



A regional assessment of chemicals of concern in surface waters of four Midwestern United States national parks

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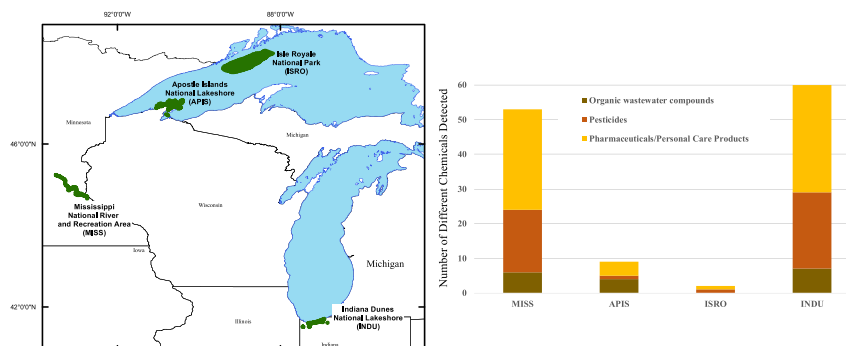
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HIGHLIGHTS

- Chemicals of concern were detected in surface waters of four U.S. national parks.
- Gabapentin and metformin frequently occurred together.
- Pesticides were detected at a higher rate than other chemicals analyzed.
- Environmental concentrations rarely exceeded reference values or standards.
- Chemicals detected at concentrations reported to elicit adverse effects to biota.

GRAPHICAL ABSTRACT



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ABSTRACT

Anthropogenic chemicals and their potential for adverse biological effects raise concern for aquatic ecosystem health in protected areas. During 2013–15, surface waters of four Midwestern United States national parks were sampled and analyzed for wastewater indicators, pharmaceuticals, personal care products, and pesticides. More chemicals and higher concentrations were detected at the two parks with greater urban influences (Mississippi National River and Recreation Area and Indiana Dunes National Lakeshore) than at the two more remote parks (Apostle Islands National Lakeshore and Isle Royale National Park). Atrazine (10–15 ng/L) and *N,N*-diethyl-meta-toluamide (16–120 ng/L) were the only chemicals detected in inland lakes of a remote island national park (Isle Royale National Park). Bisphenol A and organophosphate flame retardants were commonly detected at the other sampled parks. Gabapentin and simazine had the highest observed concentrations (>1000 ng/L) in three and two samples, respectively. At the two parks with urban influences, metolachlor and simazine concentrations were similar to those reported for other major urban rivers in the United States. Environmental concentrations of detected chemicals were often orders of magnitude less than standards or reference values with three exceptions: (1) hydrochlorothiazide exceeded a human health-based screening value in seven samples, (2) estrone exceeded a predicted critical environmental concentration for fish pharmacological effects in one sample, and (3) simazine was approaching the 4000 ng/L Maximum Contaminant Level in one sample even though this concentration is not expected to reflect peak pesticide use. Although few environmental concentrations were approaching or exceeded standards or reference values, concentrations were often in ranges reported to elicit effects in aquatic biota. Data from this study will assist in establishing a baseline for chemicals of concern in Midwestern national parks and highlight the need to better understand the sources, pathways, and potential adverse effects to aquatic systems in national parks.

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1. Introduction

The ecological health of surface waters within protected United States (U.S.) national parks is not protected from many anthropogenic chemicals, such as chemicals of concern (e.g. wastewater indicator chemicals, pharmaceuticals, personal care products). Some major sources of chemicals of concern include wastewater treatment plants (WWTPs) and agricultural lands (Pal et al., 2010). Additional sources include stormwater runoff, septic fields, landfills (Shala and Foster, 2010), and atmospheric deposition (Newton et al., 2014). Because of these varied sources, chemicals of concern occur in surface waters throughout the world (Kolpin et al., 2002; Loos et al., 2009; Terzić et al., 2008), even those located within protected lands.

U.S. national parks are mandated to preserve and protect the natural and cultural resources and values for the enjoyment, education, and inspiration of all generations (Landewe, 2008). Considering the number of chemicals in daily use and numerous pathways to the environment, protecting natural resources from chemical loading and potential ecological effects is expected to be difficult. Furthermore, some parks are located in or near highly urbanized or industrial areas that may receive inputs from both point and non-point sources such as WWTP discharges, stormwater runoff, and contaminated groundwater discharge. Although surface waters in more remote areas have fewer direct contaminant sources, chemicals of concern and other contaminants may be introduced via more diffuse pathways such as atmospheric deposition (Newton et al., 2014). Additionally, park visitors may introduce chemicals to park waters via direct use of waterways or campground use.

Surface waters located within U.S. national parks are not immune to loading of chemicals of concern. For example, pesticides can be atmospherically transported to surface waters in national parks (Mast et al.,

2012; McConnell et al., 1998). Evidence of this is demonstrated by the presence of organic contaminants in fish from remote park regions (Flanagan-Pritz et al., 2014) and bald eagles nesting in Midwestern parks (Dykstra et al., 2010). This evidence indicates that park biota at multiple trophic levels are being exposed to chemicals of concern. Although contaminants have been detected in biota, the exposure pathways and overall occurrences within national parks have not been well characterized.

Recent studies have begun to look at the occurrence of chemicals of concern in U.S. national parks in a more regional context (Weissing et al., 2013; Weissing, 2014; VanderMeulen, 2015) to better understand the threat they pose to these protected environments. These regional studies will provide needed information for prioritizing parks at risk from exposure to chemicals of concern. The current study focused on determining the occurrence of chemicals of concern in surface waters collected within and near four Midwestern U.S. national parks. A variety of surface water types were sampled, including drainage ditches, streams, rivers, lakes, and a Laurentian Great Lake. Data obtained from the study contribute to the establishment of both baseline levels of chemicals of concern in aquatic resources of U.S. national parks and a greater understanding of potential adverse effects.

2. Materials and methods

2.1. Park descriptions and site selection

Four U.S. national parks within the western Great Lakes region were sampled: Mississippi National River and Recreation Area (MISS), Apostle Islands National Lakeshore (APIS), Isle Royale National Park (ISRO), and Indiana Dunes National Lakeshore (INDU) (Fig. 1). The two more

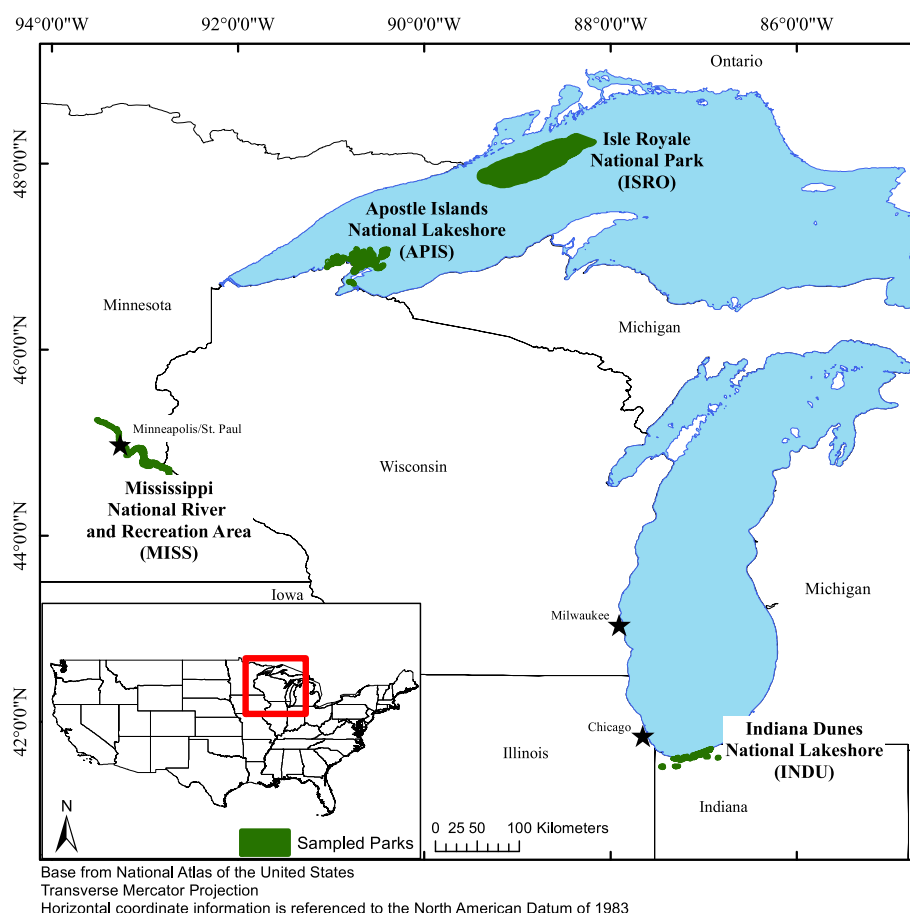


Fig. 1. Map of the four upper Midwestern United States national parks sampled during this study.

urban-influenced parks (MISS and INDU) were chosen for sampling because of numerous potential sources of chemicals of concern within the parks. Additionally, several previous and ongoing studies of a similar nature have been conducted in MISS. The two more remote parks (APIS and ISRO) were chosen for sampling because of the lack of contaminant data at the parks. Additionally, because these parks are more remote and have relatively fewer potential sources of the chemicals of interest, they would provide a sort of reference to the more urban influenced parks.

MISS includes 123 km of the upper Mississippi River that flows through the Twin Cities of Minneapolis and St. Paul in Minnesota. Water resources within MISS include parts of the Mississippi and Minnesota Rivers, perennial and intermittent tributary streams, floodplain wetlands, and standing backwaters. Four sites located on the main stem of the Mississippi River were sampled during 2013 and 2014 (Fig. S1; Table S1). The four main stem sites were selected to: (1) represent conditions upstream from the park boundary, (2) downstream from the Minnesota River confluence, (3) downstream from the Twin Cities' major Metropolitan WWTP, and (4) just upstream from the park's downstream boundary. Although one site was selected to represent conditions upstream from the park, many WWTPs discharge to the Mississippi River and its tributaries upstream from the site, potentially contributing to the overall chemical load of the river. Sites were also selected to overlap with sites from previous studies that characterized chemicals of concern in surface water, sediment, and biota (e.g. Lee et al., 2008, 2011; Route et al., 2014a, 2014b). Land cover within the park's watershed is dominated by cultivated crops. Although the percentage of developed land is relatively small in the large upper Mississippi watershed, the sampling at MISS likely accounts for much of the concentrated development in and around the Twin Cities Metropolitan area.

APIS consists of 21 islands in Lake Superior off Wisconsin's Bayfield Peninsula as well as a 19-km long shoreline unit on the mainland. Several islands and the mainland unit contain inland water resources, mostly small perennial and intermittent streams. Seven Lake Superior nearshore sites were sampled throughout the park in 2014 (Fig. S2; Table S1). Site selection was based primarily on previous data collected by the U.S. National Park Service and the U.S. Environmental Protection Agency (EPA) (Hobbs et al., 2016; Route et al., 2014a, 2014b) and proximity to trout fisheries. Land cover within the park is dominated by forest and open water.

Located in northwestern Lake Superior, ISRO is a remote island archipelago consisting of one large island surrounded by approximately 400 small barrier islands. Water resources within the park include bays, nearshore waters, offshore waters, inland lakes, wetlands, perennial streams, and many unnamed perennial and intermittent streams. Nine inland lakes, which are the focus of a separate long-term water quality monitoring program (Elias et al., 2015), were sampled for chemicals of concern during 2015 (Fig. S3; Table S1). Land cover within the park is dominated by forest, open water, and wetlands.

INDU consists of 24 km of Lake Michigan shoreline between Gary and Michigan City, Indiana. Surface-water resources within INDU include emergent wetlands, forested wetlands, bogs, lagoons, streams, and drainage ditches. In 2014 and 2015, 19 sites were sampled within INDU (Fig. S4; Table S1) that fell into two categories: (1) sites that are part of an ongoing park-specific monitoring effort of the East Branch of the Little Calumet River (EBLC) and (2) sites that are independent of the EBLC and feed directly into Lake Michigan. Many of the sites are located in drainage ditches, which have replaced natural drainage systems. Land cover within the park includes urban and industrial development, forest, wetlands, and grasslands.

2.2. Sampling methods

Sample collection methods are outlined in detail in VanderMeulen (2015). Samples were collected during the open water season, typically

between the months of April and November, which varied by park. Samples collected from APIS and ISRO were collected once a month during the months of June, July, and August. The most samples collected from one national park were collected from MISS; samples were collected once a month in April, June, and November in 2013 and July and August in 2014. Samples were collected from INDU once during November 2014 and 2015. Samples were collected in 40-mL glass amber vials that were rinsed twice with native water prior to sample collection. Grab samples were collected by dipping the sample bottle into the water to a depth of approximately 15 cm and capping the bottle underwater, when possible. Field personnel minimized use of products such as caffeine, fragrances, and insect repellent prior to and during sampling to avoid contamination of the samples. The remoteness of ISRO limited the ability to immediately ship samples to the laboratory; thus, nearly all of the samples from this park exceeded EPA's recommended holding times (EPA, 2007). However, prior to shipping the samples they were stored at the recommended temperature (4 °C). Positive detections in samples analyzed after the recommended holding time were coded as estimated values, which were used as reported by the laboratory for this analysis.

2.3. Analytical methods

Samples were analyzed at the EPA Region 8 Laboratory in Golden, Colorado. Whole water samples were analyzed for 53 wastewater indicator (WWI) chemicals by gas chromatography/mass spectrometry (GC/MS) after continuous liquid-liquid extraction following EPA method 8270D (EPA, 2014a). Samples were filtered at the laboratory and analyzed for 72 pesticides and 140 pharmaceuticals and personal care products (PPCPs) by liquid chromatography/mass spectrometry (LC/MS) after solid-phase extraction following EPA methods 8321A (EPA, 2014b) and 1694 (EPA, 2007), respectively. All samples were analyzed for pesticides and PPCPs; however, because of limited resources only a randomly selected subset of samples was analyzed for WWI in 2013 and 2014. A complete list of all chemicals analyzed in surface-water samples during 2013–15 and associated method reporting limits are provided in supplementary information (Table S2).

2.4. Field and laboratory quality assurance

Field quality-assurance measures included in this study consisted of the collection of field replicate samples. Because of funding constraints, field-blank samples were not collected during the study. A total of 14 field-replicate samples were collected from MISS, ISRO, and INDU and analyzed for pesticides and PPCPs; results are provided in Tables S3–S6. Generally, there was good agreement between chemicals detected in environmental and replicate samples. Relative percent difference was calculated as the difference between the concentration of the replicate sample and the concentration of the environmental sample divided by the mean concentration of the two replicate and environmental samples multiplied by 100. The relative percent differences for chemicals detected in both the replicate and environmental samples ranged from 0 to 166 for all chemicals (Table S7). In 20 cases, chemicals were detected in replicate samples that were not detected in the associated environmental samples (Table S7).

Quality-assurance measures used at the laboratory included laboratory blanks, matrix spikes, and calibration check standards. A total of four chemicals were detected in laboratory-blank samples (Table S8) at concentrations greater than the reporting limit. Environmental sample concentrations were determined to be compromised if they were <10 times the laboratory blank concentration and removed from the dataset prior to analyses. A total of seven data points were removed from MISS, four from APIS, and one from INDU (Tables S3, S4, S6). Three matrix spikes were analyzed throughout the study. Percent recovery of all chemicals ranged from 13 to 205, with a mean relative percent difference of 9 between duplicate matrix spikes (Table S9). Percent

recovery of 19 different chemicals was <60, and percent recovery of 22 different chemicals was >120. Mean percent recovery of calibration check standards ranged from 83.8 to 119 for all chemicals during the study (Table S10).

2.5. Data analyses

Summary statistics and detection frequencies for all data were computed using R version 3.1.3 (R Core Team, 2015). When available, human health-based screening values and/or water quality standards and aquatic biota effect values were compared with the chemical data. Health based screening values (HBSV) represent chemical concentrations in drinking water that are likely to pose little or no health risk. Although these values are established to protect groundwater and drinking water, they still provide context for environmental data. For example, if environmental concentrations are even 10% of HBSV, this could have important implications for aquatic health because of the similarity between human and aquatic vertebrate physiology. Multiple entities have established benchmarks or standards including, but not limited to, the U.S. Geological Survey (USGS) (Toccalino et al., 2014), EPA (EPA, 2016a, 2016b, 2016c), Minnesota Department of Health (Balluff et al., 2014; MDH, 2016; Suchomel et al., 2015), and Indiana Department of Environmental Management (IDEM, 2016) for select chemicals including pesticides, plasticizers, and a limited number of other WWI chemicals. Environmental concentrations were compared to the lowest chronic benchmark or standard available.

3. Results and discussion

A complete list of detected chemical concentrations for MISS, APIS, ISRO, and INDU are provided in supplemental tables S3–S6. Because of the limited data associated with WWI chemicals compared to the other chemicals, only a brief summary of WWI chemicals is provided below. More detailed summaries of PPCPs and pesticides follow.

3.1. Wastewater indicator chemicals

Samples analyzed for WWI chemicals were collected three times at two MISS sites in 2013, twice at four APIS sites in 2014, and once at

five INDU sites in 2014 (Tables S3, S4, S6, respectively). Among all samples, 14 of 53 different WWI chemicals were detected including two estrogens, four fragrances, one plastic component, two flame retardants, one plasticizer, one pesticide, and one food additive (Table 1). More WWI chemicals were detected at INDU, than MISS and APIS. Equilenin (isolated from pregnant mares, used for hormone replacement therapy) and estrone (natural estrogen secreted by vertebrates) were detected in the same sample (INDU475, sampled November 12, 2014) at concentrations of 187 and 121 (24 ng/L estradiol equivalents) ng/L, respectively (Table S6). This is noteworthy because adverse reproductive effects have been observed in fathead minnows (*Pimephales promelas*) exposed to 17 α -ethinylestradiol at concentrations around 5 ng/L estradiol equivalents (Kidd et al., 2007; Länge et al., 2001). Bisphenol A (BPA) was detected in all three parks in which it was sampled with concentrations ranging from 56 ng/L (APIS) to 350 ng/L (INDU), similar to concentrations detected in the St. Louis Bay (a tributary of Lake Superior) (Christensen et al., 2012) and other surface waters worldwide (Flint et al., 2012). Five of the 14 detected WWI chemicals were detected in 30% or more of samples collected from at least one park (Table 1). At least one plasticizer/flame retardant was detected at each of the three parks sampled for WWI chemicals. Fire retardants have also been frequently detected (at least 30% detection frequency) in several tributaries of the Great Lakes (Elliott et al., 2015, 2016; Lee et al., 2012, 2015), highlighting the ubiquitous nature of these chemicals in the environment.

3.2. Pharmaceuticals and personal care products

Samples analyzed for PPCPs were collected five times at each MISS site in 2013 and 2014, three times at each APIS site in 2014, three times at each ISRO site in 2015, and one time at each INDU site in 2014 and 2015. Among the four sampled parks, 40 (of 140) different PPCPs were detected at concentrations ranging from 10.1 ng/L (APIS) to 2790 ng/L (INDU) and represented various classes of pharmaceuticals. Only one PPCP per sample was detected in most samples collected from APIS and ISRO; the chemical varied by sample. However, two PPCPs were detected in samples collected from APIS09-09 in July 2014 (gabapentin and metformin) and from APIS09-14 in June 2014 (caffeine and DEET; Table S4). Thirteen of the 40 detected PPCPs were detected in at least 30% of samples from at least one park (Table 2). Similar to WWI chemicals, more PPCPs were detected at INDU than the other three parks. However, more individual PPCPs were detected in MISS samples compared to INDU, highlighting the influence of the major metropolitan area in the watershed. The mean number of PPCPs detected ranged from 4 to 14 per site among MISS sites (Fig. 2) and from 1 to 16 per site among INDU sites (Fig. 3). In general, the mean number of PPCP detections in MISS increased in a downstream direction and most noticeably downstream from the Twin Cities' main WWTP. Patterns were not easily discernible in INDU because of the complex system of human-made drainage ditches; many of the sample sites are not hydrologically connected. However, similar to MISS, the number of PPCPs increased downstream from a WWTP discharge (Fig. 3).

At INDU and MISS, analgesics, anticonvulsants, antidepressants, and diuretics were the most frequently detected pharmaceuticals. Gabapentin (anticonvulsant) had the highest concentration (2790 ng/L, site INDU144, sampled November 11, 2015; Table S6) of all detected pharmaceuticals. Gabapentin and metformin (antidiabetic) occurred together in 100, 12, and 24% of samples collected from MISS, APIS, and INDU, respectively. Gabapentin concentrations were greater than metformin concentrations in 80% of co-occurrences of these chemicals. One of the secondary uses of gabapentin is to treat neuropathic pain associated with diabetes (Backonja et al., 1998). This typical linked usage may explain the relatively common co-occurrence of gabapentin and metformin. Literature documenting the environmental occurrence of gabapentin is somewhat lacking; however, a monitoring program conducted in Wales, United Kingdom, observed detections of gabapentin in 100% of wastewater

Table 1
Detection frequency and maximum concentration (ng/L) of detected wastewater indicators analyzed in a subset of samples in 2013 and 2014.

Chemical	Chemical class	Detection frequency	Maximum concentration
<i>Mississippi National River and Recreation Area (MISS) 2013</i>			
Bisphenol A	Plastic component	50	232
Caffeine	Stimulant	50	43.3
Galaxolide	Synthetic fragrance	33	115
Metolachlor	Herbicide	17	867
Tributyl phosphate	Plasticizer/flame retardant	33	68.6
Triethyl citrate	Plasticizer	17	146
<i>Apostle Islands National Lakeshore (APIS) 2014</i>			
Bisphenol A	Plastic component	12	56.2
Tri(dichloroisopropyl) phosphate	Plasticizer/flame retardant	12	50.9
Triclosan	Antimicrobial	12	74.9
<i>Indiana Dunes National Lakeshore (INDU) 2014</i>			
Acetophenone	Fragrance	40	67.7
Bisphenol A	Plastic component	40	350
Caffeine	Stimulant	20	215
Camphor	Fragrance	20	89.6
Equilenin	Estrogen	20	187
Estrone	Estrogen	20	121
Methyl salicylate	Fragrance	20	53.4
Triphenyl phosphate	Plasticizer/flame retardant	20	82

Table 2

Detection frequency and maximum concentration (ng/L) of pharmaceuticals and personal care products (PPCPs) and pesticides detected in at least 30% of all samples collected at each national park.

Chemical	Chemical class	Detection frequency	Maximum concentration
<i>Mississippi National River and Recreation River (MISS) 2013/14</i>			
2,4-Dichlorophenoxyacetic acid	Herbicide	100	172
Acetochlor	Herbicide	50	265
Acetochlor oxanilic acid	Herbicide	95	896
	degradate		
Atenolol	Beta blocker	35	30.5
Atrazine	Herbicide	100	302
Atrazine de-ethyl	Herbicide	30	56.8
	degradate		
Bentazon	Herbicide	30	12.6
Caffeine	Stimulant	55	43.3
N,N-diethyl-3-methylbenzamide (DEET)	Insecticide	60	251
Desmethylenlafaxine	SNRI ¹	65	74.7
Dimethenamid	Herbicide	45	119
Dimethenamid ethanesulfonic acid	Herbicide	35	107
	degradate		
Gabapentin	Anticonvulsant	100	1080
Gemfibrozil	Cholesterol management	35	27.5
Hydrochlorothiazide	Diuretic	55	67.8
Hydroxybupropion	Antidepressant	40	42.6
	metabolite		
Imazethapyr	Herbicide	70	198
Lamotrigine	Anticonvulsant	65	85.2
Metformin	Antidiabetic	100	150
Metolachlor	Herbicide	65	867
Metolachlor sulfonic acid	Herbicide	100	555
	degradate		
Ranitidine	Antacid	42	33.1
Sulfamethoxazole	Antibiotic	55	77.7
Tramadol	Opioid, analgesic	30	28.2
<i>Apostle Islands National Lakeshore (APIS) 2014</i>			
Gabapentin	Anticonvulsant	30	13.7
<i>Isle Royale National Park (ISRO) 2015</i>			
Atrazine	Herbicide	38	14.6
N,N-diethyl-3-methylbenzamide (DEET)	Insecticide	92	119
<i>Indiana Dunes National Lakeshore (INDU) 2014/15</i>			
2,4-Dichlorophenoxyacetic acid	Herbicide	58	179
Acetochlor oxanilic acid	Herbicide	68	105
	degradate		
N,N-diethyl-3-methylbenzamide (DEET)	Insecticide	92	122
Gabapentin	Anticonvulsant	58	2790
Imazethapyr	Herbicide	42	492
Metformin	Antidiabetic	32	903
Metolachlor sulfonic acid	Herbicide	100	1550
	degradate		
Simazine	Herbicide	34	3140
Triclopyr	Herbicide	39	581

¹ serotonin-norepinephrine reuptake inhibitor.

effluent receiving waters, sometimes exceeding 1 µg/L (Kasprzyk-Hordern et al., 2009). Similarly, Writer et al. (2013) detected gabapentin in 88% of effluent samples (concentrations as large as 3100 ng/L) and 54% of downstream samples in receiving waters in Minnesota. Maximum metformin concentrations (150 and 903 ng/L in MISS and INDU, respectively; Table 2) in the current study are similar to those reported in Lake Michigan near the outfall of a major WWTP (840 ng/L) and as far as 3 km away (160 ng/L) (Blair et al., 2013). Additionally, the presence of gabapentin and metformin has recently been documented in water samples collected from the Colorado (Canyonlands National Park) and Yampa (Dinosaur National Monument) Rivers (Weissinger et al., 2013; Weissinger, 2014) at concentrations similar to those found in MISS and INDU.

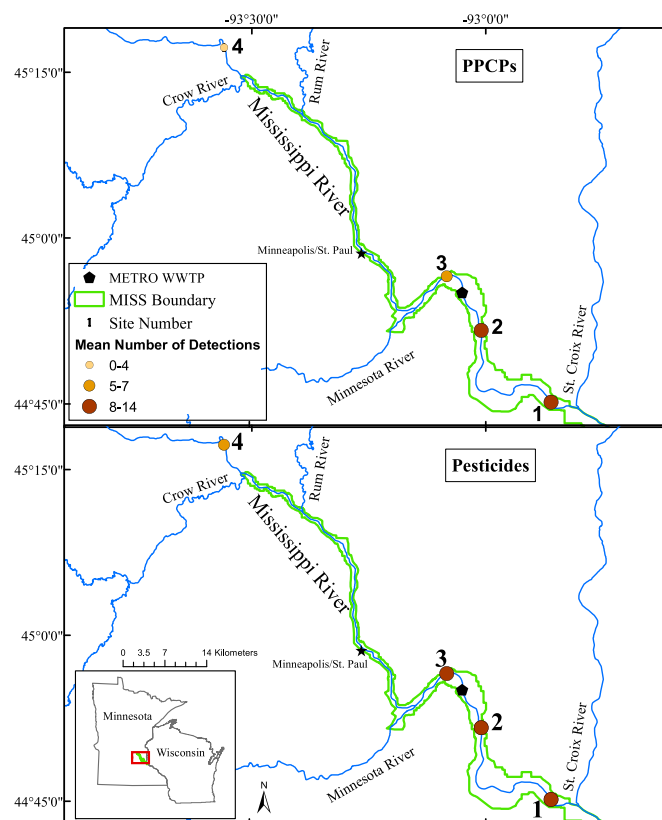


Fig. 2. Maps showing mean number of pharmaceuticals and personal care products (PPCPs) and pesticides detected per site at Mississippi National River and Recreation Area (MISS). METRO WWTP, Twin Cities Metropolitan wastewater treatment plant.

3.3. Pesticides

Pesticides were analyzed at the same frequency (parks/years/sites) as PPCPs. Among the four sampled parks, 25 (of 72) different pesticides were detected at concentrations ranging from 10.0 (ISRO) to 3140 (INDU) ng/L. Imazethapyr and atrazine were the only pesticides detected at APIS and ISRO, respectively (Tables S4–S5). Concentrations of atrazine in ISRO lakes were relatively low (<15 ng/L) and similar to previously reported concentrations (Thurman and Cromwell, 2000). Fourteen of the 25 detected pesticides were detected in at least 30% of samples from at least one park (Table 2). Within MISS, 16 different pesticides were detected, often at concentrations in the range of hundreds of ng/L (Table S3). The mean number of pesticides detected at each MISS site was similar among all sites (Fig. 2). Furthermore, many of the same pesticides were detected at all sites. This pattern reflects the relatively high agricultural influence within the Upper Mississippi River watershed. A similar pattern was observed in INDU, which also has high agricultural influence within the watershed (Fig. 3). Twenty different pesticides were detected in INDU (Table S6). Although many pesticides were detected, concentrations were similar to those previously reported in surface waters after the period of application (Hall et al., 1993), indicating that the samples collected in this study do not accurately represent the full ecological risk of these chemicals to the protected environments.

Relatively high concentrations (>1000 ng/L) of atrazine, metolachlor, and simazine have been reported for major urban streams in the Midwestern U.S. (Ryberg et al., 2014). Atrazine concentrations in samples collected from a large river (MISS), drainage ditches, streams, and small rivers (INDU) all were much less than the median 90th

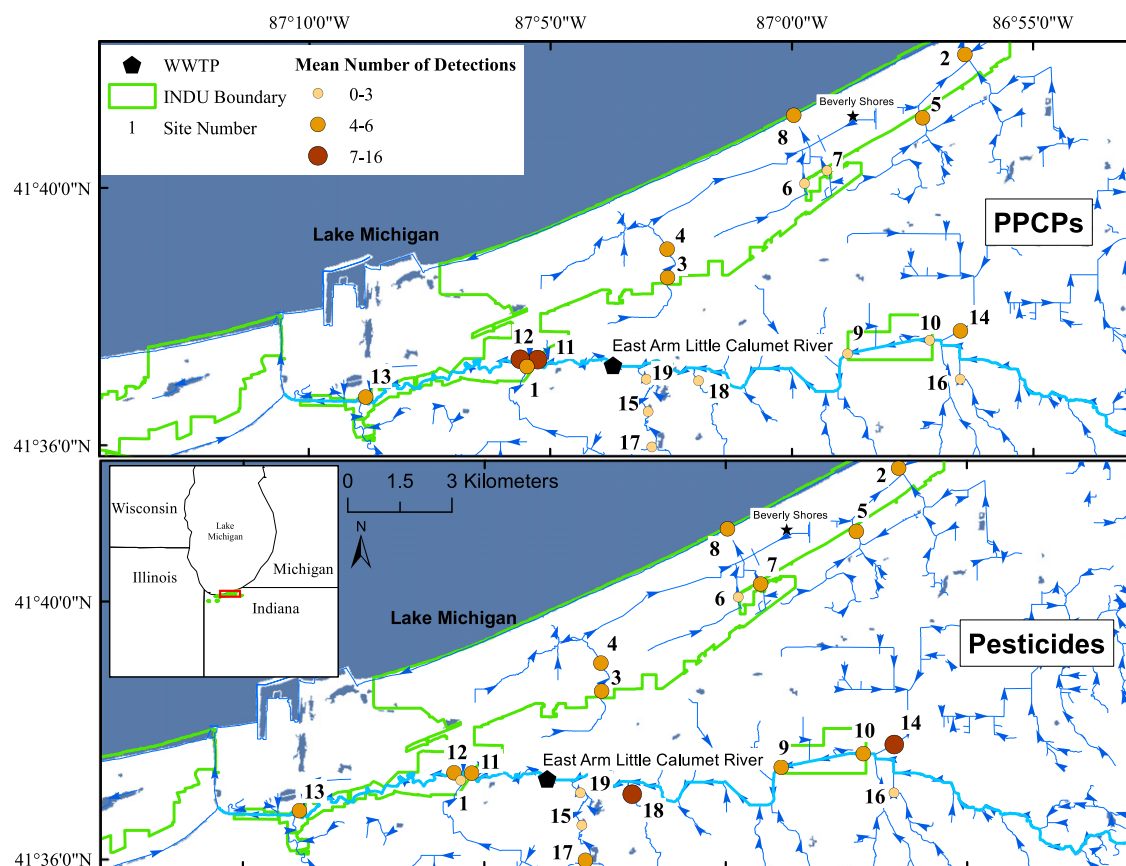


Fig. 3. Map showing mean number of pharmaceuticals and personal care products (PPCPs) and pesticides detected per site at Indiana Dunes National Lakeshore (INDU). Blue arrows indicate water flow direction. WWTP, wastewater treatment plant.

percentiles previously reported for Midwestern urban streams and rivers (Ryberg et al., 2014; Fig. 4a). Conversely, approximately one-half of the metolachlor detections in MISS and INDU and almost all simazine detections (INDU) were similar or much greater than median 90th percentiles for Midwestern urban streams and rivers (Ryberg et al., 2014) (Fig. 4b, c). The similarity in metolachlor and simazine concentrations between the two studies indicates that these pesticides are frequently present in surface waters, regardless of their inclusion in a national

park, and concerted efforts may be warranted for understanding exposure to these pesticides to fully protect the ecological health of those waters.

3.4. Comparisons of degradate and parent chemicals

Nine degradate/parent pairs of pesticides and two metabolite/parent pairs of pharmaceuticals were included in this study. Comparisons were

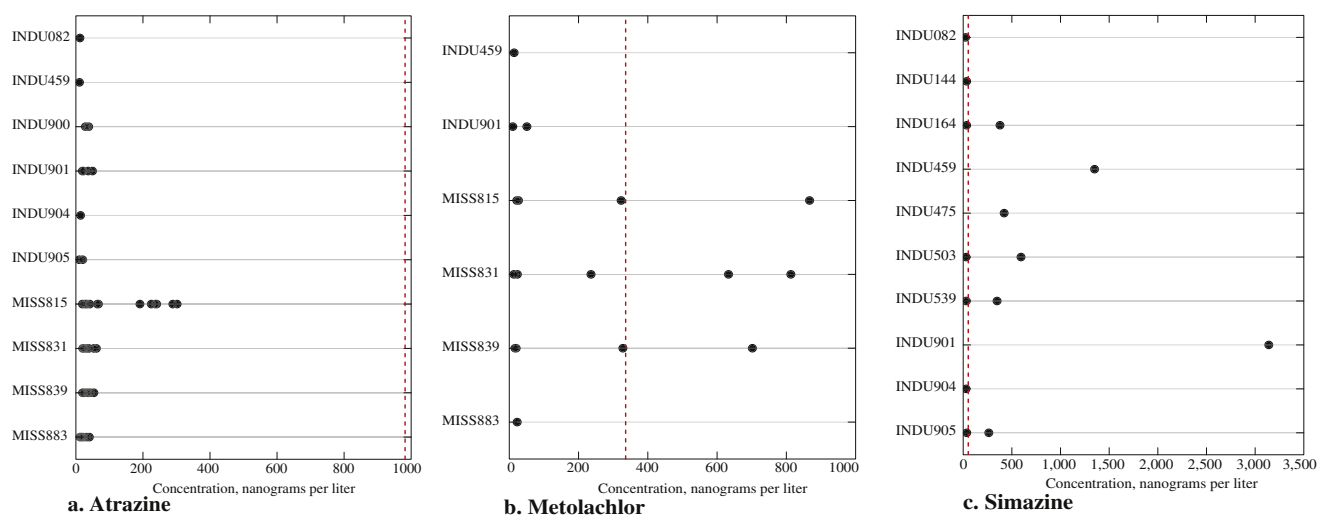


Fig. 4. Atrazine (a), metolachlor (b), and simazine (c) concentrations measured in this study compared to median 90th percentile concentrations reported in Ryberg et al. (2014) for major rivers in the Midwestern United States, as indicated by the dashed red lines.

possible for metolachlor ethane sulfonic acid (ESA)/metolachlor, dimethenamid ESA/dimethenamid, acetochlor oxanilic acid (OA)/acetochlor, atrazine de-ethyl + de-isopropyl/atrazine, desmethylvenlafaxine/venlafaxine, and 10,11-dihydro-10-hydroxycarbamazepine/carbamazepine (Fig. 5). Degradate to parent ratios were generally around one for atrazine and dimethenamid. Ratios for acetochlor, metolachlor, and venlafaxine were frequently greater than one. Metolachlor ratios were much greater in INDU samples (25–137), compared to MISS (0.4–16). A similar pattern was observed for atrazine. Although these ratios were calculated based on sparse information (e.g. few metabolites, few samples), they highlight the higher concentrations of degradates compared to parent chemicals for some chemicals in surface waters. This is of importance because degradates and metabolites can be as biologically active as (or more than) the parent chemical; however, little information regarding their ecotoxicity (either alone or in mixtures) is available.

3.5. Potential for human health effects

No environmental concentration observed during this study exceeded available HBSVs. Where comparisons were possible, environmental concentrations were typically several orders of magnitude lower than HBSVs.

The MDH has developed water screening values via rapid assessments for 119 current-use pharmaceuticals (21 in common with this study) (Suchomel et al., 2015) and 159 pesticides (24 in common with this study) (Balluff et al., 2014). Water screening values represent concentrations in water that are unlikely to pose a human-health concern and are more conservative than HBSVs. In general, environmental concentrations were <10% of water screening values. There were two exceptions. The metformin concentration in the sample collected from INDU144 on November 5, 2015 was 23% of the MDH screening value

of 4000 ng/L. And hydrochlorothiazide (a diuretic) concentrations exceeded the MDH screening value of 40 ng/L in seven total samples from INDU and MISS. These exceedances were detected at two sites within each park downstream from a WWTP, on multiple sample dates.

Maximum Contaminant Levels (MCL) for 2,4,5-TP, 2,4-D, atrazine, and simazine in drinking water have been established by the EPA (EPA, 2016a). None of the environmental samples exceeded available MCLs. One concentration of atrazine at MISS839 (sampled July 8, 2014; Table S3) was 10% of the associated MCL (and MDH HBV; MDH, 2016) of 3000 ng/L. Environmental concentrations of simazine from four INDU samples were >10% of the associated MCL of 4000 ng/L; one concentration was 78% of the MCL (3140 ng/L, INDU901, sampled November 12, 2014; Table S6). Considering that sampling occurred in November, after a typical growing season and well after typical application, observed concentrations from this study may not accurately reflect the maximum concentrations of pesticides in the parks and consequent biological/health effects. For example, the highest observed concentration of simazine may actually reflect a seasonally low concentration. Because this concentration was approaching the MCL at what is suspected to be a relatively low concentration, more intense efforts are needed to fully describe the presence and effects of pesticides within the parks. Excluding the relatively high concentrations mentioned above, most of the simazine concentrations were consistent with those reported during base-flow conditions in an urban environment (Revitt et al., 2002).

3.6. Potential for adverse ecological effects

Water-quality benchmarks intended to protect aquatic biota from exposure to chemicals of concern are currently lacking because effects are not well understood. The IDEM (IDEM, 2016), State of Minnesota (MPCA, 2016), and EPA (EPA, 2016c) have established water-quality standards for select organic chemicals (mostly pesticides) in surface waters to protect aquatic life. Comparisons between aquatic-health benchmarks and 11 chemicals (Table S11) were able to be made. Similar to comparisons with HBSVs, environmental data were <10% of standards. Using these limited standards, the risk to the ecological health of surface waters in the sampled parks appears minimal. However, several other factors must be taken into consideration when evaluating potential risk: (1) standards exist for only a few chemicals substantially limiting interpretation of overall risk, (2) standards do not account for chemical mixtures, and (3) substantial evidence exists of adverse biological effects in organisms exposed to many chemicals of concern, including some that have established standards (e.g. Bean et al., 2014; Brown et al., 2004; Fong and Ford, 2014; Segner et al., 2003).

Bisphenol A was detected at three of the four parks and at concentrations >100 ng/L, some of the highest observed concentrations in this study. Although no environmental concentration was approaching established benchmarks or standards, effects have been reported in the literature at similar concentrations. The effects of BPA exposure to aquatic biota varies, depending on the organism, exposure duration and timing, and presence of other chemicals; however, invertebrates appear to be more sensitive to BPA exposure compared to vertebrates. For example, concentrations of 80 ng/L have been demonstrated to inhibit midge (*Chironomus riparius*) development (Flint et al., 2012). Exposure to higher concentrations in the range of 230 to 320 ng/L resulted in decreased calcification of adult freshwater snail (*Lymnaea stagnalis*) shells and in deformation of developing snails, respectively (Segner et al., 2003). So although BPA was not detected at concentrations high enough to likely affect vertebrates, deleterious effects to invertebrates are possible and warrant further investigation.

Pharmaceuticals are one group of chemicals grossly underrepresented by water-quality standards even though many studies have documented the adverse effects of pharmaceutical exposure to multiple organisms. Furthermore, because pharmaceuticals often exist in complex mixtures in the environment, individual water standards may not provide accurate estimates of risk to aquatic biota. For example, a

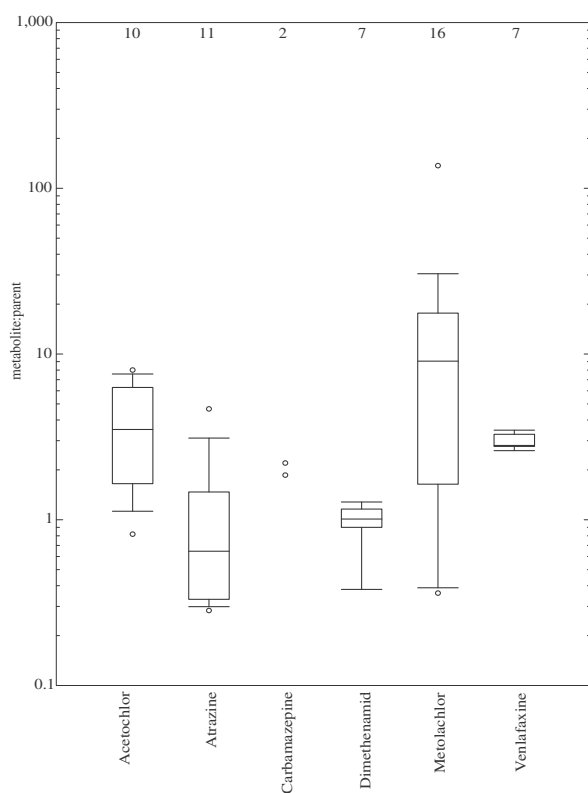


Fig. 5. Boxplots showing summary of ratios of degradate/metabolite to parent compounds. Numbers above boxplots indicate number of samples; whiskers extend to 10th and 90th percentiles; open circles are values outside of the 10th and 90th percentiles; horizontal line within the rectangle is the median.

chemical mixture of acetaminophen, carbamazepine, gemfibrozil and venlafaxine decreased embryo production and altered kidney morphology in zebrafish (*Danio rerio*) (Galus et al., 2013). Similarly, a mixture of 16 pharmaceuticals compromised the immune systems of *L. stagnalis* more than similar exposures to individual mixtures of the same 16 pharmaceuticals, but grouped by therapeutic class (Gust et al., 2013). Pharmaceuticals were often detected in complex mixtures in MISS and INDU; mixtures in MISS were often composed of 10 or more pharmaceuticals.

Antidepressants are one of the most commonly prescribed pharmaceuticals in the U.S. and thus are a fairly well-studied group of pharmaceuticals. Fluoxetine can decrease feeding behavior in fish (Hedgespeth et al., 2014) and starlings (Bean et al., 2014), as well as slow predator avoidance in fathead minnows (Painter et al., 2009). Venlafaxine concentrations as low as 31.3 ng/L can cause increased foot detachment from substrate in gastropods (Fong and Ford, 2014). Concentrations of venlafaxine in the current study were approaching 30 ng/L (maximum concentration of 27.6 ng/L, MISS831, sampled November 13, 2013; Table S3). Of important note is that although most reported effect concentrations for antidepressants are higher than typical environmental concentrations (and those observed in the current study), antidepressants can accumulate in fish tissues (Schultz et al., 2010) resulting in overall greater exposure risks. It is noted that few antidepressants were detected in the current study, but that could be an artifact of site location or sample timing. Especially given the influence of WWTPs at MISS, it is expected that more antidepressants and pharmaceuticals, in general, would be present at any given time.

Estrone was detected at 121 ng/L in INDU (INDU475, sampled November 12, 2014; Table S6), which is substantially higher than effect concentrations reported elsewhere. This concentration is more than 20 times greater than a predicted critical environmental concentration of 4.7 ng/L, which is an estimate of the surface-water concentration expected to negatively impact fish (Fick et al., 2010). Fathead minnows exposed to 50 ng/L estrone showed decreases in predator avoidance response (McGee et al., 2009). Although the high environmental concentration of estrone occurred in only one sample, note should be taken given the magnitude of the concentration. Furthermore, given that equilenin, another estrogen, was detected in the same sample (187 ng/L; Table S6), the combined estrogenic activity of the two hormones (along with other estrogenic chemicals) has the potential to affect functions of the endocrine system in aquatic biota. Given the limited scope of the study, it is hard to speculate the source of the estrone (and equilenin) at this site and may raise suspicions. Considering that laboratory quality-assurance data do not indicate any analytical issues with these hormones during the study, there is not substantial evidence to indicate that the detections were a result of contamination with sample processing and analysis at the laboratory. However, given the lack of field-blank samples collected during the study, contamination associated with sample collection and processing in the field cannot be ruled out.

Several of the chemicals detected in this study are known or suspected endocrine disruptors and have been documented to elicit effects at concentrations similar to those observed in the current study. For example, equilenin has been documented to increase plasma vitellogenin concentrations in female rainbow trout at concentrations as low as 4.2 ng/L (Tyler et al., 2009), substantially lower than the observed concentration in this study (187 ng/L). Furthermore, steroid estrogens and other weakly estrogenic chemicals have been documented to exhibit additive potency (Silva et al., 2002; Thorpe et al., 2003). Thus, although estrogens were not detected in many samples, the presence of other estrogenic chemicals such as organophosphate flame retardants (Liu et al., 2012; Liu et al., 2013) and bisphenol A (Flint et al., 2012) most likely contributes to the overall estrogenic potency of the sampled waters within the parks.

In addition to the estrogenic chemicals mentioned above, some pesticides have been associated with endocrine disruption in aquatic

organisms, particularly with respect to thyroid functions, although steroid hormones may affect the thyroid cascade in fish and mammals as well (Brown et al., 2004). Acetochlor can affect normal larvae development of rare minnow (*Gobiocypris rarus*) and decrease circulating thyroid hormone in adults at environmentally relevant concentrations (20 and 200 ng/L, respectively) (Li et al., 2009), which are similar to concentrations observed in the current study (maximum concentration of 265 ng/L, MISS815, sampled April 1, 2013; Table S3). Legacy pesticides such as PCBs, may also affect thyroid functions (Brown et al., 2004). Although these pesticides were not included in the current study, they are known to persist in the environment and can add to the effect that current-use pesticides have on aquatic organisms.

4. Conclusions

This study represents a reconnaissance survey to characterize the presence of chemicals of concern in four upper Midwestern U.S. national parks. The survey revealed that several chemicals of concern are present in surface waters of national parks at any given time. More chemicals were detected at higher concentrations in surface waters within national parks near urban or agricultural areas, and at sites downstream and nearby inputs from WWTP effluent. Flame retardants and bisphenol A were detected at least once at MISS, APIS, and INDU at concentrations up to 82 and 350 ng/L, respectively (Table 1), highlighting the ubiquitous nature of these chemicals in the environment. Of the detected pharmaceuticals, the highest concentrations were observed for gabapentin, reaching a maximum of 1080 ng/L (Table 2). Additionally, gabapentin often co-occurred with metformin; given the use of these pharmaceuticals for diabetic conditions, this co-occurrence is not unexpected. Other frequently detected pharmaceuticals included anticonvulsants, antidepressants, and diuretics. Of the detected pesticides, atrazine, metolachlor, and simazine were detected at relatively high concentrations.

With the exception of a few chemicals, detected concentrations were generally orders of magnitude less than available screening values and/or benchmarks. Metformin, hydrochlorothiazide, atrazine, and simazine concentrations either approached or exceeded (hydrochlorothiazide) available human-health benchmarks in at least one sample. Although no environmental concentrations approached or exceeded available aquatic life standards, environmental concentrations often were in ranges reported to elicit adverse effects in multiple organisms. The data obtained from this study can be compared to other surface water screening efforts focused on chemicals of concern, lead to further investigation of sources for particular chemicals, and aid in the development of adaptive management plans to help protect these U.S. national parks for the enjoyment of future generations.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.11.114>.

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