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Investigating mercury in road sediment in Michigan City, Indiana: A new type of environmental pollution record

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ABSTRACT

Mercury (Hg) is well recognized as a toxic heavy metal known to detrimentally impact the health of humans and wildlife. A common source of Hg pollution is coal combustion emissions associated with energy generation. This study takes the novel approach of using road sediment to assess the presence, distribution, and concentrations of Hg in the environment. Here, the spatial distribution of Hg in road sediment is also evaluated relative to the Northern Indiana Public Service Company (NIPSCO) Generating Station in Michigan City, Indiana, U.S.—a coal-burning power plant. Given that NIPSCO plans to decommission the plant by 2028, this data provides a baseline for evaluating Hg concentrations in the local environment and for future assessment of environmental recovery from legacy pollution and/or impacts of pollution redistribution associated with site redevelopment. Our data reveal an average concentration of 6.8 (μg/kg) of Hg and a range from 1.5 μg/kg to 28.5 μg/kg in road sediment samples ($n = 42$). Across the ~53 km^2 study area, the overall distribution of Hg is patchy and irregular spatially, however, higher concentrations are more proximal to the coal plant and are generally consistent with prevailing wind directions. Other significant Hg inputs are present in the region although, specifically two major areas of steel manufacturing located to the west of Michigan City and broadening the scope of sampling may be an essential next step. However, this investigation demonstrates that road sediment may be an effective medium for investigating Hg pollution in the environment globally.

1. Introduction

Air emissions from coal combustion are a major known source of environmental mercury (Hg) pollution in the United States and globally (e.g., (Guttikunda and Jawahar, 2014; Hu and Cheng, 2016; Liang et al., 2014; Liu et al., 2019; Rallo et al., 2011; You and Xu, 2010; Zhang and Smith, 2007)). Coal combustion is a direct source of Hg emissions due to the vaporization of the Hg components within coal, which are released after the coal is exposed to high heat (USEPA, 2023a). Mercury is a toxic element and a major pollutant of worldwide concern owing to extensive industrial emissions (Cordy et al., 2011; Huang et al., 2012; Pereira et al., 2008; Singh et al., 2017). Furthermore, Hg is also well recognized to bioaccumulate in ecosystems and impact fish (e.g., (Milestone Inc 2017; Uryu et al., 2001)), crabs (e.g., (Taylor and Calabrese, 2018; Zhao et al., 2010)), and additional animal habitats, such as birds (e.g., (Seewagen, 2018; Whitney and Cristol, 2017)) and otters (e.g., (Halbrook et al., 1994; Kruuk et al., 1997)). Not only is Hg toxic to wildlife, but it is also a major concern to human health because of its known toxicological effects. Exposure to Hg in varying forms can lead to health issues and disease in the following areas: cardiovascular, respiratory, gastrointestinal, endocrine, and more (e.g., (Genchi et al., 2017; Hu et al., 2021; Taux et al., 2022; CDC, 2015; Azevedo et al., 2012)). Since 2011, the United States Environmental Protection Agency (USEPA 2015a,b,c,d) has placed regulation standards on Hg and other pollutants resulting from coal-burning power plants (USEPA, 2023a). The decision to implement such regulations reflect their coal plant contributions to Hg pollution in addition to other toxic emissions (e.g., (USEPA, 2023a)).

Road sediment defined here as unconsolidated material that occurs in, and is associated with roadways, has the potential to provide proxy data that can be used to identify and quantify pollutants emitted into the local environment (Dietrich et al., 2022). Road sediment can be an especially efficient tool for quickly obtaining a snapshot of local

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pollutant sources and loads because it is ubiquitously present throughout the urban environment, is often publicly accessible, and it retains a chemical signature of its source(s) (e.g., (Dietrich et al., 2022; LeGalley and Krekeler, 2013; LeGalley et al., 2013; O`Shea et al., 2021)). Additionally, data obtained from the analysis of road sediment has multiple applications, for it is location-specific and often reflects issues related to environmental justice (Dietrich et al., 2018; Dietrich et al., 2019; Dietrich et al., 2022). Compared to studies of other environmental media such as water, soil, and the atmosphere, there are comparatively few studies of road sediment pollution, particularly within the U.S. Furthermore, investigations of road sediment which focus on characterizing Hg abundances are critically lacking with a limited number of analyses reported over the past 50 years (see (Dietrich et al., 2022) and references therein). The aim of this investigation is to assess whether road sediment may be an effective medium for investigating Hg pollution in the environment.

Michigan City, Indiana represents a major urban area (population ~32,000) located along the southern shore of Lake Michigan (Fig. 1). A coal-burning power plant owned and operated by the Northern Indiana Public Service Company (NIPSCO) began operations in 1931 and is a major provider of electricity to Northwest Indiana. The NIPSCO property, which includes the coal-burning power plant, cooling tower, and coal-ash waste ponds border Lake Michigan and the Indiana Dunes National Park. NIPSCO has announced plans to retire the station in 2028 and remove waste associated with coal combustion. Consequently, the Michigan City area provides a unique and important opportunity to evaluate Hg pollution in an urban setting during coal combustion operations and in the years following the closure, thus providing important insights into the fate of legacy pollution. The hypotheses evaluated in this investigation are:

1. Hg is present in measurable concentrations in road sediment collected throughout the urban area of Michigan City, Indiana.
2. Hg concentrations in road sediment will vary spatially and systematically, reflecting higher concentrations near the Northern Indiana Public Service Company (NIPSCO) coal-burning power plant in Michigan City, Indiana and lower concentrations with increasing distance from the facility.

2. Setting

2.1. Socioeconomic setting

According to the 2020 Decennial U.S. Census, Michigan City, Indiana

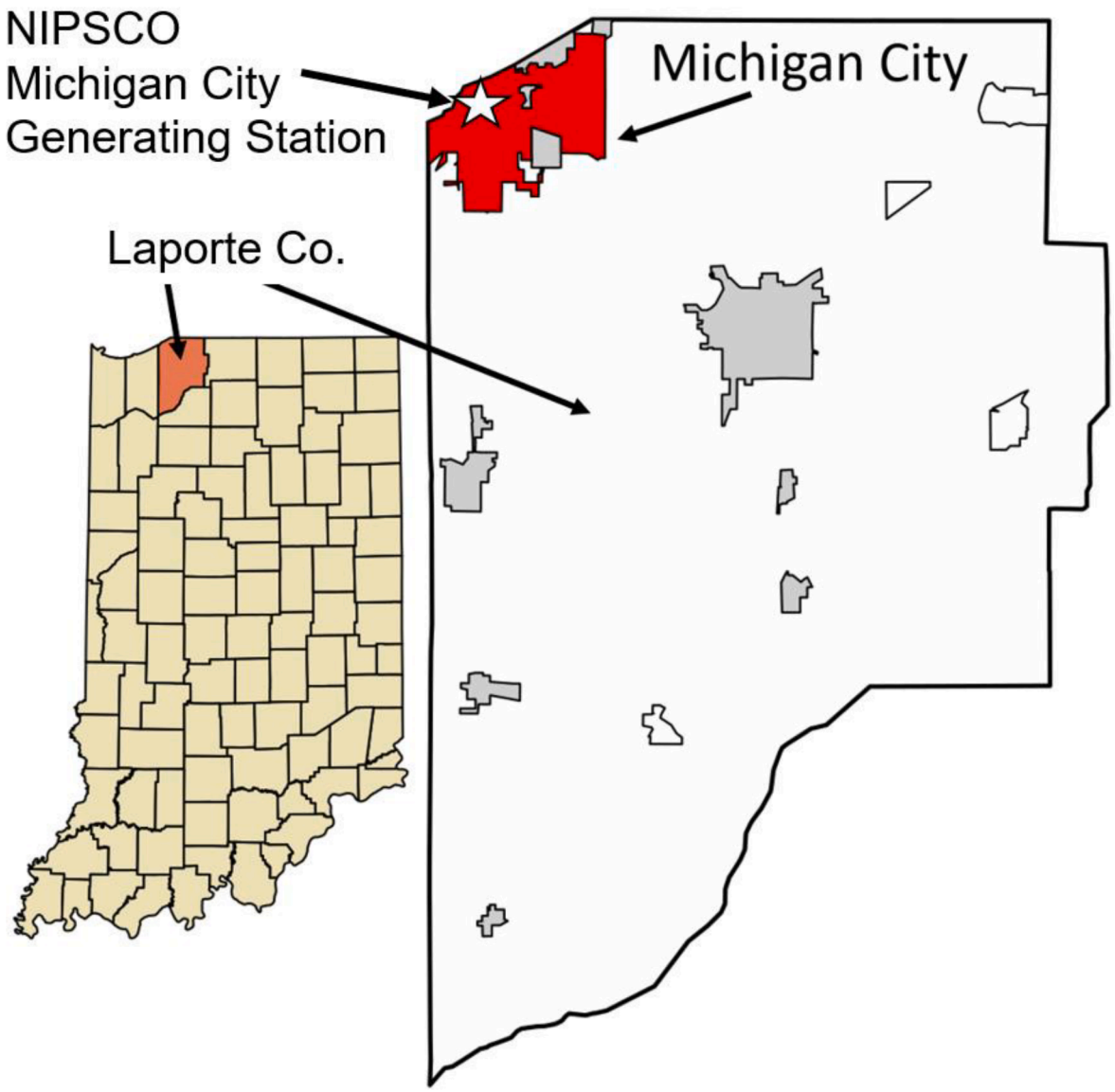

Fig. 1. Location map for Michigan City shown in the context of the state of Indiana and LaPorte County, modified after DemocraticLuntz (DemocraticLuntz, 2022).

has a population of approximately 32,075 residents with ~59 % identifying as white alone, ~27 % identifying as Black or African American, and ~10 % identifying as two or more races (US Census Bureau 2020). It is estimated that 21.2 % ± 3.4 % of this population live below the poverty line, compared to the national average of 12.6 % ± 0.1 % (US Census Bureau 2021).

Established in 1912, NIPSCO is one of the six energy delivery companies of the parent company NiSource and is the primary distributor of natural gas and electricity for northern Indiana, including Michigan City (NIPSCO.com*)*. The Michigan City Generating Station (680 MW_e) is a 130-acre site with a cooling tower that has burned coal for electricity for nearly a century. Per the U.S. EPA 2015 regulation of Coal Combustion Residuals (CCRs), the Michigan City Generating Station initiated the removal of the station's five coal ash ponds and implemented groundwater monitoring (NIPSCO 2023). Hence, the site is also relevant in the context of pollution recovery as the NIPSCO converts to renewable energy and removes coal ash ponds. This in turn allows for a future study investigating how coal pollution in the area may attenuate following this transition. It is noted however that the redevelopment of the region could also potentially initiate pollution by redistribution of ash through the deconstruction of coal ash ponds (e.g., (NIPSCO 2023)).

Other potential contributors to Hg emissions in the immediate 10-mile area may also still exist, including the following manufacturing companies, identified as toxic release inventory sites (TRI) by the U.S. EPA: Fas-Pak Inc., Sulair LLC, GAF, Triplex Plating Inc., Marley-Wylain Co., PHM Brands LLC, Shell Catalysts & Technologies LP, Diamond MFG Co. Midwest (USEPA, TRI Data and Tools, (USEPA, 2023a)). Also, important to note is the presence of major TRI sites, specifically steel manufacturing facilities, located in the towns of Gary and East Chicago, to the west and within 30 miles of the Michigan City study area.

2.2. Geologic setting

Michigan City, Indiana is located at the mouth of the Trail Creek River system in the Little Calumet-Galien subwatershed of Lake Michigan. It is part of the Calumet Lacustrine Plain physiographic unit which includes relict shorelines, dunes, interdunal and inter-shoreline wetlands and drainages formed during the evolution of modern Lake Michigan throughout the late Pleistocene and Holocene (Hartke et al., 1975). Surficial sediments are broadly characterized by low-lying complexly intermixed clay, sand, and silt deposits. The area of Michigan City area consists mainly of dune and coastal deposits associated with the Calumet Beach, a shore parallel barrier beach, and the Tolleston Beach, the most landward dune complex. Lagoonal deposits are also present, associated with the formation of the Great Marsh which borders Michigan City to the west. The developed area of Michigan City consists mainly of high-relief parabolic dunes dating to the late Holocene that were largely mined for industrial use and urban development in the early 19th century. The NIPSCO power generating station sits on the site of what was previously the largest dune in the area; Hoosier Slide. The Indiana Dunes National Park is a major Holocene dune complex (e.g., (Argyilan et al., 2015)) and is located west of Michigan City with 15 miles shoreline on Lake Michigan and 15,000 acres (National Park Service (NPS), 2022).

Underlying the surficial deposits are glacial deposits of the Pleistocene epoch that consist of mostly sand and fine gravel laid down as glacial outwash and as till inclusions, with clay-rich till units of varying thickness and areal distribution (Hartke et al., 1975). Around Michigan City, there are more than 50 m of coastal and glacial deposits which overly limestone, dolomite, sandstone, and shale of Cambrian through Devonian age.

3. Methods

3.1. Field collection

For this study, the data collection process included traveling to 42 roadside locations within the ~53 km^2 of Michigan City, Indiana In addition, a sample of a Holocene beach ridge sand, a sample of a Holocene lake clay, and a sample of the local glacial till were collected as potential background reference materials. A sample of the Ottawa sand served as a trip blank. At each location, GPS coordinates and field notes were recorded. Photographs of the locations, gathering process, and road sediment samples were also acquired and organized by sample identifier. During collection, clear plastic spoons were used to gather sediment and place them into labeled glass jars. This spoon type was necessary to prevent contamination; new spoons and jars were used for each sample. Team members wore gloves when handling all samples and safety vests when working near traffic. Road sediment samples were then stored securely in a cooler with ice per the U.S. EPA guidelines for handling samples for Hg analysis. Sample splits were then shipped to Milestone Incorporated, Connecticut, for bulk Hg analysis.

3.2. Hg analysis

A Milestone 7th Generation DMA-80 evo Direct Mercury Analyzer was used to determine Hg concentrations in sampled road sediment at Milestone's lab center in Shelton, Connecticut. Mercury analysis with the DMA-80 involved placing the weighed sample in nickel boats, which were then transferred to a 40-position autosampler. The nickel boats were then heated to evolve the Hg. Mercury is released into the system and isolated from other materials. Mercury was then emitted into measuring cells within a gold amalgamator exposed to an optical analyzer. For this study, Hg concentrations were analyzed at the μg/kg level. The software, EasyCONTROL was used to acquire and process data.

3.3. Scanning electron microscopy

For scanning electron microscopy (SEM) analyses, sample splits were obtained using a Zeiss Supra 35 VP field emission scanning electron microscope (FESEM) at the Center for Advanced Microscopy and Imaging (CAMI) at Miami University. Carbon adhesive tabs were used to mount samples on aluminum stubs. Imaging and energy dispersive spectroscopy (EDS) data was obtained using variable pressure with nitrogen (N_2) as the compensating gas and in backscatter detector mode (BSD). A Bruker Quantax EDS spectrometer with a detection limit of approximately 0.10 wt % was used for acquiring X-ray spectra. This preparation method and instrument has been extensively used in a varied set of previous investigations (e.g., (Brum et al., 2020; Cymes et al., 2020; Dietrich et al., 2018; Dietrich et al., 2019; Flett et al., 2016; Lindeman et al., 2020; Oglesbee et al., 2020; Paul et al., 2017; Armentrout et al., 2015; Barrett et al., 2011; White et al., 2013)).

3.4. Wind data analysis

Hourly wind speed and direction for the Michigan City Municipal Airport – Phillips Field (lat 41.7031, long -86.2819) were retrieved from the NOAA (National Oceanic and Atmospheric Administration (NOAA) 2023) Wind Roses - Charts and Tabular Data site and processed using the Midwest Regional Climate Center's cli-MATE tool. The period of record processed was from the first available date of January 1, 2014, to December 31, 2021. Measurement units were miles per hour (mph) and Beaufort wind speed divisions were applied. For regional context, wind rose data was also obtained for Gary, IN and is provided in the supplemental materials.

3.5. Spatial analyses

Spatial analyses were conducted using ArcGIS Pro 3.0.0. The inverse distance weighted (IDW) spatial analysis geoprocessing tool was used with parameters of power 2 and a variable search radius with the number of points set at 12. The generate near table analysis tool was utilized for calculating planar distance from each road sediment sampling location to potential Hg pollutant emitter sites.

4. Results

4.1. Hg concentrations and distributions

For sampled road sediment, Hg concentrations varied from 1.5 μg/kg to 28.5 μg/kg with a mean of 6.8 μg/kg, a median of 6.5 μg/kg, and a standard deviation of 5.5 μg/kg at 1σ (Table 1). Plotted as a histogram, the data is mostly unimodal with some concentration outliers of approximately 25 μg/kg and 28 μg/kg (Fig. 2). For the potential background reference materials, the sampled glacial till yielded 25.1 μg/kg, the Ottawa sand yielded 0.4 μg/kg, the lake clay yielded 6.2 μg/kg, while the Holocene sand also yielded 0.4 μg/kg (Table 2).

The inverse distance weighted (IDW) map of Hg concentration reflects that Hg concentrations are highest immediately south and southwest of the NIPSCO Michigan City Generating Station and appreciable concentrations occur in an irregular patchy distribution at variable distances from the generating station (Fig. 3). Generally, concentrations of Hg then dissipate or become irregular with distance from the station. The associated IDW map indicates that Hg concentrations do not uniformly decrease with increasing distance from the plant (Fig. 3). The planar distance (in meters) of potential Hg pollution sites was plotted against Hg concentrations in road sediment (Fig. 4). From this, the Spearman rank correlation coefficients and p values indicate no significant relationships ($p > 0.7$ for all sites) between distance to potential pollution emitters and Hg concentrations. This result indicates that there is no direct or precise link of Hg pollution to the NIPSCO Michigan City Generating Station, nor any other nearby TRI sites located in Michigan City.

Data for an exact Hg budget are not currently quantified for the NIPSCO Michigan City Generating Station; however, some basic semi-quantitative estimates can be made regarding Hg contribution to the road sediment samples. The Toxics Release Inventory (TRI) indicates that the NIPSCO Michigan City Generating Station has released a total of 1,269 pounds of total Hg and Hg compounds between 2013 and 2022 (USEPA, TRI Data and Tools (USEPA, 2023a,b)). The range of annual values of total Hg and Hg compounds released for the 2013-to-2022-time frame are 82 to 208 pounds per year with an average of 127 pounds per year (USEPA, TRI Data and Tools (USEPA, 2023a,b)).

Of note, the following facilities in Michigan City do not contribute to Hg emissions in the area according to their TRI data: Fas-Pak Inc., Sulair LLC, GAF, Triplex Plating Inc., Marley-Wylain Co., PHM Brands LLC, Shell Catalysts & Technologies LP, Diamond MFG Co. Midwest (USEPA, TRI Data and Tools (USEPA, 2023a,c)).

Table 1
Concentrations of Hg in μg/kg for road sediment samples.

Sample	Result (μg/kg)	Sample	Result (μg/kg)
Mc 1-Hg	7.6	Mc 21-Hg	7.5
Mc 2-Hg	2.3	Mc 22-Hg	5.3
Mc 3-Hg	6.9	Mc 23-Hg	28.5
Mc 4-Hg	6.6	Mc 24-Hg	11.6
Mc 5-Hg	3.4	Mc 25-Hg	8.2
Mc 6-Hg	10.8	Mc 26-Hg	11.1
Mc 7a-Hg	8.1	Mc 27-Hg	4.5
Mc 7b-Hg	8.5	Mc 28-Hg	3.2
Mc 7c-Hg	1.0	Mc 29-Hg	8.7
Mc 8-Hg	9.5	Mc 30-Hg	7.5
Mc 9-Hg	4.2	Mc 31-Hg	6.5
Mc 10-Hg	4.8	Mc 32-Hg	3.1
Mc 11-Hg	1.5	Mc 33-Hg	1.4
Mc 12-Hg	4.4	Mc 34-Hg	6.8
Mc 13-Hg	2.1	Mc 35-Hg	2.4
Mc 14-Hg	1.5	Mc 36-Hg	10.4
Mc 15-Hg	5.0	Mc 37-Hg	10.7
Mc 16-Hg	6.7	Mc 38-Hg	5.6
Mc 17-Hg	8.9	Mc 39-Hg	25.3
Mc 18-Hg	4.0	Mc 40-Hg	9.7
Mc 19-Hg	2.5	Mc 41-Hg	3.4
Mc 20-Hg	0.9	Mc 42-Hg	8.3

4.2. Scanning electron microscopy

Scanning electron microscopy of spatially representative samples at increasing distances from the coal plant (MC7C, MC3, MC29) identified technogenic spherule particles (Fig. 5). These observations are consistent with previous studies of road sediment in other areas of the U.S. (e.g., (Dietrich et al., 2019; LeGalley and Krekeler, 2013; O'Shea et al., 2021)). These particles are consistent with an origin associated with coal combustion. They exhibit variable compositions with major silica, calcium, and iron components, and diameters from 1 to 20 μm. It is important to note that discrete Hg-bearing particles were not observed in SEM, suggesting that the form of Hg is either elemental or in nanoparticle forms too small (or at too low of concentrations) to be readily observed with SEM. This is consistent with the low bulk Hg concentrations (see earlier), such that it might not be expected that discrete Hg-bearing particles would be readily observed. Technogenic spherules were common and observed in multiple additional samples (Fig. 6), suggesting that coal pollution is a common component of road sediment in the sampled area. A significant proportion of the technogenic spherules (~85 %) were characterized by smooth, glassy textures. This is consistent with both near source atmospheric deposition and a lack of post-depositional transport. The remainder of the technogenic spherules exhibited variable textures including concentric rings likely from cooling, and abraded surfaces likely from mobilization and transport within the road sediment.

Examples of other particles interpreted as pollutants were also observed. These included lead, steel, iron-rich corroded particles, sponge-textured materials, slag, rods, barite, zinc-bearing particles, and copper-bearing particles (Fig. 7). These particles had average diameters between 15 and 250 μm (Fig. 7), are similar to those observed in road sediment in other recent U.S. studies, and commonly exhibited angular textures consistent with being locally-derived (e.g., (Dietrich et al., 2019; Dietrich et al., 2022; LeGalley and Krekeler, 2013; O'Shea et al., 2021)).

4.3. Wind data analysis

Wind data presented in Fig. 3 indicates that winds within the vicinity of Michigan City were variable during the period of record available (National Oceanic and Atmospheric Administration (NOAA), 2023). The lowest wind speeds and durations are associated with winds from the north-northeast (NNE) to the south-southwest (SSW). Winds blew most frequently from the west-southwest (WSW 230 degrees) to south (S 170 degrees) for 28.1 % of the time and from the north-northwest (NNW 330 degrees) to north (10 degrees) 14 % of the time. Maximum hourly wind speeds in the range of 19 – 25 mph were recorded only from the west to southwest (190 – 260 degrees) and north (350 – 0 degrees). According to the data, the predominant winds reflect offshore winds from the south-southwest (SSW, 180 – 230 degrees) and onshore winds from the north (350 to 10 degrees). For regional context, and as shown in supplementary Fig. 1 for Gary, IN (~30 miles west of Michigan City), winds blew most frequen tly from the west (W) and the southwest (SW).

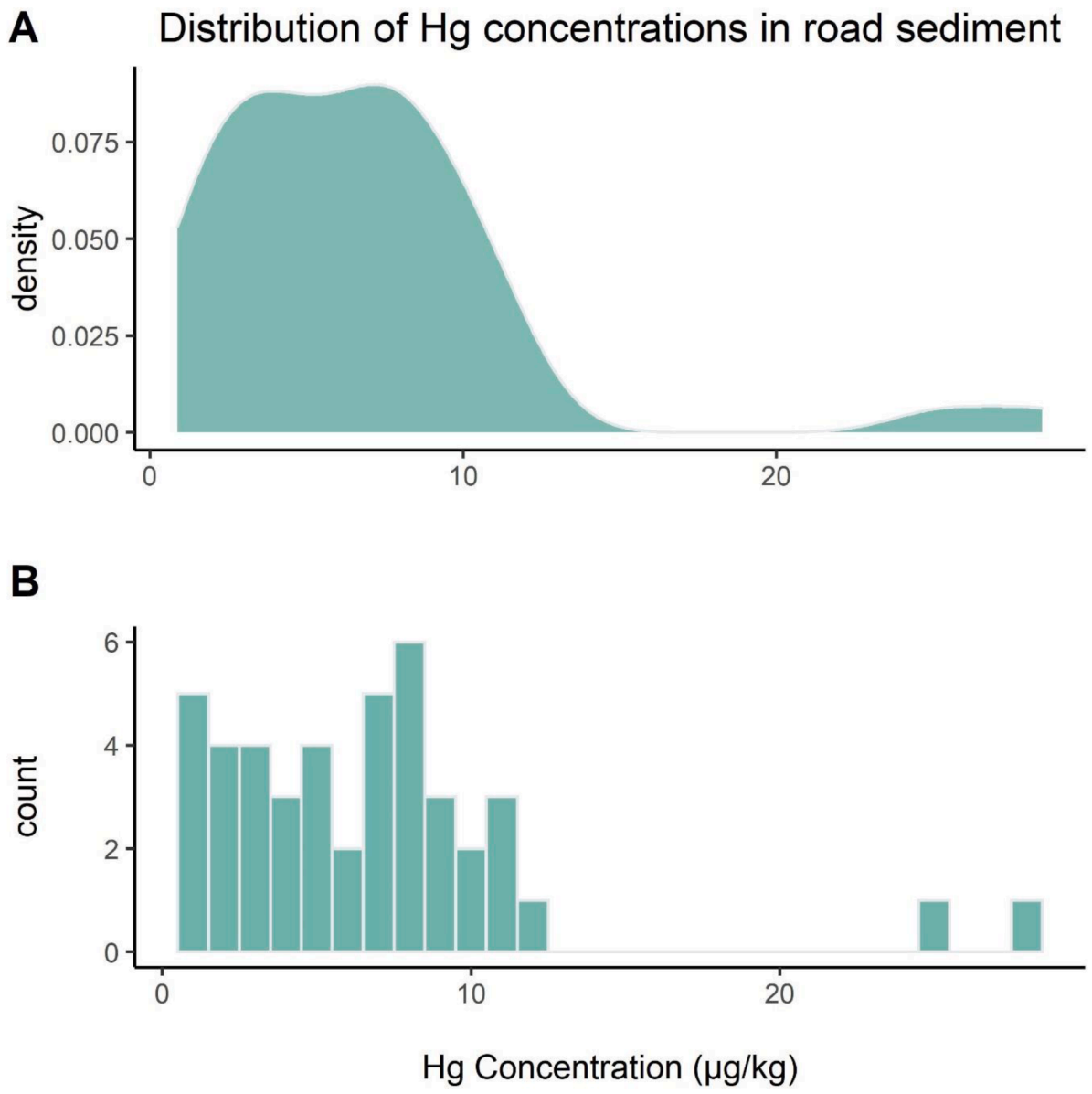

Fig. 2. Smoothed kernel density estimate (A) and histogram (B) showing the distribution of concentrations of Hg in road sediment samples in µg/kg.

Table 2
Concentrations of Hg for standards and reference samples near the study area. Dorm sample designations are Milestone standards. The certified value for Dorm-5 is 316 ± 17 µg/kg and Dorm-4 is 410 ± 0.055 µg/kg. Note that both trip blank (Ottawa sand) and background sand (MC 19 Hg Sand) are ~0.4 µg/kg.

Sample	Result (µg/kg)
Dorm-4	412.7
Dorm-5	310.3
Ottawa Sand	0.4
ID Clay Hg	6.2
ID Till Hg	25.1
MC 19 Hg Sand	0.4

5. Discussion

5.1. The NIPSCO Michigan city generating station as a potential Hg source

Several lines of evidence support the interpretation that the NIPSCO Michigan City Generating Station is a contributing source of Hg pollution detected in road sediment samples. TRI data are generally consistent with the levels of Hg pollution observed throughout the study area. For the available data for the time periods of 2013 to 2023, 1,269 pounds of total Hg and Hg compound emissions is equivalent to 5.7×10^{11} µg. The majority of this was emitted as stack air emissions and as off-site release, although stack air Hg release emissions were more common dating back to 2000 (Fig. 8). This mass as distributed throughout the 53 km^2 of Michigan City indicates a simplified average of 10,860 µg/m^2. Assuming a soil density average of 1700 kg/m^3, the road sediment sample average of 6.8 µg/kg across 1 m depth of soil over time is broadly consistent with this crude estimate (~6.4 µg/kg). However, exact budgeting or knowledge of Hg cycling at soil/sediment depth is not possible without more detailed work in the area. While these

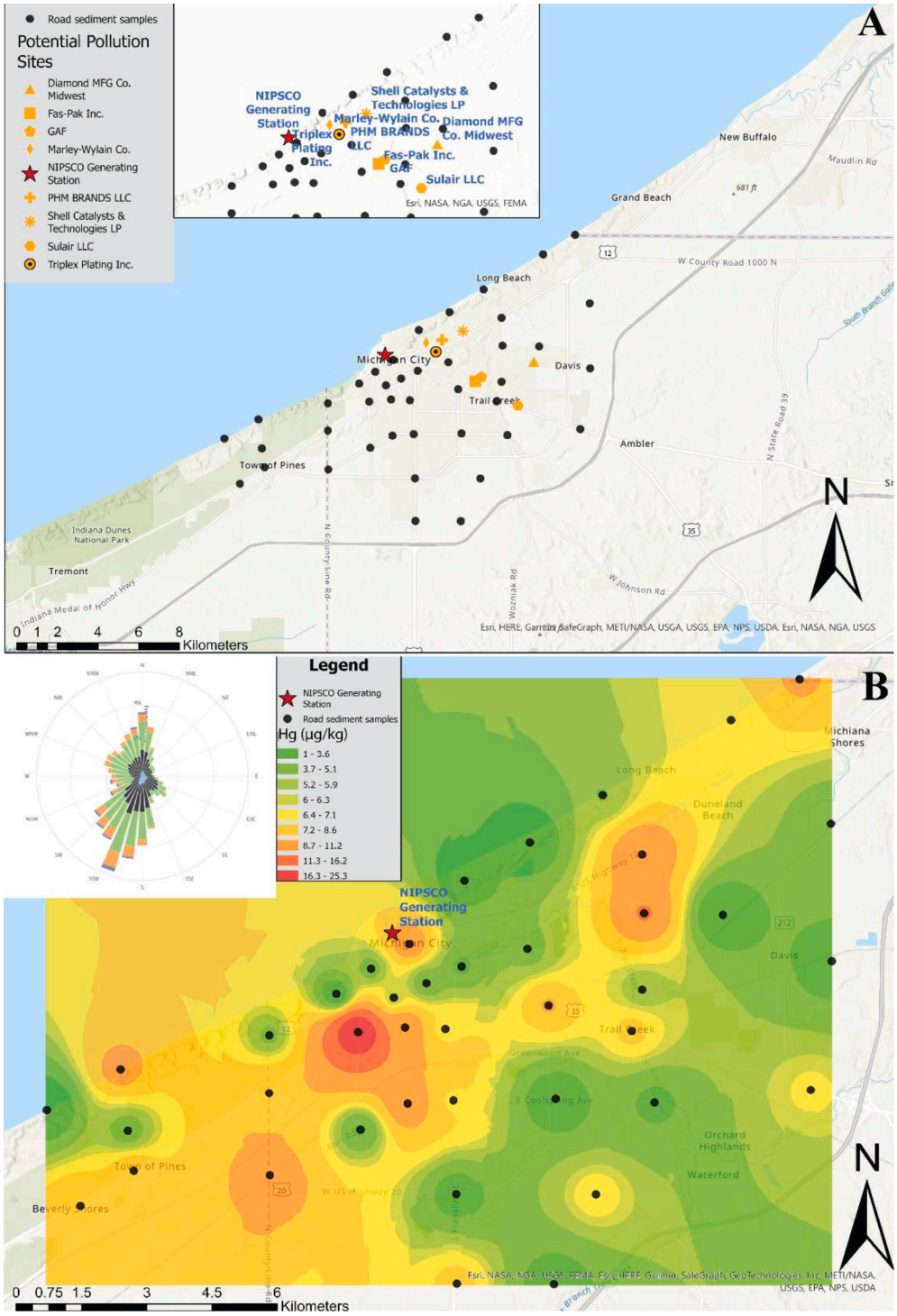

Fig. 3. Maps of: (A) Sampling locations and potential pollutant sites, including the NIPSCO generating plant and (B) Inverse distance weighted (IDW) map of Hg concentrations (in µg/kg) with the wind rose diagram for the area (National Oceanic and Atmospheric Administration (NOAA), 2023).

concentrations are what would be expected from TRI emissions alone from the NIPSCO coal plant, minor amounts of observed Hg may originate from other sources such as metal particulate (Fig. 7), which have the potential to travel far distances (e.g., (Marina-Montes et al., 2020)), e.g., from steel plants in Gary, IN (Dietrich et al., 2019).

Although an exact Hg budget cannot be established, the data suggest that much of the Hg sourced from the NIPSCO site (and other additional sources) is likely mobilized over time and is not fully retained in the road sediment. Given that most of the road areas sampled were not thoroughly covered in sediment, it is inferred that road sediment (and Hg) are being transported out of the system. There is no current constraint on the age of road sediment in Michigan City and research in this area may help better understand Hg retention and transport. Constraining the age of road sediment is notably challenging and Dietrich et al. (2022) suggests further development in this area.

The common occurrence of technogenic spherules in multiple samples throughout the area is interpreted as direct evidence that coal pollution is impacting the local environment. Such particles are consistent in size and texture with spherules observed in road sediment from other urban areas impacted by coal pollution (Dietrich et al., 2018;

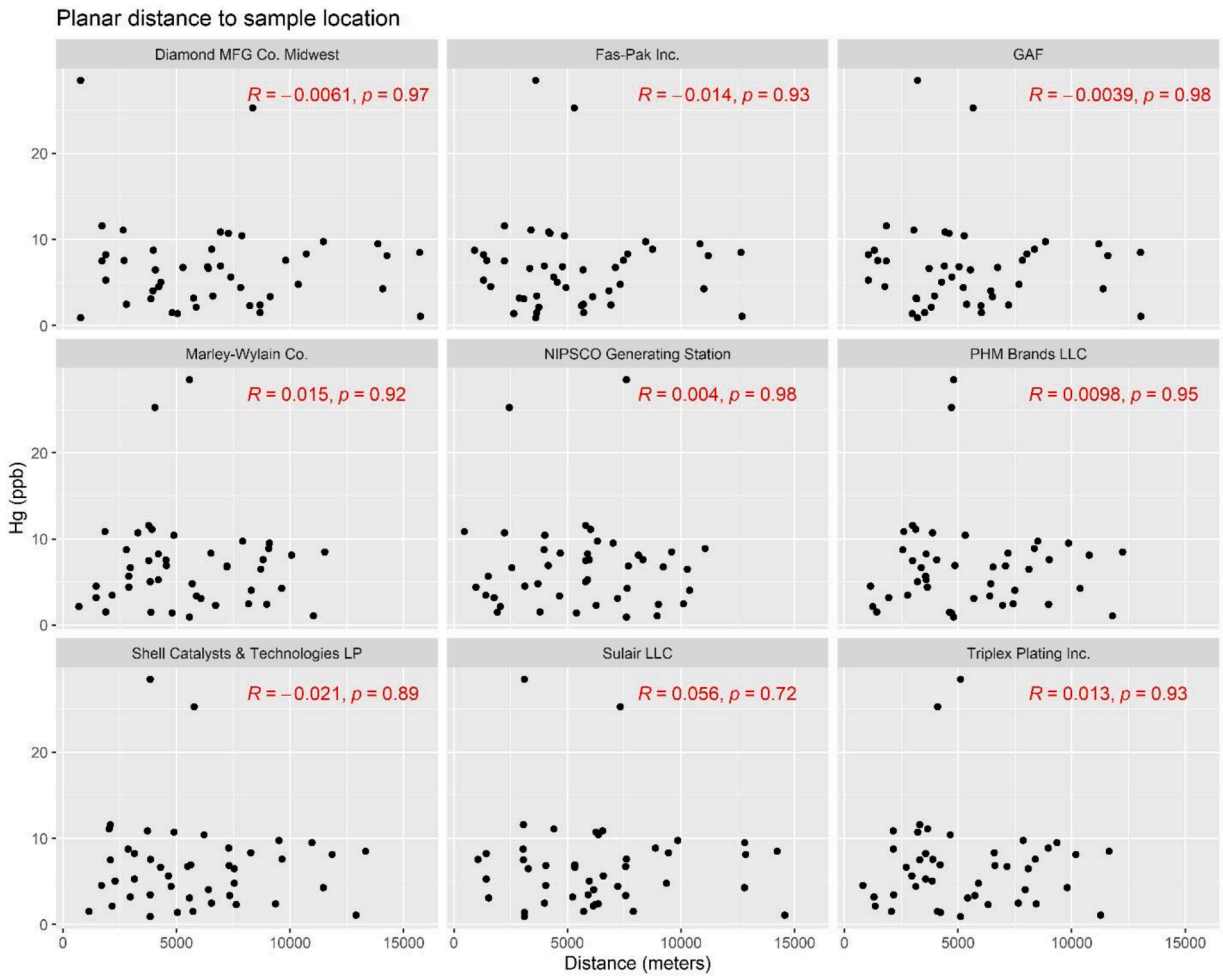

Fig. 4. Bivariate plots of planar distance (in meters) from road sediment sampling locations to potential Hg pollution sources, plotted against Hg concentrations in road sediment. Spearman rank correlation coefficients and p values indicate no significant relationships ($p > 0.7$ for all sites) between distance to potential pollution emitters and Hg concentrations.

Dietrich et al., 2019; LeGalley and Krekeler, 2013). The EDS detection limit is approximately 0.10 wt. % (1000 ppm), hence if Hg is present in observed technogenic spherules, it is likely far below the detection limit.

Additional information supporting the interpretation that Hg is at least partly derived from the Michigan City Generating Station is that Hg is known to be emitted from coal stacks in the U.S. (e.g., (Charnley, 2006)) and internationally (e.g., (Feng and Qiu, 2008; Meij and te Winkel, 2006; Wang et al., 2014)). Examples of emissions of Hg from coal stacks in the U.S. include 40 % of the 48 metric tons of atmospheric emissions (Charnley, 2006; USEPA 1999). Streets et al. (Streets et al., 2019) indicate that global coal combustion contributed a release of 558.3 Mg/year for 2015. International outputs of Hg owing to coal combustion are around 200 metric tons in China (Wang et al., 2014) with a total gaseous mercury (TGM) concentration of 8.4 ng/m^3. This is attributable to coal plants and smelting facilities (Feng and Qiu, 2008). The dominant forms of Hg in coal stack emissions are thought to be sulfide-bound, clay-bound, and organic matter-bound mercury (Zhao et al., 2019).

The spatial distribution of road sediment Hg concentrations is a supporting line of evidence that at least some Hg pollution present in the environment may be derived from the NIPSCO Michigan City Generating Station. The IDW map summarizes that the highest Hg concentrations occur near the generating station and to the S-SW. However, the large amount of spatial variability suggests that any Hg sourced from the NIPSCO plant, has likely been largely reworked and distributed, or perhaps largely deposited to the N-NE in Lake Michigan based on the predominant direction of wind from the S-SW (Fig. 3).

An additional consideration is that winds in the Lake Michigan shoreline region of Indiana are highly variable and highly seasonal. The wind rose from the Michigan City Municipal airport indicates that the strongest hourly average winds in the range of 19-25 mph are from the south-southwest (offshore) and also from the north (onshore winds). Atmosphere circulation also plays a complex role in dispersion, transformation, and removal of pollutants, as the dispersion of pollutants from source emitters (e.g., smokestacks) will be affected by crosswind mixing in both horizontal and vertical directions. Furthermore, meteorological variables, including wind speed, wind direction, temperature, humidity, precipitation (process of removal), and atmospheric pressure are the main drivers of variation in pollutant concentrations and dispersion (Bates and Caton, 2002). Additionally, post-depositional processes and transport of road sediment through run-off can have a significant impact on cycling and dispersion of Hg and other trace metals (e.g., (Dietrich et al., 2022)).

The occurrence of additional pollutants found in sediment samples via SEM may influence the distribution of Hg throughout the research area; however, this cannot currently be quantified. Analysis via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) may provide insight on Hg concentrations in individual pollutant particles and background materials, provided feasible particle separation and beam size constraints can be met. To improve constraints on the Hg budget of this sampled area, an analysis of Hg in different potential pollutant source materials is needed, such as coal ash from the NIPSCO

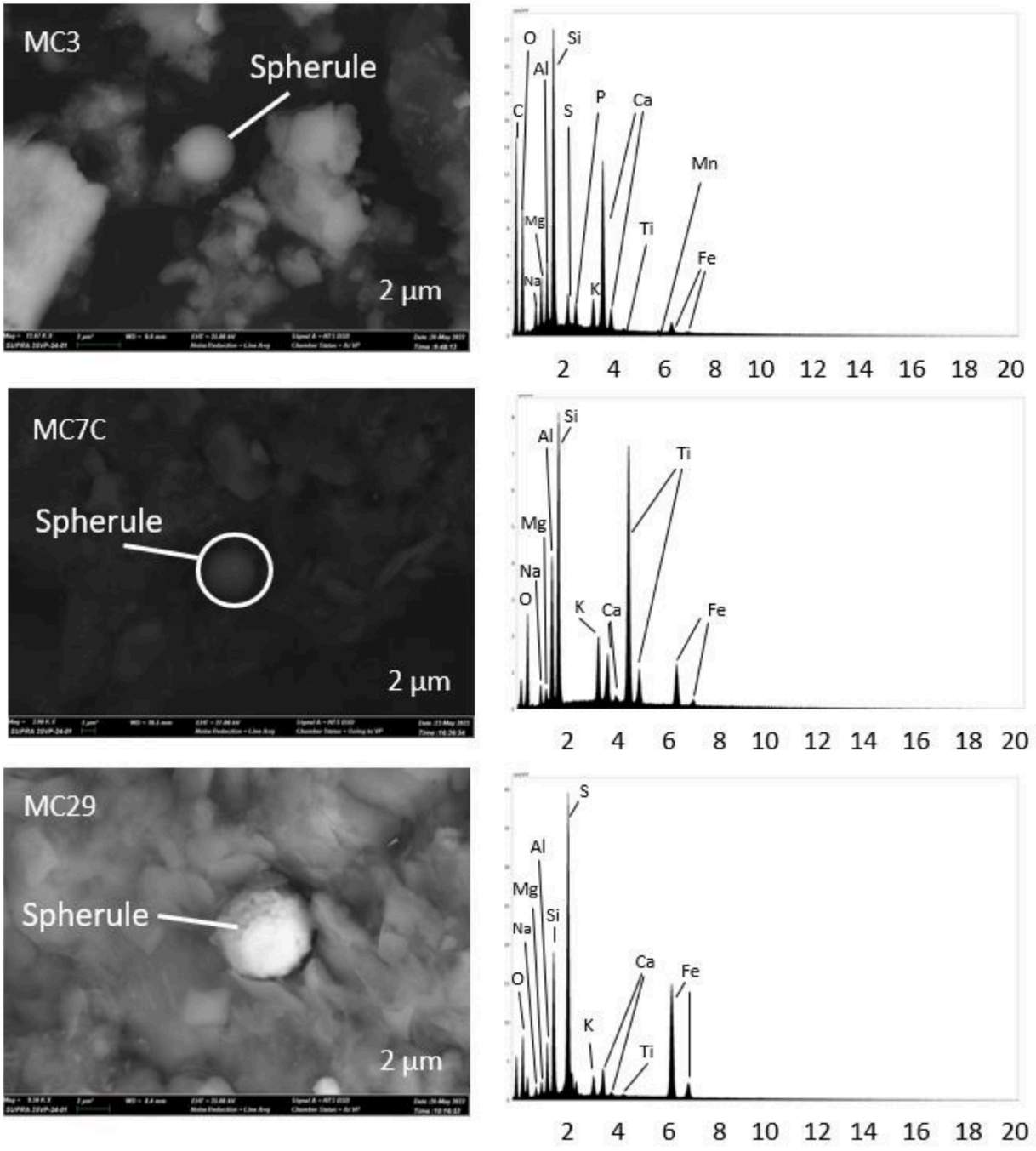

Fig. 5. Examples of micrometer (µm) scale technogenic spherules with paired EDS spectra having major lines labeled. A lack of peaks beyond 8 keV indicates Pb and As are below detection limit. Spherules are approximately 2 µm in diameter and have a variety of chemical compositions. Examples show a variety of textures, including a smooth and discrete spherule (top), an embedded spherule in matrix (middle) and a partially corroded spherule (bottom). These particles are consistent with coal pollution input into the system.

plant. At present, this study provides a benchmark for future investigations of Hg concentrations in road sediment in the U.S. and elsewhere. As environmental remediation is planned later this decade (e.g., coal ash pond clean-up; (NIPSCO 2022)), data from this investigation presents an opportunity to evaluate success.

5.2. Background and complexities of other sources

Establishing the background concentration of Hg in the natural environment is important, yet challenging to achieve. Studies spanning from 1967 to 2003 indicate varying Hg compositions within the Earth's continental crust (Rudnick and Gao, 2003). Compiled data estimates that Hg makes up 0.05 µg/g of the upper continental crust (Rudnick and Gao, 2003). The extent of pollution over time makes it challenging to establish an environmental background for Hg concentrations in urban settings. In areas less impacted by Hg pollution, like the North Sea, ~6 µg/kg Hg per square meter is reported (Wängberg et al., 2007) whereas Michigan City road sediment samples are approximately 100 to 300 times that level. We also note that the glacial till and the lake clay in the study area may not represent true background anymore because of the contributions from natural and anthropogenic Hg over time. This may explain why the till sample in this study has such elevated Hg. We also note that the Ottawa Sand (trip blank) sample has a concentration of 0.4 µg/kg as a reference point and the Holocene dune sand sample has a

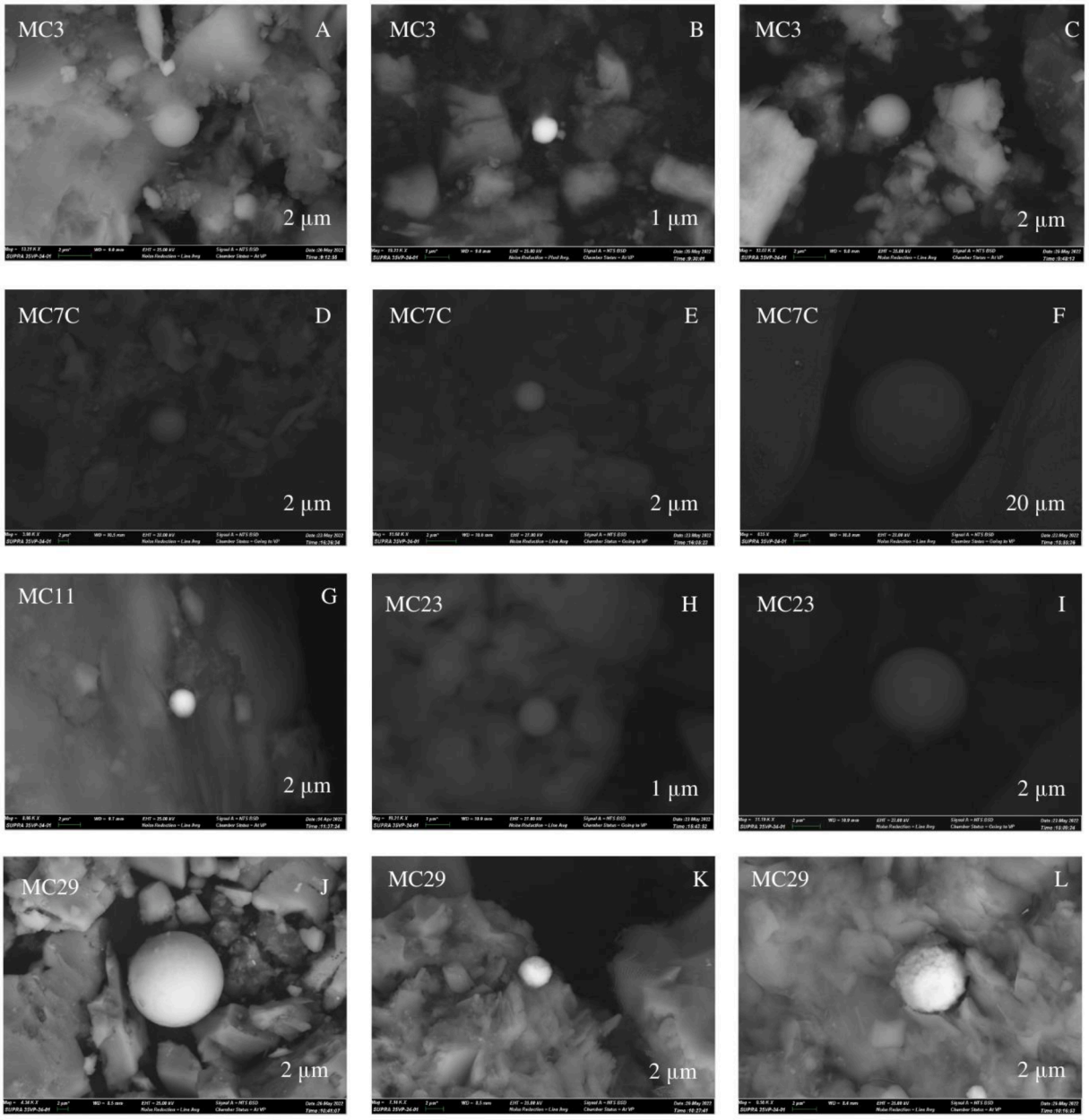

Fig. 6. Examples of micrometer (µm) scale (1 to 20 µm in diameter) technogenic spherules from multiple samples throughout Michigan City. These technogenic spherule particles are consistent with coal pollution throughout the road sediment system.

concentration of 0.4 µg/kg, supporting the inference that the elevated concentrations of Hg observed in road sediment are from pollution (see Table 2). Given the context of background and the record of TRI emissions, Hg concentrations are thus interpreted as being above background, anthropogenically influenced, and are in part attributed to the NIPSCO Michigan City Generating Station.

It is acknowledged that other pollutants were present in the road sediment (e.g., lead particles, steel and iron-rich corroded particles, sponge-textured materials, slag, rods, barite, zinc-bearing particles, and copper-bearing particles; Fig. 7), and that these pollutants may contain trace amounts of Hg, which cannot be reasonably constrained at present. These pollutants suggest other sources of Hg in addition to coal combustion may be possible or occur. However, these are likely non-point sourced pollutants based on the lack of significant correlations between planar distance from other potential Hg emission sources (TRI sites) to road sediment samples and their corresponding Hg concentrations, as well as a large degree of heterogeneity in the Hg spatial distributions around these sites (Fig. 3). However, as stated previously when discussing possible NIPSCO plant Hg sourcing, Hg transport and reworking may be significant enough to eliminate most spatial distribution signals in road sediment. Regardless, the fact that TRI emission data does not document any form of Hg emissions for other TRI sites in the area suggests that there is minimal, if any, sourcing of Hg directly from other nearby point sources. It is of course possible that undocumented emissions occur, or transport of Hg from sources outside Michigan City (e.g., Gary) through atmospheric particulates has occurred.

5.3. Future directions

Mercury budgets are challenging to evaluate and the new constraints on Michigan City road sediment provide an opportunity for future work to better quantify the Hg budget in regions impacted by coal combustion activities. Approximately 50 % of the anthropogenic Hg emissions at a global scale are from coal pollution and comparisons of Hg isotope

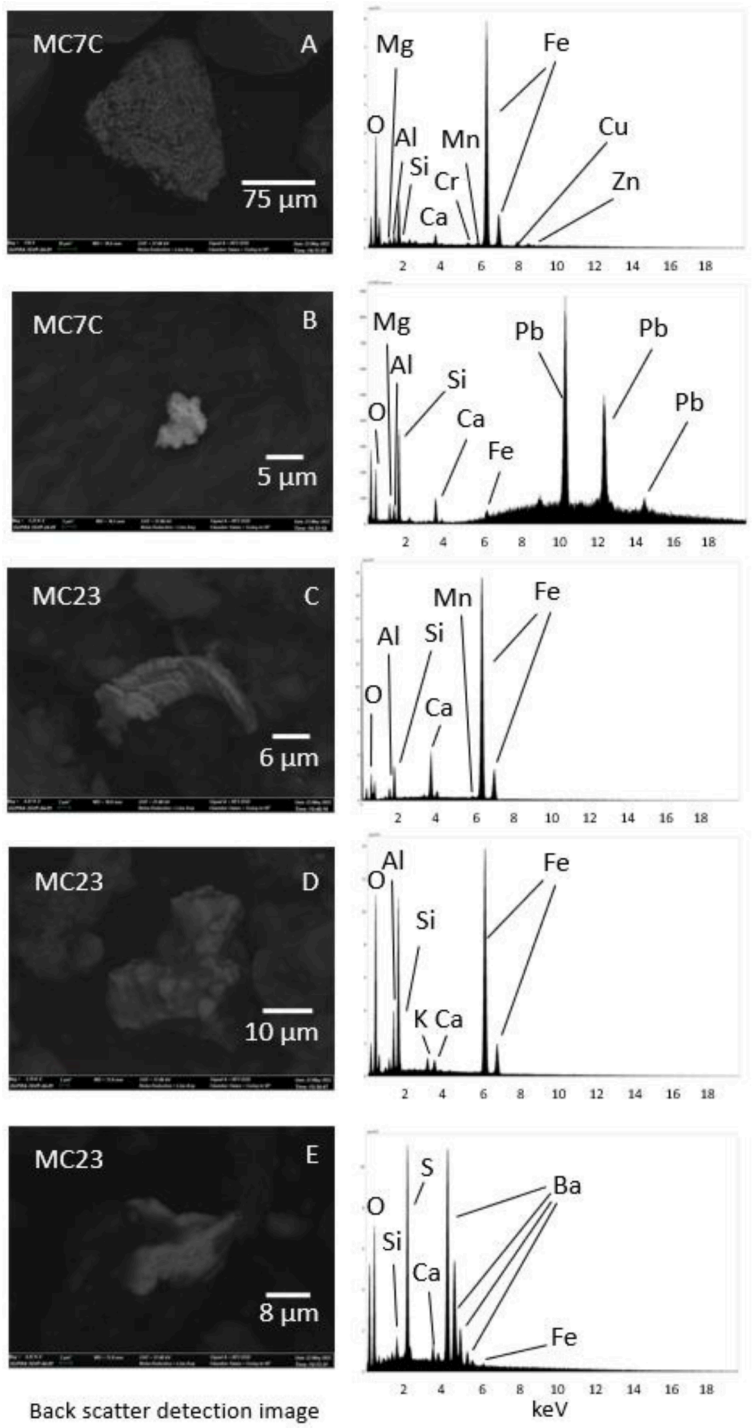

Fig. 7. SEM images of a variety of pollutant types, indicating other possible sources of Hg input into the system may exist. Images are paired with respective EDS spectra with major elements of concern labelled. A) A corroded Fe-Cu-Zn particle approximately 100 µm in diameter, B) Lead particle approximately 8 µm in diameter, C) Particle interpreted as a steel shaving or fragment approximately 20 µm in diameter, D) A particle interpretted as Fe-rich slag with near euhedral equant crystals approximately 28 µm in diameter in a lower density matrix, E) A particle of barite intimately mixed with minerals approximately 20 µm in diameter.

compositions of eight other regions globally show that they are statistically distinguishable on the basis of δ^{202}Hg, Δ^{199} Hg, or both (Sun et al., 2014). Mercury isotopes may therefore have potential as a tracer of local Hg emission and sources in Michigan City as the road sediment Hg concentrations are defined and the nature of pollutant particles documented (e.g., lead particles, steel and iron-rich corroded particles, sponge-textured materials, slag, rods, barite, zinc-bearing particles, and copper-bearing particles). This investigation of Michigan City road sediment indicates that this medium likely can provide new insight on Hg concentrations through northwest Indiana and may help provide some constraints on identifying locations for quantifying gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate-bound mercury (PBM) in the future.

Road sediment research is gaining interest and use in the U.S. as a medium to investigate pollution at a community scale (e.g., (Dietrich et al., 2018; Dietrich et al., 2019; Dietrich et al., 2022; Flett et al., 2016; O'Shea et al., 2021; White et al., 2014; LeGalley and Krekeler, 2013; LeGalley and Krekeler, 2013)). This is the first detailed study of Hg

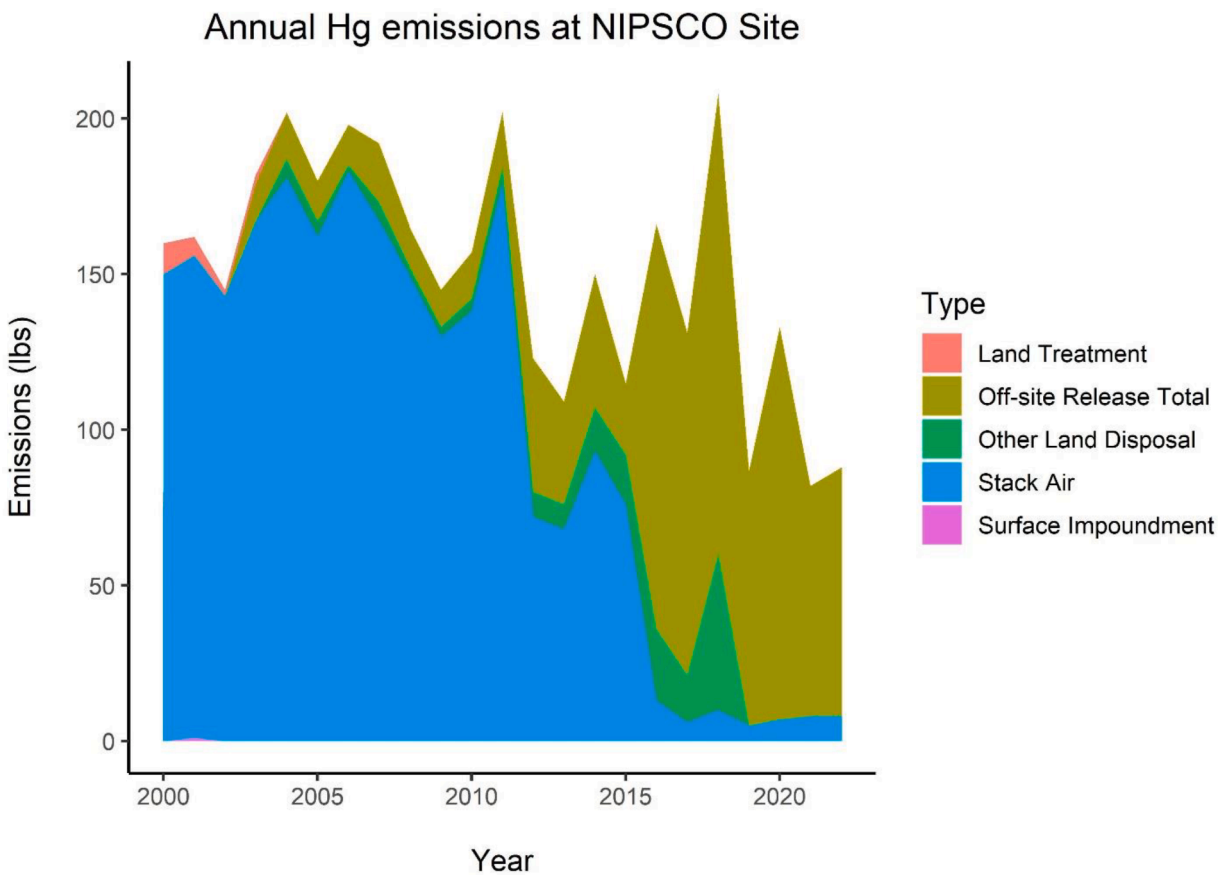

Fig. 8. Annual Hg emissions (in pounds) from the NIPSCO site in Michigan City, IN, categorized by emission type (USEPA, TRI Data and Tools (USEPA, 2023a)).

concentrations in road sediment within the U.S. with a comparatively large sample size (n= 42) and spatially consistent sampling. It is noted that many road sediment investigations have much lower numbers of samples (e.g., n=15; (LeGalley and Krekeler, 2013)) or slightly lower numbers of samples (e.g., n=27; (Flett et al., 2016)). In general, Hg road sediment research is sparse, as Dietrich et al. (2022) found that only 4 studies in the U.S. reported Hg analysis for road sediment. Thus, the dataset reported here for Michigan City is significant within the context of ongoing and future road sediment studies globally.

This work specifically provides benchmark concentrations of Hg within the study area and opens opportunities for several future studies. Results of this investigation indicate Hg pollution in part, has originated from the NIPSCO Michigan City Generating Station and is deposited in the road sediment system. Understanding the fate and transport and other mediums in which Hg emissions could locally occur and contaminate the broader environment, including Lake Michigan, is a direction to pursue. More specifically, the percentage of Hg entering Lake Michigan from point sources and from road sediment as nonpoint source pollution, should be quantified to better understand the potential impacts on the surrounding aquatic environment. The potential impact on Lake Michigan aquatic environments is especially important to study, as Hg bioaccumulates in the food chain (e.g., Milestone, 2022; (Uryu et al., 2001)). Additionally, due to the predominant S-SW wind direction in the area (Fig. 3), atmospheric deposition of Hg is likely high over Lake Michigan.

As road sediment is publicly accessible as waste, relationships between Hg concentrations in road sediment and other media should be explored for estimating Hg concentrations throughout the urban landscape. It is therefore recommended that additional media be studied such as lake/stream cores and tree bark to evaluate Hg concentrations and spatial distributions throughout the region. Ideally, such investigations should be done commensurately to determine atmospheric deposition fluxes and forms of Hg. Moreover, Hg isotope studies should be done in parallel.

Another area requiring future analysis is the impact of decommissioning the NIPSCO Michigan City Generating Station on the concentrations and distribution of Hg. Fundamentally, the question to be addressed is how long will it take the road sediment, and the surrounding region in general, to attenuate from the current levels of Hg pollution? Comparative analysis of Hg concentrations and spatial distributions after this change should be undertaken to understand the impact of plant shutdown, if other sources are significant, and enable predictions on the effects of coal plant shutdown in other analogous settings.

Because there were no discrete Hg-bearing phases (e.g., sulfides, sulfates, oxides, selenides, selenates) observed via SEM in this study, the exact form of Hg is not known. However, forms may be expected to be similar to those observed in other examples of coal combustion, such as Zhao et al. (2019), which are sulfide-bound, clay-bound, and organic matter-bound Hg. It is therefore also recommended that future studies of road sediment conduct detailed particulate matter analysis across a range of scales (i.e., from mm to nm). This would enable a better understanding of overall Hg cycling in the environment. This additional next step may be particularly useful in understanding how Hg will attenuate over time.

5.4. *Hypothesis evaluation*

The hypothesis that Hg is present in measurable concentrations in road sediment throughout the urban area of Michigan City, Indiana is supported. The hypothesis that Hg concentrations vary spatially and systematically reflecting higher concentrations near the Northern

Indiana Public Service Company (NIPSCO) coal-burning power plant in Michigan City, Indiana and lower concentrations away from the facility, is only partially supported, as indicated by the IDW map and spatial statistical correlations. Considering known Hg emissions from the TRI inventory and the context of spatial distributions of Hg in road sediment, the NIPSCO coal plant is likely a contributor in part to Hg pollution in Michigan City, Indiana and surrounding areas. However, more detailed source apportionment work is needed in order to fully constrain this, including widening the spatial footprint of sampling to include potentially larger contributors to Hg emissions in the heavily industrialized portions of the region.

6. Conclusions

Road sediment samples collected in Michigan City Indiana were analyzed for their Hg concentrations to assess the NIPSCO Michigan City Generating Station's potential contribution to Hg pollution in the area. From 42 bulk analyses, Hg in bulk road sediment samples range from 1.5 μg/kg to 28.5 μg/kg with an average concentration of 6.8 μg/kg. The IDW map generated based on these findings depicts higher concentrations of Hg near some regions associated with the generating station, consistent with the variable wind direction. However, there is large spatial variability in Hg concentrations, suggesting complex overall sourcing and mixing within the environment. Based on TRI data available from local industries, it was also determined that these local potential sources do not contribute significantly to Hg emissions. The data indicate that the NIPSCO coal plant is in part a likely source of Hg pollution in the Michigan City, Indiana area. However, other major industrial sources in the region (e.g., Gary, IN) cannot be excluded. Road sediment continues to show promise as an environmental medium to evaluate Hg contamination and provides constraints for future investigations which should quantify Hg budgets and assess the impact of Hg on the environment.

CRediT authorship contribution statement

Audrey Allen: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Matthew Dietrich:** Validation, Software, Methodology, Investigation, Formal analysis. **Claire L. McLeod:** Formal analysis, Writing – review & editing. **Morgan Gillis:** Writing – original draft, Methodology, Investigation. **Kailee Gokey:** Methodology, Investigation. **Mirielle Fouh Mbindi:** Field work and Discussion. **Mark P.S. Krekeler:** Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Project administration, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.envadv.2024.100483.

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