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Sedimentary record of antibiotic accumulation in Minnesota Lakes

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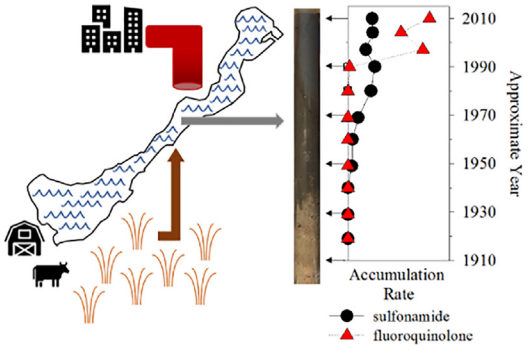
HIGHLIGHTS

- The study determined antibiotics are present in lake sediment cores.
- Two extraction and analysis methods provided similar results.
- Sediment cores successfully captured historical trends of ten antibiotics.
- Synthetic, human-use (wastewater derived) antibiotics were more commonly detected.

GRAPHICAL ABSTRACT

Profiles of antibiotics were collected in lake sediment cores revealing the role of wastewater effluents as a source of these compounds to aquatic systems.



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ABSTRACT

The widespread detection of antibiotics in the environment is concerning because antibiotics are designed to be effective at small doses. The objective of this work was to quantify the accumulation rates of antibiotics used by humans and animals, spanning several major antibiotic classes (sulfonamides, tetracyclines, fluoroquinolones, and macrolides), in Minnesota lake-sediment cores. Our goal was to determine temporal trends, the major anthropogenic source to these lacustrine systems, and the importance of natural production. A historical record of usage trends for ten human and/or animal-use antibiotics (four sulfonamides, three fluoroquinolones, one macrolide, trimethoprim, and lincomycin) was faithfully captured in the sediment cores. Nine other antibiotics were not detected. Ofloxacin, trimethoprim, sulfapyridine, and sulfamethazine were detected in all of the anthropogenically-impacted studied lakes. Maximum sediment fluxes reached 20.5 ng cm^{-2} yr^{-1} (concentration 66.1 ng/g) for ofloxacin, 1.2 ng cm^{-2} yr^{-1} (1.2 ng/g) for trimethoprim, 3.3 ng cm^{-2} yr^{-1} (11.3 ng/g) for sulfapyridine, and 1.0 ng cm^{-2} yr^{-1} (1.6 ng/g) for sulfamethazine, respectively. Natural production of lincomycin may have occurred in one lake at fluxes ranging from 0.4 to 1.8 ng cm^{-2} yr^{-1} (0.1 to 5.8 ng/g). Wastewater effluent appears to be the primary source of antibiotics in the studied lakes, with lesser inputs from agricultural activities.

1. Introduction

The health care system was revolutionized with the discovery of antibiotics in the 1930s. The ability to treat and prevent microbial infections resulted in antibiotics being one of the greatest inventions of the 20th century. The effectiveness of antibiotics has led to their mass production and widespread use. In 2011 and 2012, an estimated 17,900 tons of antibacterials were sold and distributed by retail and non-retail channels in the United States for use in humans and animals (FDA, 2012; FDA, 2014; Zhang et al., 2015). Given the large quantities of antibiotics used, it is important to understand their potential impact in aquatic systems.

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Only a fraction of the antibiotics administered is metabolized by humans and animals; up to 90% of the dose is excreted in urine and feces (Kumar et al., 2005). Wastewater treatment plant (WWTP) effluents are point sources of human-use antibiotics to aquatic systems due to incomplete removal by conventional treatment technologies (Miao et al., 2004; Glassmeyer et al., 2005). Concentrations of antibiotics in municipal wastewater are typically in the low μg/L range, and receiving water levels range from low to high ng/L (Kümmerer, 2009a; Kolpin et al., 2002; Ferrey et al., 2015; Bai et al., 2014; Yang and Carlson, 2003; Kim and Carlson, 2007; Gibs et al., 2013; Janecko et al., 2016). The agriculture industry uses antibiotics to treat and prevent microbial illnesses and as growth promoters in livestock. Agricultural practices contribute to antibiotic pollution in water bodies by surface runoff from fields to which manure contaminated by antibiotics is applied (Yang and Carlson, 2003; Kim and Carlson, 2007; Davis et al., 2006).

Antibiotics have also been detected downstream of wastewater outfalls in sediment (Kümmerer, 2009a; Bai et al., 2014; Kim and Carlson, 2007; Janecko et al., 2016; Zhou et al., 2011; Yang et al., 2010). Compounds, such as tetracyclines and fluoroquinolones, that strongly adsorb onto particles, accumulate in sediment (Gu and Karthikeyan, 2005; Zhang et al., 2011). Similar to surface water, the highest observed levels of antibiotics in sediments were downstream of metropolitan (industrial and municipal wastes) and agricultural and aquaculture areas (feedlots and fish ponds) (Kim and Carlson, 2007; Janecko et al., 2016; Zhou et al., 2011). In addition to their mass production, some antibiotics are naturally produced in the environment, such as select tetracyclines, penicillin, erythromycin, tylosin, and lincomycin (Demain, 2009; Greenwood, 2003a).

Different from other classes of contaminants of emerging concern, antibiotics are designed to have an effect on microorganisms (Kümmerer, 2009a). Ecosystem health may be influenced by antibiotics by hindering the growth of algae and benthic invertebrates (Janecko et al., 2016; Baran et al., 2006; Brain et al., 2004). Use of antibiotics may increase the occurrence of antibiotic resistance in bacteria, which poses a risk to human and veterinary health by reducing the ability of antibiotics to treat microbial illnesses (Andersson and Hughes, 2014; Hernando et al., 2006). Lethal concentrations cause a specific immediate response, but prolonged sub-inhibitory levels of antibiotics can also select for and promote the dispersion of antibiotic resistant genes (ARGs) (Andersson and Hughes, 2014; Hughes and Andersson, 2016). Recent studies have shown conflicting findings as to whether environmental samples show correlations between antibiotic and ARG levels (Zhang et al., 2014; Huerta et al., 2013; Pruden et al., 2006; Oberlé et al., 2012).

The objective of this work is to quantify the current and historical levels of selected human- and animal-use antibiotics in lake sediment cores. Measuring levels of antibiotics in dated sediments is a useful tool to reconstruct chemical pollution of water bodies over time. Antibiotic levels in surface waters and surface sediments due to anthropogenic inputs have been well studied (Yang and Carlson, 2003; Kim and Carlson, 2007; Davis et al., 2006; Zhou et al., 2011). This study, however, aims to assess the temporal trends of environmental levels of antibiotics during the past century due to anthropogenic inputs. Previous research has investigated the presence and persistence of human-use pharmaceuticals (including antibiotics) in a sediment core from a sewage-impacted estuarine system (Lara-Martín et al., 2015) and in river sediments (Thiebault et al., 2017; Tamtam et al., 2011). Select antibiotics (including sulfamethazine, trimethoprim, and ofloxacin) were found to be resilient to degradation in the sediment, be successful at capturing human-usage trends, and have limited mobility throughout the sediment bed (Lara-Martín et al., 2015; Thiebault et al., 2017; Tamtam et al., 2011). These features indicated antibiotics could be used as potential chronological markers in sediment cores (Thiebault et al., 2017). Our study, however, solely focuses on the presence of antibiotics in multiple aquatic systems with varying degrees and types of anthropogenic influences. The performance of two extraction methods (accelerated solvent and ultrasound assisted extraction) for removal of antibiotics from sediment was assessed and compared. Also investigated is whether synthetic or naturally produced antibiotics are more persistent in the environment, what the dominant source of antibiotic pollution is in the targeted lakes, and whether the degree of anthropogenic impact is reflected in the historical trends. The potential pressure of antibiotics selecting for ARGs provides motivation for further understanding in the abundance and persistence of antibiotics in the environment. Thus, historical levels of 19 antibiotics (including those from the fluoroquinolone, tetracycline, sulfonamide, and macrolide classifications) were quantified in sediment cores from four Minnesota lakes.

2. Methods

2.1. Sediment core collection

Sediment cores were collected in August and September 2014 from four Minnesota lakes (Fig. S1 and Table S1). Lake Pepin (GPS coordinates: 44.499750, −92.294170) and the Duluth Harbor of Lake Superior (46.732783, −92.065333) were selected because they have large watersheds and receive multiple waste inputs. Lake Winona (45.87501, −95.40402) has a small watershed with one municipal wastewater discharge, and Little Wilson Lake in the Superior National Forest (47.656138, −91.067905) lacked any major waste inputs and served as a control site. Coring locations were sited in known depositional areas of each lake, generally deeper regions where fine-grained, organic-rich sediments (to which antibiotics adsorb) accumulate conformably.

The cores were collected via a piston corer equipped with a polycarbonate tube and deployed into the sediment from the surface using Mg-alloy rods. The sediment cores were extruded vertically top-down and sectioned on site into 2–4 cm intervals in the field, except for Lake Pepin. The Lake Pepin core was sectioned on a laboratory benchtop after measuring its magnetic susceptibility profile, which was matched with that of previously dated cores from the same location to determine the deposition date of the core sections (see below). The outer circumference of the core was removed to prevent carryover of younger to older sediment via smearing during extrusion. Sections were stored in cleaned glass jars, homogenized, and a subsample was taken for radiometric dating. Samples were cooled to 4 °C in the field and were subsequently kept at −20 °C for long term storage.

Loss-on-ignition analysis of homogenized subsamples were used to determine water, organic carbon, carbonate, and inorganic content of sediment by weighing the sediment after heating for 12 h at 105 °C, 4 h at 550 °C, and 2 h at 1000 °C, respectively. An aliquot of sediment (approx. 10 g dry weight equivalent) at select intervals was freeze-dried and then stored at −20 °C until extraction for antibiotic analysis.

2.2. Compounds of interest

The antibiotics selected for this study include six sulfonamides (sulfachloropyridazine, sulfadiazine, sulfadimethoxine, sulfamethazine, sulfamethoxazole, and sulfapyridine), three macrolides (erythromycin, roxithromycin, and tylosin), four tetracyclines (chlortetracycline, doxycycline, oxytetracycline, and tetracycline), four fluoroquinolones (ciprofloxacin, enrofloxacin, norfloxacin, ofloxacin), and three non-categorized antibiotics (carbadox, lincomycin, and trimethoprim). The compounds chosen for this study were based on one or more of the following criteria: 1) known natural products; 2) had human and/or animal uses; 3) were part of several major classifications; and 4) had been previously detected in sediment samples. The compounds, their abbreviations, and uses are given in Table 1. Degradation products of chlortetracycline (epi-chlortetracycline, isochlortetracycline, and epi-isochlortetracycline) and erythromycin (erythromycin-H_2O) were also included and summed into their respective parent compound concentrations. Roxithromycin was included in the study to monitor for carry-over contamination. Roxithromycin is a synthetic compound

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