Environmental Pollution 178 (2013) 211–219

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

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

Cadmium and associated metals in soils and sediments of wetlands across the Northern Plains, USA

Donna L. Jacob[a,c,*,1], Alex H. Yellick[a], La Toya T. Kissoon[a], Aida Asgary[a], Dimuthu N. Wijeyaratne[a], Bernhardt Saini-Eidukat[b,c], Marinus L. Otte[a,c]

[a] Wet Ecosystem Research Group, Department of Biological Sciences, NDSU Department 2715, P.O. Box 6050, Fargo, ND 58108-6050, USA
[b] Department of Geosciences, NDSU Department 2745, North Dakota State University, Fargo, ND 58108-6050, USA
[c] ND INBRE Metal Analysis Core, NDSU Department 2715, P.O. Box 6050, Fargo, ND 58108-6050, USA

A R T I C L E I N F O

Article history:
Received 10 December 2012
Received in revised form
14 February 2013
Accepted 1 March 2013

Keywords:
Prairie potholes
Riparian
Floodplains
Shallow lakes
Zinc

A B S T R A C T

Cadmium, present locally in naturally high concentrations in the Northern Plains of the United States, is of concern because of its toxicity, carcinogenic properties, and potential for trophic transfer. Reports of natural concentrations in soils are dominated by dryland soils with agricultural land uses, but much less is known about cadmium in wetlands. Four wetland categories – prairie potholes, shallow lakes, riparian wetlands, and river sediments – were sampled comprising more than 300 wetlands across four states, the majority in North Dakota. Cd, Zn, P, and other elements were analyzed by ICP-MS, in addition to pH and organic matter (as loss-on-ignition). The overall cadmium content was similar to the general concentrations in the area's soils, but distinct patterns occurred within categories. Cd in wetland soils is associated with underlying geology and hydrology, but also strongly with concentrations of P and Zn, suggesting a link with agricultural land use surrounding the wetlands.

1. Introduction

Cadmium occurs locally in high concentrations in the Northern Plains of the United States due to the prevalence of shale-derived soils (Holmgren et al., 1993; Garrett, 1994; Hopkins et al., 1999). The metal accumulates in organisms and is of concern because of its relative toxicity and its carcinogenic properties (Waalkes, 2000; Goyer et al., 2004; Satarug et al., 2010), and has been banned in the European Union in a wide array of products (Communication Department of the European Union, 2011).

The Northern Plains region is highly productive in terms of agriculture and wildlife, and both may be impacted by Cd in the environment. Cadmium occurs in some foods, including grains and fish (Department of Health and Human Services, 2008; European Food Safety Authority, 2009). While there have been no direct reports of excessive concentrations of Cd in food from the Northern Plains, North Dakota sunflower seeds have the potential to exceed the maximum allowance designated by food safety regulators overseas (Comis, 1995). As for wildlife, the millions of small wetlands covering the Prairie Pothole Region support more than half of the important migratory bird species in the US (Kantrud et al., 1989), in addition to resident birds, animals, and plants. Although there have not been any confirmed negative impacts of cadmium on wildlife in the region, there is concern about low-level exposure to the metal and transfer to higher trophic levels, including humans (Li et al., 1997; Burger, 2008; Pillatzki et al., 2011; Rojas-Cifuentes et al., 2012).

Knowledge about the natural distribution of Cd in wetlands, the most productive of terrestrial ecosystems, has been sketchy at best despite the fact that its relative toxicity and carcinogenicity have been long known. Large-scale databases containing data on Cd distribution in soils are made available by government organizations, but these are substantially limited concerning wetland systems. The Geochemical Survey (US Geological Survey website) reports cadmium concentrations across the US, including some wetland soils and sediments, but mostly from drylands (we prefer the term 'dryland' to 'upland' as the opposite of 'wetland', because 'upland' is an ambiguous term – 'uplands' are elevated lands, such as hills and mountains, in British English), and with relatively high detection limits (2 mg kg^{-1}). The EPA's metadata analysis of Cd in soils (US EPA, 2003) reflects mostly dryland soils. The PLUTO database (US Geological Survey, 2001) includes soils as well as sediments from wet ecosystems, but the Cd detection limits are

* Corresponding author.
E-mail addresses: donna.jacob@ndsu.edu (D.L. Jacob), bernhardt.saini-eidukat@ndsu.edu (B. Saini-Eidukat), marinus.otte@ndsu.edu (M.L. Otte).
[1] Present address: NDSU Department 2715, P.O. Box 6050, Fargo, ND 58108-6050, USA.

0269-7491/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.envpol.2013.03.005

high; in many cases 2 mg kg^{-1} and sometimes even 20 mg kg^{-1}, resulting in most samples with non-detectable concentrations of Cd. The Geochemical Atlas of Europe (Forum of European Geological Surveys website) reports Cd concentrations, to low detection limits (0.02 mg kg^{-1}), in a variety of sediment types, including streams and floodplains. This database is useful for comparison with the United States.

Smaller-scale Cd distribution studies in our study area specific to wetlands are few and not very detailed. An early study on Cd and associated metals in riverine wetlands and prairie potholes by Martin and Hartman (1984) reported values from 13 Waterfowl Production Areas and National Wildlife Refuges across five states in the region. That study was valuable because it was probably the first report on Cd levels in wetlands in the area. However, the sampling density was very low and so the data did not sufficiently assess the variation in Cd in wetlands across the region, which comprises hundreds of thousands of wetlands. The same applies to their comparison of six riverine wetlands with five prairie potholes – the low number of observations across that huge region was simply not enough to come to meaningful comparisons between the two types of wetlands. The Minnesota Geological Survey sampled stream sediments in our sampling area, but not lakes (Lively and Thorleifson, 2009).

Our research group focuses predominantly on cycling of elements, most of which are metals, in wet ecosystems. Over recent years, we collected and analyzed the element composition of soils and sediments from wetlands across the Northern Plains in the US, mostly from North Dakota (ND) and Minnesota (MN), but also some from Montana (MT) and South Dakota (SD). Here we report the distribution of Cd and associated metals based on four separate studies on multi-element composition of (1) prairie wetland soils and (2) riparian floodplains in ND, MT, and SD; (3) shallow lake sediments in MN, and (4) sediments of two rivers of environmental concern in ND, the Souris and Turtle rivers. We included the latter, because sediments make up an important part of riparian floodplain soils. These studies combined provide an extensive dataset of Cd concentrations and other elements in wetland soils and sediments across the landscape.

The aims of this paper are to (1) understand the spatial distribution of Cd and associated elements in soils and sediments of wetlands across the region, (2) assess the associations of Cd with other elements, and (3) assess whether or not consistent differences exist between types of wetlands. Even though this study was carried out in the Northern Plains of the United States, the landscape and ecology are similar to, and the information we provide thus relevant to, other large areas of partly glaciated landscapes with prairie pothole-like wetlands and shallow lakes in the Northern Hemisphere (e.g. Canada, northern Europe, and northern Asia). Our reported limit of detection at 0.089 nmol g^{-1} (0.01 mg kg^{-1}) was much lower than most of the existing databases. This is the first study over a wide geographic area with a large sample set that specifically addresses the distribution of Cd in wetlands.

The biogeochemistry of metals in the environment, particularly in wetlands, is a major influence on distribution and movement in ecological systems. Cadmium concentrations can be affected by wetland conditions in several ways, including sediment transport, oxidation/reduction, pH, and organic matter content. Franzen et al. (2006) reported higher values of DTPA-extractable Cd concentrations in 'depressional' landscape positions compared to slope or 'upland' landscape positions. These observations may mean that the total amounts of Cd per weight unit were higher in depressional landscape positions due to downward movement of Cd from upslope to downslope, or the chemistry at depressional landscape positions rendered more Cd extractable at similar total amounts. If we assume that the extractability of Cd did not change much across landscape positions, then wetlands, particularly prairie potholes, being situated in depressions in the landscape, would be expected to act as sinks of metals. This might result in generally higher levels of metal concentrations compared to dryland conditions. However, we did not sample drylands adjacent to the wetlands in our studies, nor do such data exist in enough detail from other studies to make in-depth comparisons.

A typical characteristic of flooded wetland soils is the development of anoxic, reduced conditions. This results in accumulation of organic matter in the soil, formation of metal sulfides, and commonly near-neutral pH. Cd can remain immobilized in wetland soils under these conditions (Gambrell, 1994; Jacob and Otte, 2003). We thus expected a correlation between sediment Cd concentrations and organic matter content due to binding/adsorption (Salomons and Förstner, 1984; Gambrell, 1994; Spurgeon et al., 2008). Other factors affecting Cd concentrations include the particle size distribution of the soils/sediments – most metals bind predominantly smaller particles, particularly the fraction smaller than 63 μm – and pH (Salomons and Förstner, 1984). Because our samples were sieved through either 63 μm or 180 μm sieves before analysis, and did not otherwise assess particle size distributions on the samples, we are unable to assess the relationship between particle size of soils/sediments and Cd concentrations for our data. Similarly, differences between the data sets in determination of pH limit our ability to make comparisons across the entire data set.

It was further expected that Cd concentrations would correlate with Pb, Zn, and perhaps Ag, As, and S concentrations, because the chemistry of the metals is known to be similar and associated with S chemistry (Salomons and Förstner, 1984; Chaney, 2010). As Chaney (2010) pointed out, Cd and Zn should always be considered together, because they have similar biogeochemical behavior in soils and accumulation in organisms. However, as Schultz et al. (1980) noted, they can be decoupled and have low overall correlation in Pierre Shale. In addition, there can be anthropogenic additions of Cd and Zn to soils and sediments from the use of mineral P fertilizers (Mortvedt, 1996).

We also expected relationships between Cd concentrations and the underlying geology, with higher Cd concentrations in wetlands occurring where the surface geology, and thus the soil via pedogenesis, was higher in Cd. In the central and eastern portion of the region, multiple glacial advances from a north-northwesterly direction deposited shale-bearing tills, most recently during late Wisconsin time. In eastern North Dakota, these tills overlie bedrock that itself is shale, typically the Cretaceous Pierre Shale. Schultz et al. (1980) studied the geochemistry of the Pierre Shale across the western U.S. The presence of shale as bedrock, and as a lithologic component of the substrate on which wetlands were formed, is an important influence on soil and wetland chemistry in the region. For example, we expected higher Cd values for the sediments of the Turtle River in ND and for the wetlands in the northeast corner of ND, which are adjacent to the Pembina escarpment. There the Pierre Shale outcrops and the Pierre aquifer is near the surface. These units are known for their relatively high concentrations of metals including Cd (Hopkins et al., 1999). The Pierre aquifer partly supplies water to the Turtle River (Dalrymple and Dwelle, 2012).

2. Materials and methods

Four different data sets were collated and will be referred to as 'Potholes', 'Shallow Lakes', 'Riparian Floodplains', and 'River Sediments'. In the 'Potholes' project, the majority of the wetlands sampled were located in regions that had been formed by glaciation, and thus are depressional wetlands, or potholes. Some of the 'pothole-like' wetlands included in this study were in soils unaffected by the most recent glaciation events, but for ease of description, they are included in the 'Potholes' group. For all data sets, samples were taken (typically at least 5 replicates per