Ecotoxicology and Environmental Safety 166 (2018) 354–358

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Assessing mercury pollution in Amazon River tributaries using a Bayesian Network approach

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ARTICLE INFO

Keywords:
Amazon waters
Bayesian Networks
Environmental modelling
Hg contamination
Water pollution

ABSTRACT

Mercury pollution of water bodies exerts significant human and ecosystem health impacts due to high toxicity. Relatively high levels of mercury have been detected in the Amazon River and its tributaries and associated lakes. The study employed a Bayesian Network approach to investigate the contribution from geogenic sources to mercury pollution of lakes in the Madeira River basin, which is the largest tributary of the Amazon River. It was found that the source indicators of naturally occurring mercury have both, positive and negative relationships with mercury in lake sediments. Although the positive relationships indicated the influence of geological and soil formations, the negative relationships implied that the use of mercury amalgam for gold extraction in artisanal and small-scale mining (ASM), which is the primary anthropogenic source of mercury, also contribute to mercury in Amazon tributaries. This was further evident as mercury concentrations in lake sediments were found to be significantly higher than those in the surrounding rocks. However, potential anthropogenic mercury was attributed to historical inputs from gold mining due to the recent decline of ASM mining practice in the region.

1. Introduction

Amazon, as the world's most biodiverse system of tropical rainforests, is the home to a large number of species of freshwater flora and fauna (Castello et al., 2013; Junk et al., 2007). However, this water environment is subject to significant risks due to the presence of a range of toxicants of natural and anthropogenic origin, and one of the major concerns is mercury (Hg) pollution of Amazon River tributaries. As a highly toxic pollutant, Hg can pose risks to human health once ingested through contaminated fish.

In fact, Amazon waters can be polluted by Hg due to: (1) geogenic factors such as transport of naturally occurring Hg in soil into waterways and atmospheric emissions from Andes volcanic eruptions (Bonotto and Vergotti, 2015); and (2) use of Hg amalgam for gold extraction from ore in artisanal and small-scale mining (ASM) (Pacyna et al., 2010; UNEP_Chemicals_Branch, 2008). However, it is important to note that ASM gold mining has decreased in intensity over the past years (Bastos et al., 2006). Therefore, it can be hypothesised that the current Hg content in river waters and sediments could be sourced from naturally occurring Hg as well as historical inputs from previous ASM gold mining.

The investigation discussed in this paper characterised the potential degradation of Amazon ecosystem due to geogenic Hg inputs, and thereby identified any potential contributions from anthropogenic sources of Hg. This is due to the practical constraints in the Amazon region to collect reliable data on ASM gold mining activities, as a consequence of the wilderness, difficulty in terrestrial access and zones of conflicts with indigenous people, among others. The study adopted Bayesian Networks (BNs), which is a novel approach in the context of environmental systems modelling. BNs are a graphical modelling approach embedded with straightforward interpretability, and has been used for understanding complex environmental systems. Past studies include, prediction of species abundance as a function of habitat characteristics (Howes et al., 2010), assessment of influential factors in the occurrence of cyanobacterial blooms in tropical lakes (Rigosi et al., 2015), modelling the impact of vehicular traffic on the build-up of

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https://doi.org/10.1016/j.ecoenv.2018.09.099
Received 7 June 2018; Received in revised form 19 September 2018; Accepted 22 September 2018

hydrocarbons on urban roads (Li et al., 2017), evaluation of the influence of land use change on urban receiving waters (Wijesiri et al., 2018a), assessment of human health risks in developing countries due to poor urban water quality (Wijesiri et al., 2018b), and comparison of the impact of urbanisation in different geographical regions on stormwater pollution (Wijesiri et al., 2018c).

Further, BNs have emerged as an effective modelling approach as it facilitates the utilisation of expert elicited information and historical data for developing the model structure. It enhances the handling of sparse data and the derivation of scientifically robust inferences (Stefanini, 2008). However, it is also important to note that expert elicitation needs to be performed in a way that it does not lead to inaccurate discretisation of variables (limits the capture of the characteristics of observed data) and derivation of less reliable prior information (Uusitalo, 2007).

Accordingly, the main objective of the current study was to develop a BN model to assess the contribution from geogenic sources to Hg in the sediments of Amazon lakes. The outcomes of the research study are expected to contribute to the formulation of effective planning and management strategies to minimise the impact of Hg, and thereby safeguard the Amazon aquatic ecosystem.

2. Materials and methods

2.1. Study sites

The study was based in the Madeira River basin located in Rondônia State, Brazil. As shown in Fig. S1 in the Supplementary information, Madeira is the largest of several basins that comprise the system of Amazon rainforests. The sediment sampling sites were located in nine lakes (0.6–5 km in length and 0.3–1.2 km in width) as shown in Fig. 1, and their main features have been detailed in Bonotto and Vergotti (2015). Further, the population in the surrounding area of the lakes varies from 120 inhabitants to 2000 inhabitants. The major economic activities of the population include fishing, agriculture (rice, corn, manioc, banana, coffee, coconut and water melon) and extractive industries (chestnut and açaí).

In addition to sediments from the nine lakes, a total of six rock samples were collected at Teotônio and Santo Antônio waterfalls (Fig. S2 and Table S1 in the Supplementary information). The petrographic, geochemical, and geochronological aspects of the rock formations were characterised by Payolla (1994). The major lithologies consisted of coarse-grained igneous rocks comprising granites, syenites and monzonites.

2.2. Sample collection and laboratory analysis

The core sediment samples were collected over a maximum depth range of 20–80 cm from the lake bed by driving a 1 m long and 7 cm diameter PVC tube attached to an iron outliner. Samples were collected approximately in the central area of each lake, and each sample was cut into 5 cm thick slices and transferred into polyethylene bags, stored in iceboxes, and then transported to the laboratory. The maximum depth (and respective number of slices) of core sediments collected at each lake was: Samuel – 20 cm (4); Paca – 25 cm (5); Demarcação – 35 cm (7); Brasileira – 55 cm (11); Conceição – 50 cm (10); Araçá – 80 cm (16); Tucunaré – 65 cm (13); Santa Catarina – 50 cm (10); and Nazaré – 25 cm (5). Quality Assurance and Quality Control procedures were followed during sample handling and storage (Azcue et al., 1994).

The sediment samples collected were analysed for elemental Hg and indicators of geogenic Hg, namely, major oxides (Al_2O_3, Fe_2O_3, TiO_2, SiO2, MgO, CaO, Na_2O and K_2O) and organic carbon. The selected oxides are typical parameters analysed to perform geochemical balance of the composition of rocks, soils and sediments (Faure, 1991) and largely influence Hg transport through soil, while organic carbon content indicates the likelihood of forming Hg-organic complexes (Belzile et al., 2008; Brigham et al., 2009; Gu et al., 2011).

To determine the concentration of elemental Hg in lake sediments, the samples were first digested, and then analysed using atomic absorption spectrometry with cold vapour generation by following the Method 7471B (USEPA, 2007). For the rock samples collected, only the elemental Hg was analysed. The rock fragments were initially crushed using jaw crushers in two stages, first, from 5 cm to 1.5 cm size, and then 1.5 cm to 3–5 mm. Subsequently, crushed rock samples were further size reduced to $< 400\ \mu m$ in an oscillating mill and submitted to the same analytical procedure adopted for Hg determination in the lake sediments.

The concentrations of oxides were determined using X-ray Fluorescence (XRF) method as described by Beckhoff et al. (2007). Total Organic Carbon (TOC) in sediments was determined using spectrophotometry as described by Hach (1992).

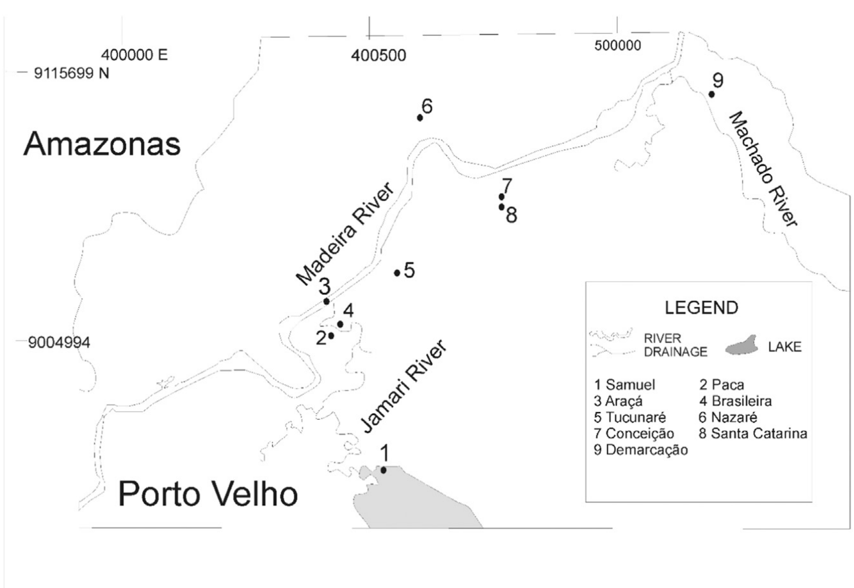

Fig. 1. Locations of lakes (adapted from Bonotto and Vergotti, 2015).

2.3. Bayesian network modelling approach

BN modelling builds relationships between random variables using *Structure Learning Algorithms* to learn the model structure. A typical structure of a BN model is shown in Fig. S3 in the Supplementary information. Subsequently, the model parameters are commonly estimated based on *Maximum Likelihood Estimates* (Ben-Gal, 2007; Scutari, 2009; Uusitalo, 2007). As can be seen in Fig. S3, given a set of random variables $V = \{X_1, X_2, ..., X_6\}$, the BN structure defines a factorisation of the global probability distribution of V (i.e. joint probability distribution) into local probability distributions of individual variables. This factorisation is based on the *Markov Property* of BNs (Eqs. (1) and (2)) which states that any given variable depends on its parent variables (Korb and Nicholson, 2010).

$$P(X_1, X_2, ..., X_6) = \prod_{i=1}^{6} P(X_i \mid \prod X_i),\text{for discrete variables} \tag{1}$$

$$f(X_1, X_2, ..., X_6) = \prod_{i=1}^{6} f(X_i \mid \prod X_i),\text{for continuous variables} \tag{2}$$

In this study, a BN was proposed to investigate the relationships between concentration of Hg in lake sediments in Madeira river basin and indicators of the origin of geogenic Hg (as discussed in Section 2.2) and sediment depth. The predictive analysis was conducted by fitting the probability density functions corresponding to the proposed BN model with observed data of model variables (i.e. Hg concentration in sediments, geogenic source indicators, and sediment depth) using the ***bnlearn*** R statistical computing package. Hence, the model parameters were estimated in the form of conditional regression coefficients, such that the difference between observed and predicted values is minimised. The estimated parameters were then used to predict the concentrations of Hg in lake sediments. The type (positive/negative) and the magnitude of estimated parameters quantitatively informed the contribution from geogenic sources to Hg pollution of the aquatic environment.

3. Results and discussion

3.1. Development of the BN model

Fig. 2 depicts the structure of the proposed BN that describes relationships between Hg concentrations in lake sediments at different depths and geogenic source indicators. It is important to note that the predictive analysis undertaken was conditional on the proposed model structure. However, this structure can be modified as new knowledge become available, in order to enhance the replication of the system being modelled, and thereby to improve the model prediction performance (Uusitalo, 2007). Table 1 shows estimated model parameters, and it can be noted from the variation in predicted values against observed data and residual plots (Fig. 3), that the prediction performance of the BN model is satisfactory.

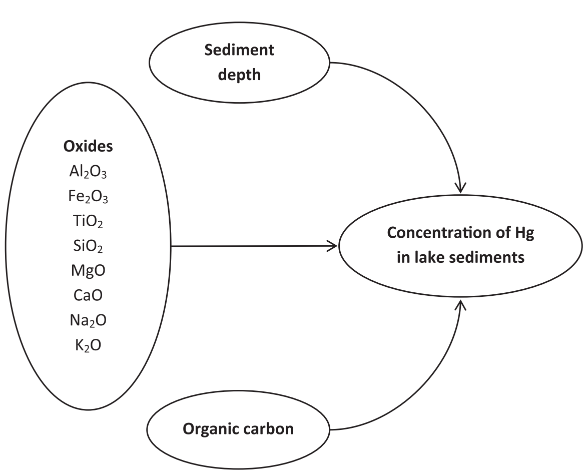

Fig. 2. Structure of the Bayesian Network (BN) for visualising the relationships between Hg in lake sediments and geogenic source indicators.

3.2. Impact of geogenic Hg on the degradation of lakes

In order to evaluate the relationships between Hg concentrations and geogenic source indicators, leave-one-out cross validation was undertaken using R *linear model – lm()* function. It was noted that there exists statistically significant linear relationships between Hg concentration in lake sediments and CaO (p-value = 0.000926 at 0.01 significance level), Fe_2O_3 (p-value = 0.0119 at 0.05 significance level) and K_2O (p-value = 0.0202 at 0.05 significance level). This implies that it is unlikely that Hg concentrations are not directly related (positively or negatively) to CaO, Fe_2O_3 and K_2O concentrations in sediments, compared to other geogenic source indicators.

Moreover, as evident from Table 1, Hg concentrations in lake sediments show positive relationships (i.e. positive conditional regression coefficients) with Al_2O_3, CaO, MgO and organic carbon. On the other hand, as evident from the negative relationships (i.e. positive conditional regression coefficients), low Hg concentrations are expected where there are high Fe_2O_3, K_2O, Na_2O, SiO_2 and TiO_2 concentrations in sediments. Further, Hg concentrations have negative relationships also with sediment depth. However, given that sediment depth shows the weakest negative relationship and the current study accounted for sediments of 0–20 cm depth, it can be concluded that the variation in Hg concentrations with depth is minimal compared to that in response to other factors.

In order to further confirm the relationships identified between Hg in sediments and geogenic source indicators, it was important to evaluate geological and soil formations around the lakes studied. Fig. S4 in the Supplementary information shows the geological map of Rondônia State. Accordingly, the study area largely comprises of alluviam-colluviam sediment formations, lacustrine deposits and laterites (containing Al and Fe oxides). The area also has small patches of amphibole-biotite formations which contain Al, Fe, K, Mg and Si. Further, according to the soil map of Rondônia State (Fig. S5 in the Supplementary information), the study area has red-yellow argisol soils (includes majority of soils previously classified as podzolic soils) and red and yellow latosol soils, which are rich in organic carbon and Fe and Al oxides (Benedetti et al., 2011). Accordingly, some of the major positive relationships revealed by the BN model (Al_2O_3 and MgO) could be attributed to the presence of geogenic formations that contain Al and Mg. However, Hg concentrations in lake sediments also show negative relationships with geogenic source indicators, in particular, Fe_2O_3 and K_2O, which are abundant in the typical minerals and soils in the study area. This implies that sources other than natural sources, potentially gold mining activities also contribute to Hg in lake sediments.

In fact, although the geological formations in all the nine lakes are similar, the predictions of Hg concentrations in sediments shown in Fig. 4 are particularly significant in the case of Samuel, Paca, Demarcação and Brasileira lakes. Moreover, it was also found that the Hg concentrations in the surrounding rock formations (Table S1 in the Supplementary information) are significantly lower than Hg concentrations in lake sediments (p-value = 2.46×10^{-12} at 0.01 significance level). This implies that gold mining activities could potentially release Hg into these lakes. In recent years, with gold mining in the Madeira River basin decreasing in intensity (Bastos et al., 2006), the sediment contamination is attributed to historical inputs. Thus, it could be concluded that the Amazon tributaries continue to be contaminated by Hg despite the diminishing anthropogenic inputs. Accordingly, strict regulations need to be imposed on the use of hazardous materials in mining in order to protect the Amazon waters.

Table 1
Estimated conditional regression coefficients for Hg concentration in lake sediments (conditional Gaussian distribution).

Conditional density: Hg | oxides: organic carbon: sediment depth										
Intercept	250.50									
Parent Variable	Oxides								Organic Carbon	Sediment Depth
	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	Na_2O	K_2O	SiO_2		
Estimated coefficient	6.96	− 18.16	− 30.72	67.23	474.56	− 99.58	− 60.31	− 2.37	0.42	− 0.39

Note 1: Conditional density refers to the probability density function of 'Hg' given 'oxides', 'organic carbon' and 'sediment depth'.
Note 2: High Hg concentrations can be expected where those variables with positive coefficients have relatively high values (e.g. higher the Al_2O_3 concentration, higher the Hg concentrations), and low Hg concentrations can be expected where those variables with negative coefficients have relatively high values (e.g. higher the Fe_2O_3 concentration, higher the Hg concentrations).

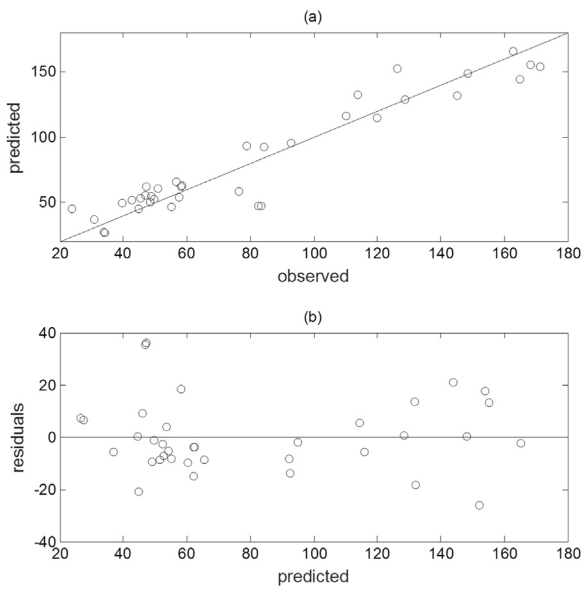

Fig. 3. Analysis of prediction performance of the Bayesian Network (BN) model: (a) observed vs predicted; (b) predicted vs residuals.

4. Conclusions

This study employed BN modelling to characterise the contribution of geogenic and anthropogenic sources of Hg in Amazon lakes in Rondônia State, Brazil. Accordingly, it was evident that Hg in lake sediments are both, positively and negatively related to oxides (typically representing the composition of rocks, soils and sediments) which influence the transportation of Hg, and organic carbon which enables Hg-organic complexation. The positive relationships are attributed to geological and soil formations in the Amazon ecosystem and the negative relationships imply that Hg in lake sediments could also be originating from anthropogenic sources, potentially from gold mining. Further, it was also found that significantly high concentrations of Hg are recent in lake sediments compared to the Hg concentrations in the surrounding rocks. Given the significant decrease in gold mining over the past years in the region, it can be concluded that historical inputs of Hg from previous mining activities still contribute to the high Hg concentrations in lake sediments.

Acknowledgements

Sprint Grant 2016/50327-4 funded jointly between FAPESP-Foundation for Supporting Research in São Paulo State and Australian Technology Network (ATN) of which Queensland University of Technology (QUT), Brisbane, Australia, is a partner.

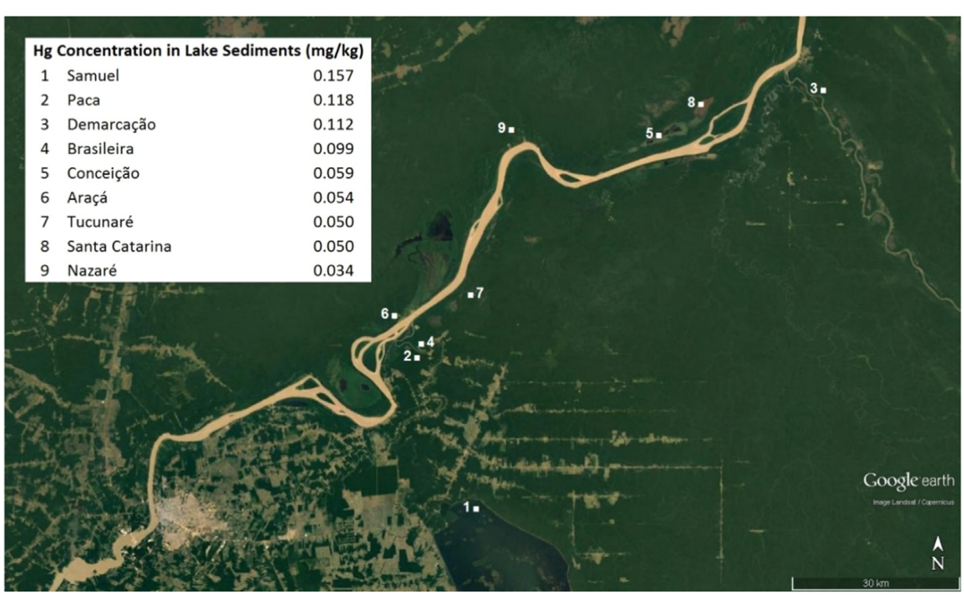

Fig. 4. Predicted concentrations of Hg in sediments (average over depths of 0–5 cm, 5–10 cm, 10–15 cm and 15–20 cm) of lakes in Madeira River basin (Map data: Google, DigitalGlobe).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2018.09.099.

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