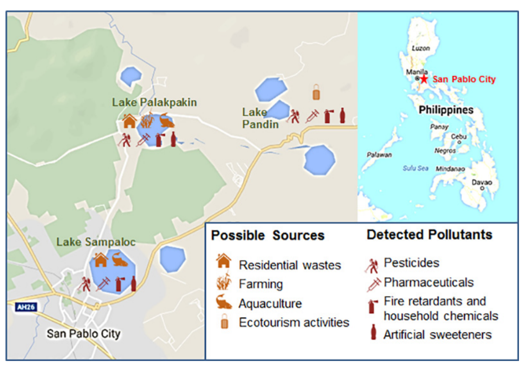
Ian Ken D. Dimzon [a], Ann Selma Morata [b,c], Janine Müller [a], Roy Kristian Yanela [b], Stephan Lebertz [d], Heike Weil [a], Teresita R. Perez [b], Jutta Müller [a], Fabian M. Dayrit [b], Thomas P. Knepper [a,]*

[a] Hochschule Fresenius, University of Applied Sciences, Limburger St. 2, 65510 Idstein, Germany
[b] Ateneo de Manila University, Ateneo Innovation Center and Department of Chemistry, Katipunan Ave., Loyola Heights, 1108 Quezon City, Philippines
[c] University of the Philippines-Visayas, Department of Chemistry, Miagao, Iloilo 5023, Philippines
[d] SGS Institut Fresenius, Im Maisel 14, 65232 Taunustein, Germany

HIGHLIGHTS

- Three small neighboring lakes have distinctive pollutant profiles.
- Dominant human activity in lake vicinity affects the pollutant profile of the lake.
- Detected compounds are from farming, aquaculture, domestic and eco-tourism sources.
- Pollutants included pesticides, artificial sweeteners and surfactants.
- Also detected were fire retardants, insect repellent and pharmaceuticals.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 April 2018
Received in revised form 17 May 2018
Accepted 17 May 2018
Available online xxxx

Editor: D. Barcelo

Keywords:
Philippines
Small lakes
Artificial sweeteners
Pesticides
Aquaculture
Surfactants

ABSTRACT

More than half of the freshwater lakes in the Philippines are small with surface areas of <2 km^2. The dynamics in these lakes are different from those in the bigger lakes. This study was conducted to determine the organic pollutants and their sources in three of the seven lakes of San Pablo City in Laguna, Philippines: lakes Palakpakin, Sampaloc, and Pandin. Gas Chromatography-Mass Spectrometry (GC–MS) and Liquid Chromatography - Tandem Mass Spectrometry (LC-MS/MS) were used in the targeted and non-targeted analysis of the lake water samples. The three lakes are all volcanic crater lakes but are exposed to different anthropogenic activities, which includes domestic activities, livelihood (farming and aquaculture) and eco-tourism.

Due to the presence of rice fields and fruit plantations, chlorpyrifos was detected in the three lakes while other pesticides like cypermethrin, picolinafen and quinoxyfen were additionally found in Lake Sampaloc, which is the biggest of the three lakes and located within the urbanized section of the city. Traces of different surfactants (linear alkylbenzene sulfonates, secondary alkyl sulfonates, alkyl sulfates, alkyl ether sulfates), biocide benzalkonium chloride, insect repellent diethyltoluamide, antibiotics (sulfadiazine and sulfamethoxazole), hypertension drug telmisartan, phosphate-based fire retardants, and artificial sweeteners (acesulfame, cyclamate, saccharin and sucralose) were detected in lakes Sampaloc and Palakpakin. The same surfactants, artificial sweeteners, insect repellant and phosphate-based fire retardants were also found in Lake Pandin, which is mainly used for eco-tourism activities like swimming and boating.

* Corresponding author.
E-mail address: knepper@hs-fresenius.de (T.P. Knepper).

https://doi.org/10.1016/j.scitotenv.2018.05.217

The results of this study suggest that the organic pollutants present in the small lakes can be linked to the various human activities in the immediate lake environment. Because small lakes are more prone to environmental stresses, human activities in the said lakes must be regulated to ensure sustainable development.

1. Introduction

With the general global decline in open fish catch due to overfishing and pollution, aquaculture has become an increasingly important source of livelihood, commerce, and food security accounting for about 42% of total fish production in 2012, up from about 26% in 2000 (Food and Agriculture Organization of the United Nations, 2014). Freshwater aquaculture can be carried out in freshwater bodies, such as lakes, or in constructed fish ponds. In the Philippines, small-scale aquaculture is carried out in freshwater lakes, which are managed by the local community following regulations set by the national government and respective local governments.

The interaction of aquaculture and the environment is two way, and is complex (Edwards, 2015). On the one hand, intensive modern aquaculture introduces agro-industrially manufactured feed and a variety of other supplements into the water. On the other hand, agricultural, domestic and industrial pollution can lead to poor aquaculture. This interaction can be better understood if the different pollutants are known and are linked to their possible sources. Numerous researches have been conducted to determine such pollutants in surface waters and to develop strategies to mitigate their effects. Organic compounds, such as pesticides, surfactants, pharmaceuticals, artificial sweeteners, fire retardants and insect repellants make up one large group of pollutants (Lange et al., 2012; Pal et al., 2010; Rivera-Utrilla et al., 2013; Yadav et al., 2015). Mass spectrometry is the method of choice to determine the presence of organic pollutants. However, there are many procedures that have been developed for sample preparation, chromatographic separation, ionization and mass analysis techniques for various groups of organic compounds (Lopez de Alda et al., 2003; Lutz et al., 2006; Reemtsma, 2003).

This project was undertaken to determine the level of chemical pollution in three of the seven small crater lakes in San Pablo City, Philippines. This study is relevant in three ways. First, although many studies have been conducted in Philippine freshwater lakes, these have focused the bigger lakes, such as Laguna de Bay (in Luzon Island). In contrast, there were only a few studies on small lakes (with surface area < 2 km^2) despite the fact that these lakes make-up three-fourths of the country's total number of lakes (Brillo, 2016). Moreover, smaller lakes are more prone to irreversible ecological damages (Brillo, 2016) brought about by natural and anthropogenic factors. The information derived from the studies on small lakes will be essential in developing measures to protect them and to plan for their sustainable use. Second, the anthropogenic impacts on each of the three lakes differ, and the results of the analysis can provide insights regarding how the pollutants are introduced into the lake. Third, the three lakes can be representative models of the various types of lakes in Southeast Asia and other tropical regions.

We monitored various organic pollutants using an array of techniques depending on their chemical properties. Targeted analysis was performed to determine pesticides, pharmaceuticals, artificial sweeteners, insect repellants and fire retardants using gas chromatography–mass spectrometry (GC–MS) and liquid chromatography – tandem mass spectrometry (LC-MS/MS). Non-targeted analysis using LC – High Resolution MS was performed to expand the coverage of pollutants. To trace qualitatively the sources of fire retardant pollutants, a method was developed to extract the said compounds from their potential sources.

2. Methods

2.1. Sampling and sample preparation

2.1.1. Collection of lake water samples

This study was conducted in three of the seven lakes of San Pablo City: Palakpakin (PAL), Sampaloc (SAM), and Pandin (PAN). These are volcanic crater lakes, which are located within a catchment area of 27.5 km^2 (Laguna Lake Development Authority, 2008). The lakes are within the watershed of Laguna de Bay. The lakes are also located within the city limits of San Pablo City, which has a population of about 250,000 (Philippine Statistics Authority, 2010). Each lake is subjected to different anthropogenic impacts from human activities within the lake and along its surrounding area.

The description of the three lakes is given in Table 1 while the maps showing the lakes and their vicinity are shown in the Supplementary data (Fig. S1). PAL is surrounded by farmland and residences within a village with a population of about 8000 (Philippine Statistics Authority, 2010), and is used for aquaculture by the local fishing community. SAM is located near the city center with an approximate population of 40,000 (Philippine Statistics Authority, 2010), and is surrounded by residences, government offices, and commercial establishments. PAN has no surrounding residences, has minimal agriculture and aquaculture activity, and it is used mainly as a community-managed ecotourism site.

Lake water samples were collected five times from February 2015 to August 2016, which covers both dry and wet seasons. Six sampling sites were selected in PAL and three each in lakes SAM and PAN (see aerial view in the Supplementary data Fig. S1). The lake water samples were collected at the surface, and at depths of 1, 3, and 6 m using a Kemmerer device and then transferred to 1-L amber bottles, which had been washed with acetone and deionized water and rinsed 3 times with the water sample. The water samples were stored at 0–4 °C. During sampling, conventional water parameters such as surface temperature, pH and dissolved oxygen were measured.

2.1.2. Preparation of lake water samples and standards

The water samples were filtered through a 0.45 μm cellulose acetate membrane filter. The solid phase extraction (SPE) cartridges (Oasis HLB, Waters) were conditioned before use with 3 × 2.0 mL MeOH and 5 × 2.0 mL deionized (DI) water. A 10 μL portion of a 30 μg/mL atrazine-D5 internal standard was added to each aliquot of 200 mL water sample and the water sample was extracted through the SPE cartridge using a vacuum manifold at a flow rate of 20 mL/min at a pressure 5 mm Hg. The SPE cartridges were then dried for 45 min under a stream of nitrogen gas.

The elution of compounds was then carried out with 3 × 1.5 mL 1:1 acetone-ethyl acetate solution. For GC–MS, the extracts were evaporated under nitrogen gas until the volume reached approximately 150 μL. The sample was then diluted to 200 μL with 1:1 acetone-ethyl acetate solution and were transferred to GC vials for analysis. For LC-MS, the extracts were evaporated to dryness under nitrogen gas. The samples were reconstituted with 1 mL 95:5 water:methanol with 50 mM ammonium acetate. The solution was then passed through a syringe filter with cellulose acetate membrane into 1-mL vials for analysis.

To prepare the calibration solutions, 30, 50, 100, 300, and 500 ng of the standard mix was added to 400 mL deionized water