



Contents lists available at ScienceDirect

Journal of Hazardous Materials

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



Occurrence of *N*-nitrosamines in U.S. freshwater sediments near wastewater treatment plants

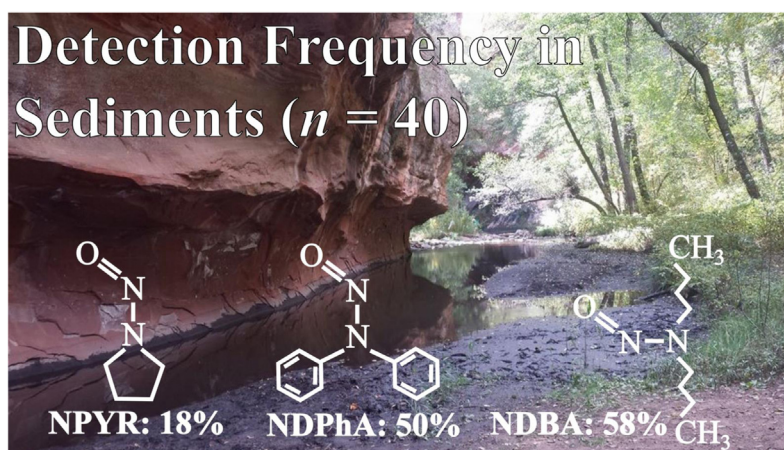
Adam J. Gushgari¹, Rolf U. Halden*, Arjun K. Venkatesan¹

Center for Environmental Security, The Biodesign Institute, Global Security Initiative, Arizona State University, 781 E. Terrace Mall, Tempe, AZ 85287, United States

HIGHLIGHTS

- Carcinogenic nitrosamines are discovered in U.S. freshwater sediments nationwide.
- *N*-Nitrosodibutylamine, *N*-nitrosodiphenylamine, and *N*-nitrosopyrrolidine are detected.
- At least one nitrosamine occurs in 70% of sediments analyzed.
- Contamination is only loosely linked to wastewater treatment plant inputs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 January 2016
Received in revised form 28 March 2016
Accepted 30 March 2016
Available online xxx

Keywords:

N-Nitrosamine
Sediment contamination
Wastewater treatment plant
Environmental fate

ABSTRACT

In the present study, 40 freshwater sediments collected near 14 wastewater treatment plants (WWTPs) across the United States were analyzed for eight *N*-nitrosamines by liquid chromatography-tandem mass spectrometry (LC-MS/MS). Three *N*-nitrosamines were detected for the first time in freshwater sediments in units of ng/g dry weight at the specified detection frequency: *N*-nitrosodibutylamine (NDBA; 0.2–3.3; 58%), *N*-nitrosodiphenylamine (NDPhA; 0.2–4.7; 50%), and *N*-nitrosopyrrolidine (NPYR; 3.4–19.6; 18%). At least one *N*-nitrosamine was detected in 70% (28/40) of sediments analyzed. Non-detect values in units of ng/g dw were obtained for *N*-nitrosodimethylamine (NDMA; <10.2), *N*-nitrosomethylethylamine (NMEA; <1.7), *N*-nitrosodiethylamine (NDEA; <3.9), *N*-nitroso-di-*n*-propylamine (NDPA; <1.7), and *N*-nitrosopiperidine (NPIP; <3.6). Principal component analysis specifically points to two of multiple potential pathways explaining *N*-nitrosamine occurrences in sediment: NDBA and NDPhA were positively correlated with bulk water ammonia and pH levels, and NPYR with sediment content of organic carbon and iron. Interestingly, *N*-nitrosamine occurrences up- and downstream of WWTPs were statistically

* Corresponding author.

E-mail addresses: rolf.halden@asu.edu, halden@asu.edu (R.U. Halden).

¹ These authors contributed equally.

indistinguishable ($p > 0.05$). This is the first report on the occurrence of the carcinogenic *N*-nitrosamines NDBA, NDPhA, and NPYR in U.S. freshwater sediments. Discovery of this phenomenon warrants further research on the compounds' origin, environmental persistence, aquatic toxicity, and risks posed.

© 2016 Published by Elsevier B.V.

1. Introduction

N-Nitrosamines are a large group of emerging contaminants of ecological and human health concern due to their carcinogenic potential. Over 300 congeners have been reported and may affect humans through a number of different exposure routes, including ingestion of food and water, use of tobacco products, occupational exposure, and the use of certain cosmetic or pharmaceutical products [1]. *N*-Nitrosamine sources in industrial, commercial and residential settings are known to increase the quantities detected in raw wastewater [2]. The International Agency for Research on Cancer (IARC) has classified 24 different *N*-nitrosamines with respect to their carcinogenic potential to humans. Two of these, *N*-nitrosornicotine and 4-(*N*-nitrosomethylamino)-1-(3-pyridyl)-1-butanone, have been classified as Group 1 known human carcinogens [3]. The remainder are classified as either probably carcinogenic to humans (Group 2A), possibly carcinogenic to humans (Group 2B), or not yet classifiable (Group 3) [3]. Although the United States Environmental Protection Agency (U.S. EPA) recognizes the existence of sub-populations at risks of multiple exposures, quantifying the latter remains challenging and incomplete due to the ubiquitous nature of *N*-nitrosamines [4]. As of today, a total of five *N*-nitrosamines are included in the U.S. EPA Contaminant Candidate List 3 (CCL-3), and the same five have been listed again in the U.S. EPA CCL-4 draft: these are *N*-nitrosodiethylamine (NDEA), *N*-nitrosodimethylamine (NDMA), *N*-nitroso-di-*n*-propylamine (NDPA), *N*-nitrosodiphenylamine (NDPhA) and *N*-nitrosopyrrolidine (NPYR) [5,6].

One area of increasing concern is the unintentional formation of *N*-nitrosamines as disinfection byproducts (DBP) in drinking waters. For instance, chlorination and chloramination of waters containing secondary and tertiary amines can result in the formation of NDMA, a widely studied probable human carcinogen [6–8]. Other documented or hypothesized pathways of *N*-nitrosamine formation include generation in waters containing ammonia, organic nitrogen, or other inorganic nitrogenous substances; UV-induced formation in the presence of chlorinated dimethylamine and monochloramine; and formation via oxidation of dimethylacetamide to hydroxylamine in ozonation processes [9–12].

Because of the lower partitioning coefficients of most *N*-nitrosamines, it is generally believed that *N*-nitrosamine occurrence is limited to only aqueous matrices; therefore, little research has been conducted on the occurrence and sorption behavior of these compounds in solid environmental matrices. A recent study reported the occurrence of eight *N*-nitrosamines in nationally representative U.S. biosolids samples with a detection frequency of 88%, suggesting either *in situ* formation or sorption of *N*-nitrosamines to biosolids during secondary or sludge treatment in wastewater treatment plants (WWTPs) [5]. Detection frequency of *N*-nitrosamines in sludge samples linearly correlated with their *n*-octanol water partitioning coefficient (K_{OW}), suggesting hydrophobic sorption as a mechanism governing *N*-nitrosamines accumulation in solid environmental matrices [5]. Numerous *N*-nitrosamines and their secondary amine precursors have been detected in WWTP effluent, as well as in wastewater-impacted aquatic environments [13–16]. It has also been shown that common water constituents, such as the presence of ammo-

nia and chloramine, can increase the rate of *N*-nitrosamine formation [17]. Motivated by a lack of data on *N*-nitrosamine occurrences in freshwater bed sediments proximal to WWTP discharges, we screened for the following eight *N*-nitrosamines: NDMA, *N*-nitrosomethylethylamine (NMEA), NDEA, NDPA, *N*-nitrosodibutylamine (NDBA), NPYR, *N*-nitrosopiperidine (NPIP), NDPhA. To the best of our knowledge, only one peer-reviewed study exist in the literature that reports the occurrence of NDMA in bulk sediments acquired from the Calumet River (Indiana Harbor, Indiana) [18]. Reported NDMA concentrations from this study ranged from 0.16 to 1.69 mg/kg dry weight with a detection frequency of 60% ($n = 10$) [18]. Another study that examined the extraction methods of *N*-nitrosamines in solid matrices screened for *N*-nitrosamines in freshwater sediments ($n = 4$), but were not able to detect levels above the method detection limit of the study [19]. In order to address this important knowledge gap, the objectives of the present study were to: (i) quantify and provide the first occurrence data of eight *N*-nitrosamines in freshwater bed sediments collected near WWTPs from three geographically distinct regions of the United States; and, (ii) apply principal component analyses of water and sediment quality parameters to inform on potential mechanisms explaining any given detections of harmful *N*-nitrosamines in freshwater sediments.

2. Materials and methods

2.1. Chemicals

Analytical standards of *N*-nitrosamines and other chemicals were purchased from Sigma-Aldrich (St. Louis, MO), including NDMA, NMEA, NDEA, NDPA, NDBA, NPYR, NPIP, NDPhA, dichloromethane (DCM) (HPLC grade), methanol (LC–MS grade), water (HPLC grade), ammonium acetate, and acetic acid. The deuterated isotopes NDMA- d_6 , NDPA- d_{14} and NDPhA- d_6 were purchased from Cambridge Isotope Laboratories (Andover, MA). The deuterated isotope NPIP- d_{10} was purchased from C/D/N Isotopes Inc. (Quebec, Canada).

2.2. Sediment samples

Grab samples were collected from the top 10 cm of surficial freshwater sediments in 40 U.S. locations near 14 WWTPs between 2009 and 2015. Samples were collected from the Southern, Mid-western and Western U.S. during spring, fall and winter seasons, respectively. Due to confidentiality agreement with municipalities, the location of the facilities is not revealed in the present study and spatial analyses were not part of the scope of work. After collection, samples were stored in amber glass jars at -20°C until analysis. The flow volume processed by the sampled WWTPs varied: three processed <3.8 million liters per day (ML/d), seven between 3.8 and 38 ML/d, two between 38 and 380 ML/d, and two treated >380 ML/d. The majority of sediment samples (39 of 40) were collected within 3000 m of the corresponding WWTP, either upstream (30% of the samples) or downstream of the plant (60% of the samples).

Download English Version:

<https://daneshyari.com/en/article/4979943>

Download Persian Version:

<https://daneshyari.com/article/4979943>

[Daneshyari.com](https://daneshyari.com)