

# Concentrations of select dissolved trace elements and anthropogenic organic compounds in the Mississippi River and major tributaries during the summer of 2012 and 2013

Derek D. Bussan · Clifford A. Ochs ·  
Colin R. Jackson · Tarun Anumol · Shane A. Snyder ·  
James V. Cizdziel

Received: 23 June 2016 / Accepted: 16 January 2017  
© Springer International Publishing Switzerland 2017

**Abstract** The Mississippi River drainage basin includes the Illinois, Missouri, Ohio, Tennessee, and Arkansas rivers. These rivers drain areas with different physiography, population centers, and land use, with each contributing a different suites of metals and wastewater contaminants that can affect water quality. In July 2012, we determined 18 elements (Be, Rb, Sr, Cd, Cs, Ba, Tl, Pb, Mg, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) and chlorophyll-a (Chl-a) in the five major tributaries and in the Upper Mississippi River. The following summer, we determined both trace elements and 25 trace organic compounds at 10 sites in a longitudinal study of the main stem of the Mississippi River from

Grafton, Illinois to Natchez, Mississippi. We detected wastewater contaminants, including pharmaceuticals and endocrine disrupting compounds, throughout the river system, with the highest concentrations occurring near urban centers (St. Louis and Memphis). Concentrations were highest for atrazine ( $673 \text{ ng L}^{-1}$ ), DEET ( $540 \text{ ng L}^{-1}$ ), TCPP ( $231 \text{ ng L}^{-1}$ ), and caffeine ( $202 \text{ ng L}^{-1}$ ). The Illinois, Missouri, and Yazoo rivers, which drain areas with intense agriculture, had relatively high concentrations of Chl-a and atrazine. However, the Ohio River delivered higher loads of contaminants to the Mississippi River, including an estimated  $177 \text{ kg day}^{-1}$  of atrazine, due to higher flow volumes. Concentrations of heavy metals (Ni, V, Co, Cu, Cd, and Zn) were relatively high in the Illinois River and low in the Ohio River, although dissolved metal concentrations were below US EPA maximum contaminant levels for surface water. Multivariate analysis demonstrated that the rivers can be distinguished based on elemental and contaminant profiles.

**Electronic supplementary material** The online version of this article (doi:10.1007/s10661-017-5785-x) contains supplementary material, which is available to authorized users.

D. D. Bussan · J. V. Cizdziel (✉)  
Department of Chemistry and Biochemistry, University of  
Mississippi, University, MS 38677, USA  
e-mail: cizdziel@olemiss.edu

C. A. Ochs · C. R. Jackson  
Department of Biology, University of Mississippi, University, MS  
38677, USA

T. Anumol · S. A. Snyder  
Department of Chemical and Environmental Engineering,  
University of Arizona, 1133 E James E Rogers Way, Harshbarger  
108, Tucson, AZ 85721-0011, USA

T. Anumol  
Agilent Technologies Inc., 2850 Centerville Road, Wilmington,  
DE 19808, USA

**Keywords** Mississippi River · Trace elements · Trace  
organic compounds · Chlorophyll-a · Atrazine

## Introduction

Surface runoff, including wastewater discharges from municipalities and industry, from much of the central USA flows through the Mississippi River to the Gulf of Mexico. The Mississippi River Basin (MRB)

encompasses area from 31 states and two Canadian provinces and is the fourth largest watershed in the world (Brown et al. 2005). There are six major Mississippi River sub-basins: the Upper Mississippi, Ohio, Missouri, Tennessee, Arkansas-Red-White, and the Lower Mississippi. Each of these watersheds varies substantially in physiography, population density, and land use/cover. For example, within the Missouri and Lower Mississippi River sub-basins, there is intensive agriculture, whereas in the Ohio River sub-basin, there is more industry. Consequently, the tributaries have different physical-chemical characteristics and could be expected to have disparate chemical profiles (Jackson et al. 2014; Millar et al. 2015). For instance, the Missouri watershed yields the highest load of suspended sediments, whereas the Upper Mississippi has the largest total nitrogen load and yield (Turner and Rabalais 2003). The runoff from these watersheds can affect water quality, not only in the Mississippi River but also at its terminus in the Gulf of Mexico, an infamous example being the zone of hypoxia that occurs annually near the mouth of the Mississippi River due to an influx of nutrients (Rabalais et al. 2002). Poor water quality not only impacts fish and wildlife but also can have major economic impacts for residents of the Gulf Coast (Rabalais et al. 2002; Rabotyagov et al. 2014). Linkages between land use/cover and water quality in the MRB have generally been well documented; however, there is surprisingly little information on trace elements and anthropogenic trace organic compounds.

Concentrations of trace metals in rivers can provide information on the state of the environment and development over large areas (Garbarino et al. 1996). Data for trace elements in large river basins is also needed to evaluate the impact of changing climate and land use; however, data over broad spatial scales is often lacking (Huser et al. 2011). Trace elements can also be used as indicators of anthropogenic impacts. For example, U, Co, and Cu have been found to be elevated in groundwater underneath agricultural areas (Levins and Gosk 2008). Moreover, while certain trace elements, such as B, Cu, Fe, Mn, Mo, and Zn, are essential for plants and animals (Lindsay 1984; Loomis and Durst 1992), others, such as As, Cr, Se, and Pb, have the potential to be toxic to animals even at low concentrations (Garbarino et al. 1996). Despite the importance of monitoring trace elements in aquatic systems, current information in the Mississippi River system is limited, with measurements for the last large-scale spatial studies

occurring nearly a quarter of a century ago (Garbarino et al. 1996; Shiller 1997). For the Mississippi River, Shiller (1997) observed that for a number of elements, there was a seasonal pattern, particulate trace element concentrations tended to follow suspended matter concentrations, and, except for Mo and U, particulate concentrations were generally greater than dissolved concentrations.

Trace organic compounds (TOCs) are another important class of pollutants for which there is little information in the Mississippi River system, particularly on a broad spatial scale. TOCs cover a diverse range of substances including pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs). Ever increasing numbers and types of TOCs are being discovered in water, in large part due to improved analytical methods (Daughton and Ternes 1999; Snyder et al. 2003; Richardson et al. 2005; Snyder 2014). Concentrations of PPCPs in natural waters tend to be high near wastewater treatment plant (WWTP) discharges because these facilities were generally not designed to handle PPCPs (Ternes et al. 2004). Although many of the compounds have a relatively short half-life in the environment, their near continual discharge replenishes them and effectively increases their impact (Buseti and Heitz 2011). PPCPs pose multiple risks to both the aquatic biotic community and humans that depend on these sources of water (Hernando et al. 2006). Fish communities can be feminized by EDCs, such as 17 $\beta$ -estradiol (a natural estrogen present in urine) and ethinylestradiol (an ingredient in birth control pills), at concentrations as low as several nanograms per liter (Purdum et al. 1994; Desbrow et al. 1998). The PPCPs ciprofloxacin (an antibiotic), triclosan (an anti-microbial agent), and tergitol NP 10 (a surfactant) have also been found to shift the community structure of natural freshwater algae assemblages (Wilson et al. 2003). Other concerns about the presence of PPCPs in natural waters include bacteria becoming resistant to anti-microbial drugs, especially in a waterbody used for drinking water (Koczura et al. 2012; Michael et al. 2013). Some TOCs can be transformed in the natural environment to either more toxic forms or even regenerating the original parent structure (Cwiertny et al. 2014).

Similar to the sparse data for trace elements, information on TOCs in the Mississippi River is quite limited. Boyd et al. (2004) examined nine different PPCPs and EDCs in stormwater canals of New Orleans, Louisiana,

as well as in surrounding bayou waters and found measureable concentrations of naproxen, ibuprofen, triclosan, and bisphenol A in two stormwater canals and detectable concentrations of naproxen and bisphenol A in bayou waters. However, there has been no large-scale spatial study of TORCs in the Mississippi River system, and the last major study involving mass transport of pesticides and herbicides in the system was conducted in the 1990s by the US Geological Survey (USGS) (Pereira et al. 1995). That study found that the Upper Mississippi River Basin contributed just 22% of water to the total Mississippi River drainage basin but contributed 40% of the total atrazine, and 50% or more of many other pesticides were found in the Mississippi River (Pereira et al. 1995). The study also found that while Iowa and Illinois are the sources for much of the agricultural chemicals transported by the Lower Mississippi River, the Ohio River Basin was the source of >50% of the simazine, and the Missouri River Basin was the predominant source of trifluralin (Pereira et al. 1995).

Given that toxic metals and anthropogenic organic compounds can cause water quality deterioration and affect wildlife and human health, we sought to assess the concentrations and spatial distribution of a wide range of metals and TORCs, including PPCPs, hormones, and pesticides, along a large transect of the Mississippi River and in its major tributaries. There are a few limitations of this study that should be acknowledged. The study was not designed to track temporal changes in concentrations and loadings of elements and TORCs in these rivers. Whereas samples were collected from a wide geographic area, for logistical reasons, the sampling frequency was limited. During the summer of 2012, we focused on major tributaries of the Mississippi River, and the following summer on a longitudinal study of the main stem of the Mississippi River. Thus, this work represents “snapshots” of the system during the summer low flow period. That said, there are two important findings from this research: (1) major rivers of the Mississippi River Basin can be distinguished from each other based on trace metal and contaminant profiles, likely reflecting different industry, land use, and soil characteristics within the sub-basins, and (2) a variety of anthropogenic TORCs, including PPCPs and EDCs, are present in the river system, with the highest concentrations occurring near urban centers. Moreover, the data from this report can serve as a baseline for

future studies and for assessing potential remedial action in the MRB.

## Materials and methods

### Sampling the Mississippi River and its tributaries

Our general sampling approach was described in detail in a previous report (Jackson et al. 2014). Briefly, we collected sub-surface water samples during a 2-week sampling campaign in July 2012 from a total of 18 sites from six major tributaries of the Lower Mississippi River (i.e., Upper Mississippi, Illinois, Missouri, Ohio, Tennessee, and Arkansas rivers) (Table 1). The volume of water in the Mississippi River approximately doubles at the confluence of the Ohio and Mississippi Rivers, a location that is also generally accepted as the dividing line between the Upper and Lower Mississippi River. A second sampling campaign was conducted in July 2013 along a ~1250 km longitudinal transect in the Lower Mississippi River from Grafton, Illinois to Natchez, Mississippi (Fig. 1). Along this longitudinal transect, we also included samples at the mouth of five major tributaries (Illinois, Missouri, Ohio, Arkansas, Yazoo rivers). Concentrations of metals and contaminants in the Mississippi River depend on several factors including water level and season (Shiller and Boyle 1987; Shiller 1997). We collected grab samples mid-channel ~0.5 m below the surface during summer low (base level) flow, when weather conditions were stable with no major storm events the prior 10 days. Depth profiles of temperature and oxygen revealed no evidence of vertical stratification in these large and generally turbulent rivers.

In July 2012, we sampled three sites in each of the Arkansas, Missouri, Ohio, and Upper Mississippi rivers; two sites in the lower portion of the Illinois River; and four sites on the Tennessee River: two in Kentucky Lake, a large (469 km<sup>2</sup>) open reservoir just before the river merges with the Ohio River, and two in the more upstream region. The most downstream sample sites were 25 to 50 km upstream of the confluence of the river with the larger system, and other sample sites were progressively 50–80 km upstream of that. In July 2013, samples were collected daily approximately every 120 river km, roughly corresponding to the mean flow of the Mississippi River per day during the summer, in a downstream direction starting from near Grafton,

**Table 1** Sampling location on the Mississippi River and major tributaries

Year 2012				Year 2013				
Nearest city	River	Latitude	Longitude	Site no.	Nearest city	River	Latitude	Longitude
Louisiana, MO	Upper Mississippi	39.45	-91.045	1	Grafton, IL	Illinois	38.965	-90.496
Hamburg, IL		39.229	-90.724	2	Grafton, IL	Upper Mississippi	38.946	-90.475
Golden Eagle, IL		38.865	-90.568	3	Hartford, IL		38.828	-90.111
Hardin, IL	Illinois	39.169	-90.614	4	Hartford, IL	Missouri	38.826	-90.134
Grafton, IL		38.966	-90.495	5	Ste. Genevieve, MO	Upper Mississippi	38.003	-90.047
New Haven, MO	Missouri	38.6	91.2	6	Cape Girardeau, MO		37.335	-89.483
Washington, MO		38.583	-91.029	7	Cairo, IL		37.027	-89.217
Defiance, MO		38.657	-90.735	8	Cairo, IL	Ohio	37.026	-89.176
Uniontown, KY	Ohio	37.799	-87.916	9	New Madrid, MO	Lower Mississippi	36.579	-89.522
Sturgis, KY		37.534	-88.07	10	Blytheville, AR		35.886	-89.768
Burna, KY		37.215	-88.447	11	Memphis, TN		35.224	-90.075
Adamsville, TN	Tennessee	35.149	-88.316	12	North Tunica, MS		34.743	-90.45
Clifton, TN		35.386	-88.006	13	Rosedale, MS		33.817	-91.048
New Concord, KY		36.625	-88.055	14	Rosedale, MS	Arkansas	33.810	-91.109
Hardin, KY		36.802	-88.132	15	Mayersville, MS	Lower Mississippi	32.900	-91.066
Moscow, AR	Arkansas	34.169	-91.739	16	Vicksburg, MS		32.347	-90.963
Dumas, AR		33.988	-91.363	17	Vicksburg, MS	Yazoo	32.389	-90.916
Watson, AR		33.954	-91.21	18	Natchez, MS	Lower Mississippi	31.561	-91.41

Cities are provided solely for reference to location. 2013 sites are listed north to south

Illinois to near Natchez, Mississippi, ~1250 km to the south. Samples were also collected from five major tributaries (Illinois, Missouri, Ohio, Arkansas, and Yazoo rivers) a few kilometers upstream from their confluence with the Mississippi River.

For trace elements and other water quality parameters, water was collected into acid-washed polyethylene bottles. Water pH and temperature were measured in the field using a YSI professional plus water quality meter. Water samples for trace metals were filtered through 0.45- $\mu\text{m}$  filters and preserved to 2% acid ( $v/v$ ) with high-purity concentrated  $\text{HNO}_3$  (Optima grade; Fisher Scientific). For organic analytes, samples were collected into 4-L amber bottles and adjusted to a  $\text{pH}<2$  by addition of concentrated  $\text{HCl}$  (Optima grade). Samples were placed in a cooler containing ice and transported back to the laboratory where they were stored at  $\sim 5^\circ\text{C}$ .

#### Determination of trace elements

Trace metal samples were determined by sector field inductively coupled plasma mass spectrometry (SF-ICPMS) using a Thermo Fisher Element-XR. The

instrument utilizes reverse Nier-Johnson geometry that is capable of high resolving power ( $m/\Delta m \approx 10,000$ ). Sample introduction utilized a glass concentric nebulizer with a cyclonic spray chamber. The instrument was tuned prior to analysis for sensitivity and stability. Data acquisition parameters are given in Table 2.

Typically, we achieved  $\sim 1$  million counts  $\text{s}^{-1}$  for  $1 \text{ ng g}^{-1}$  of  $^{115}\text{In}$  in low-resolution mode and  $<4\%$  relative standard deviation (RSD). External calibration was used to quantify the elements. Rhodium was added as an internal standard in-line using a mixing chamber (Trident, Glass Expansion). In 2012, we determined 18 elements (Be, Rb, Sr, Cd, Cs, Ba, Tl, Pb, Mg, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) in the five major tributaries and in the Upper Mississippi River. In 2013, the same elements, along with Li, Na, Ca, Ga, Ag, and U, were determined at 18 sites in a longitudinal study of the main stem of the Mississippi River from Grafton, Illinois to Natchez, Mississippi. Mean values for NIST SRM 1643e (trace elements in natural water) were within  $\pm 20\%$  of certified values, except for Na, Sr, Mg, and Ca, which were within  $\pm 30\%$ . Precision of replicate samples was  $<15\%$  relative percent difference.



**Fig. 1** Locations in the Mississippi River Basin that were sampled in 2012 (open circles) and 2013 (dark circles). Major cities and state boundaries are shown for reference

**Table 2** ICP-MS instrumental settings

Plasma parameters	
Cool gas flow	16 L min <sup>-1</sup>
Aux. gas flow	0.9 L min <sup>-1</sup>
Sample gas flow	1.19 L min <sup>-1</sup>
RF power	1280 W
Data acquisition parameters	
Low resolution (LR)	<sup>9</sup> Be, <sup>23</sup> Na, <sup>85</sup> Rb, <sup>88</sup> Sr, <sup>107</sup> Ag, <sup>111</sup> Cd, <sup>133</sup> Cs, <sup>137</sup> Ba, <sup>205</sup> Tl, <sup>208</sup> Pb, <sup>238</sup> U
Medium resolution (MR)	<sup>24</sup> Mg, <sup>27</sup> Al, <sup>44</sup> Ca, <sup>51</sup> V, <sup>52</sup> Cr, <sup>55</sup> Mn, <sup>56</sup> Fe, <sup>59</sup> Co, <sup>60</sup> Ni, <sup>63</sup> Cu, <sup>66</sup> Zn, <sup>69</sup> Ga
Mass window	20% LR; 150% MR; 200% for HR
Points per peak	50 for LR; 20 for MR
Scan type	E-scan
Integration time	10 ms
Passes and runs	3 and 2

### Determination of chlorophyll-a

Chlorophyll-a (Chl-a) was determined with a Beckman DU 530 Life Science UV/Vis spectrophotometer using standard methods (Wetzel and Likens 2000). Briefly, 250 mL of river water was filtered through Whatman GF/F filters, which were subsequently extracted using 90% NH<sub>4</sub>OH-buffered acetone. The absorbance of released Chl-a in the extract was measured at 655 and 750 nm.

### Determination of trace organic compounds

TORCs in the water were determined by automated online solid-phase extraction (SPE) coupled to liquid chromatography-tandem mass spectrometry (Anumol and Snyder 2015). The methodology was developed to target a wide range of TORCs based on literature reports about the compounds occurrence, toxicological relevance, and ability to pose as “indicators” of water quality (Anumol and Snyder 2015). Information regarding the target analytes and isotopic surrogates used in the study are shown in Table 3.

Briefly, samples were filtered using 0.2-µm polyethylene styrene filter prior to analysis. Automated pre-concentration of all samples was performed using an Agilent FlexCube SPE module, which required only 1.7 mL of sample. During the elute phase, there is a gradient elution of the target analytes onto the analytical column. The liquid chromatography was conducted using an Agilent 1290 UHPLC binary pump. An Agilent Poroshell 120 EC C-18 (2.1 mm × 50 mm, 2.7 µm) column was used for separation of analytes. Mass spectrometry was performed on an Agilent 6460 triple quadrupole mass spectrometer. The mass spectrometer was run in dynamic multiple reaction mode and data acquisition, and analysis was performed on MassHunter software (Ver. 06.01). Optimized parameters and retention times are provided elsewhere (Anumol and Snyder 2015). Method reporting limits in ultrapure water range from 0.1 to 15 ng L<sup>-1</sup>. Analytical standards were high purity (>97%) and purchased from Sigma-Aldrich (St. Louis, MO) or Alfa Aesar (Ward Hill, MA).

### Statistical analysis

Analysis of variance (ANOVA) and Tukey’s HSD test were used to test for differences among groups. Differences were deemed significant at the *p* < 0.05 level.



**Table 3** Class and use of TORCs selected in this study with isotopes used for quantification

Compound	Use	Category	Isotope
Atenolol	$\beta$ -Blocker	Pharmaceutical	Atenolol-d7
Carbamazepine	Anti-seizure		Carbamazepine-d10
Clofibrilic acid	Lipid regulator		Bisphenol A-13C12
Diltiazem	Anti-histamine		Diltiazem-d3
Diphenhydramine	Anti-arrhythmic		Diphenhydramine-d5
Fluoxetine	Anti-depressant		Fluoxetine-d5
Gemfibrozil	Anti-cholesterol		Gemfibrozil-d6
Ibuprofen	Analgesic		Ibuprofen-d3
Meprobamate	Anti-anxiety		Meprobamate-d7
Naproxen	Analgesic		Naproxen-13C1d3
Primidone	Anti-convulsant		Primidone-d5
Trimethoprim	Antibiotic		Trimethoprim-d3
Caffeine	Stimulant	Personal care product	Caffeine-13C3
<i>N,N</i> -diethyl- <i>m</i> -toluamide (DEET)	Insect repellent		DEET-d6
Propylparaben	Cosmetic preservative		Propylparaben-d4
Triclocarban	Antibiotic		Triclocarban-13C6
Triclosan	Anti-microbial		Triclosan-13C12
Perfluorohexanoic acid (PFHxA)	Surfactant	Industry	PFHxA-13C12
Perfluorooctanoic acid (PFOA)			PFOA-13C4
Perfluorooctane sulfonate (PFOS)			PFOS-13C4
Tris(2-chloropropyl)phosphate (TCPP)	Flame retardant	Industry	TCPP-d12
Testosterone	Androgen	Hormone	Testosterone-d3
Atrazine	Herbicide	Herbicide	Atrazine-d3
Simazine			Simazine-d3

Principal component analysis (PCA) was used to evaluate and interpret commonalities or differences in the elemental data. PCA was not amenable to the TORCs data because of limited data and samples with target compounds below the instrumental detection limit. Statistical analysis was done using JMP 11.0 (SAS Institute; Cary, NC).

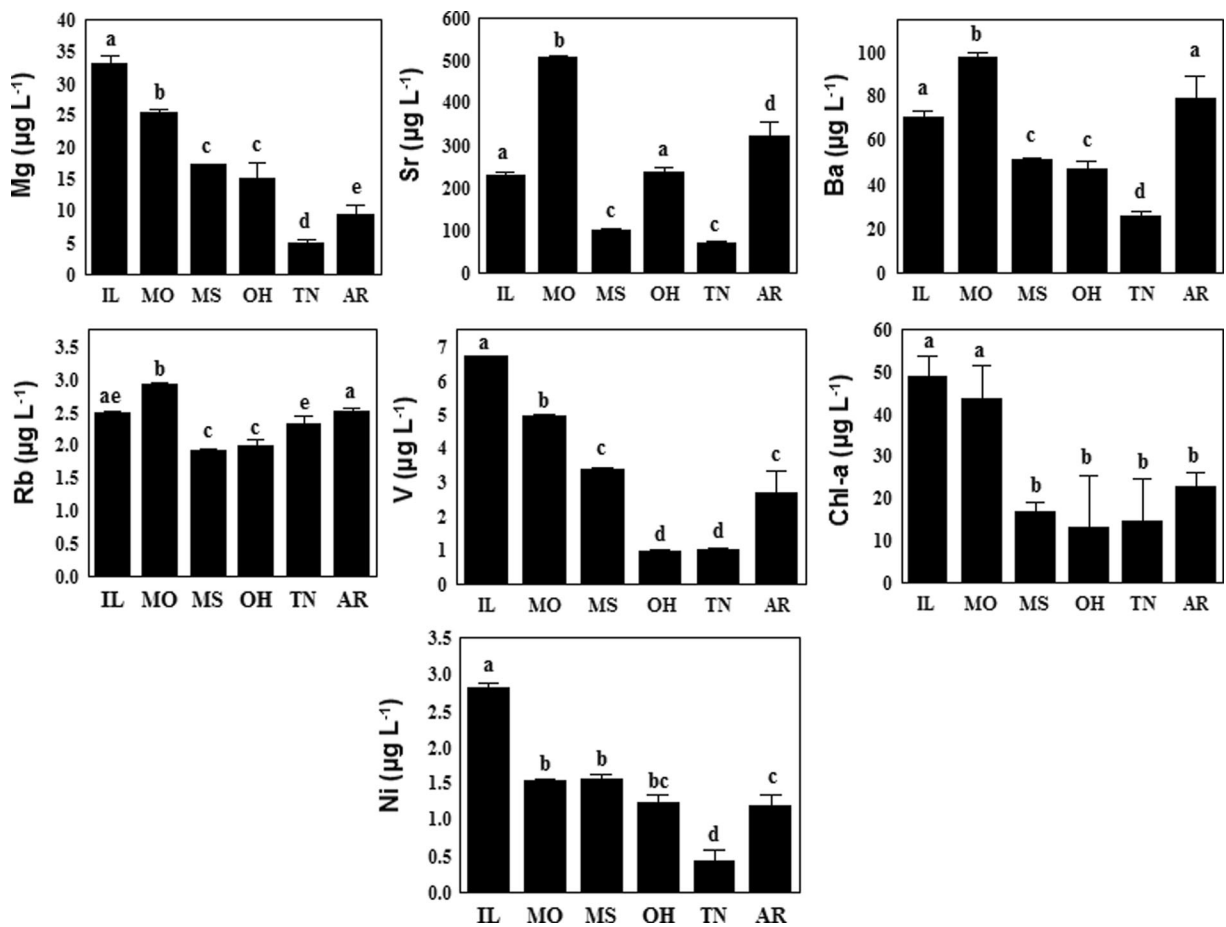
## Results and discussion

### Chlorophyll-a

Chl-a is used as a water quality parameter to assess algal abundance and biomass, and, in turn, algal abundance and biomass can be used to evaluate nutrient loading to aquatic systems (Gannon and Stemberger 1978; Buck et al. 2000). Algal biomass is responsive to nitrogen and phosphorus enrichment and thus is greatly impacted by

runoff containing fertilizers (Harding and Perry 1997) or animal manure (Edwards and Daniel 1993; Mozaffari and Sims 1994; Edwards et al. 1996). The World Health Organization gives a guideline level of 20,000 cyanobacteria cells mL<sup>-1</sup> (corresponding to 10  $\mu$ g Chl-a under conditions of cyanobacterial dominance) for protection from irritation or allergenic effects of cyanobacterial compounds. A level of 100,000 cyanobacterial cells mL<sup>-1</sup> (equivalent to ~50  $\mu$ g Chl-a L<sup>-1</sup> if cyanobacteria dominate) is used as a guideline value for a moderate health alert in recreational waters.

In this study, the highest concentrations of Chl-a were in the Illinois River (27.1 to 52.3  $\mu$ g L<sup>-1</sup>) and the lowest concentrations were in the Ohio River (10.6 to 26.6  $\mu$ g L<sup>-1</sup>) (Fig. 2). The concentrations in the Illinois River were similar to results reported a decade earlier (Royer et al. 2008), suggesting that fertilizer use in this corn-producing region remains high (Eghball and



**Fig. 2** Bar graphs representing mean concentrations of six metals and Chl-a in major tributaries of the Lower Mississippi River for the 2012 sampling trip. Concentrations are in micrograms per liter, except for Mg ( $\text{mg L}^{-1}$ ). Error bars represent 1 SD. Letters above each bar indicate whether the levels are statistically different

( $p < 0.05$ ) from one another within each plot; bars that do not share a letter are statistically different. Rivers are labeled as IL Illinois, MO Missouri, MS upper Mississippi, OH Ohio, TN Tennessee, and AR Arkansas

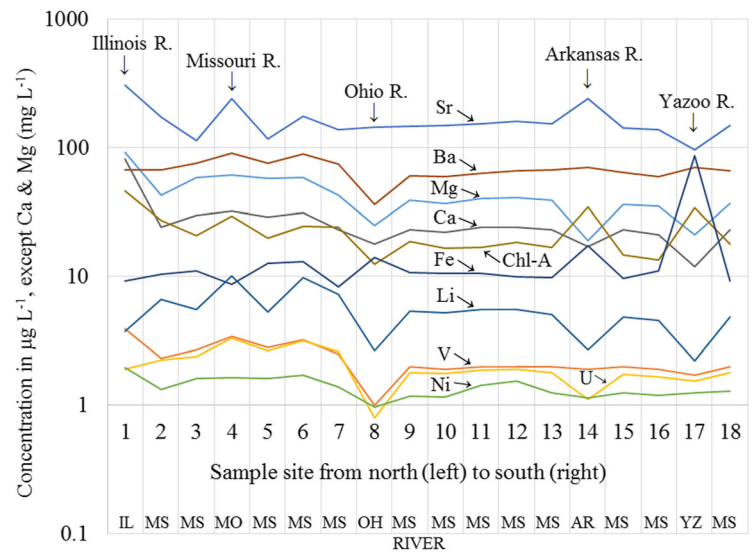
Power 1999). According to the Illinois Department of Agriculture, 4,282,890 t of fertilizer was distributed in the state in 2012 and 3,875,739 t in 2013. The Yazoo, Missouri, and Arkansas Rivers, which also drain intensive agricultural areas, also had relatively high Chl-a concentrations compared to the Ohio River and the main stem of the Mississippi River (Fig. 3). Cyanobacteria were a major component of the microbial community in our samples (Jackson et al. 2014).

Trace elements

Metal and Chl-a concentrations for the 2012 study are given in Table 4. pH values ranged from 7.4 to 8.2, generally considered to be in the normal range and similar to earlier studies (Shiller and Boyle 1987).

Within this pH range, many elements are not strongly partitioned to the adsorbed phase (Shiller 1997). Each of the elements measured were below maximum contaminant levels for drinking water established by the US Environmental Protection Agency (Table 4). Six elements (Mg, Sr, Ba, Rb, V, and Ni) and Chl-a, in particular, exhibited relatively large differences in concentration between rivers (Fig. 2). For example, V and Ni were significantly higher in the Illinois and Missouri Rivers compared to the Tennessee River. Dissolved metals in the rivers stem from both natural and anthropogenic sources. Trace elements like V and Ni are released to the environment through weathering of rocks and erosion of soil (Fischer et al. 2009). Metal concentrations in the soil vary in the river sub-basins due to different geology (Smith et al. 2014). Concentrations of V and

**Fig. 3** Metal and chlorophyll-a (*Chl-a*) concentrations (logarithmic scale) in a longitudinal study of the Mississippi River from Grafton, Illinois (site 1) to Natchez, Mississippi (site 18) and some of its major tributaries in 2013. For clarity, not all elements are shown; all data is provided in supplement Table 1. River symbols: *IL* Illinois, *MS* Mississippi, *MO* Missouri, *OH* Ohio, *AR* Arkansas, *YZ* Yazoo



Ni in the soil of the Illinois and Missouri River basins are generally higher than the Tennessee basin (Mast et al. 1973). Anthropogenic sources of V and Ni include fossil fuel combustion and steel production (Henry and Knapp 1980; Hope 1997). In 2008, the latest year for which data was available, air emissions of Ni were higher in Illinois (19,500 kg) compared to Tennessee (14,800 kg) (Office of Air Quality and Standards 2008); V data was not reported. While there are several large-scale steel production facilities located just north of Peoria along the Illinois River, Shiller (1997) concluded that the weathering rate and type of source rock, rather than solution chemistry or anthropogenic influences, are the most important factors determining fluvial dissolved V concentrations. Like Shiller (1997), we found a statistically significant correlation between V and pH ( $r = 0.63$ ), as well as between V and Chl-a ( $r = 0.81$ ). Others have shown that V can stimulate chlorophyll production by algae (Wilhelm and Wild 1984).

Metal and Chl-a concentrations for the 2013 (longitudinal) study are shown in Fig. 3, with specific values given in Supplemental Table 1. Concentrations and patterns among the rivers were generally similar to the prior year. The Illinois had relatively high concentrations of Pb, V, Ni, Co, Zn, Ca, Sr, and Mg, and the Ohio had low concentrations of Mg, V, Pb, U, Ni, Ba, Ca, and Chl-a. The Missouri River was elevated in Sr, Li, V, Pb, and U. The Arkansas River showed distinct features with higher concentrations of Fe, Sr, and Chl-a and lower concentrations of Li, Mg, and U, relative to

the Lower Mississippi River into which it drains. The Yazoo River was high in Al, Fe, Mn, and Chl-a and low in Li, Ca, and Mg compared to the Lower Mississippi River.

The Ohio River, in particular, stands out in the altering concentrations of metals in the Mississippi River, as seen in Fig. 3, by the dip in the lines representing metal concentrations in the Ohio River and by the lower levels in the Mississippi River downstream of the Ohio River compared to upstream. Indeed, mixing appears adequate to account for the concentrations of some elements and Chl-a downstream of where the Ohio River enters the Mississippi River (Fig. 4). However, this interpretation should be made cautiously as many trace elements exhibit non-conservative behavior during tributary mixing and in-stream processes may impact concentrations (Shiller and Boyle 1985; Shiller 1997). The spread in the “Upper Mississippi” river data cluster (Fig. 4) may stem from influence of the Missouri and Illinois rivers which discharge upstream of these sampling points. V and Ni show a strong correlation ( $r = 0.92$ ) regardless of location, suggesting similar sources and environmental behavior (Fig. 4d).

#### Trace organic compounds

Our results indicate the presence of a variety of anthropogenic TOrcs throughout the Mississippi River and its major tributaries (Table 5). Of the 25



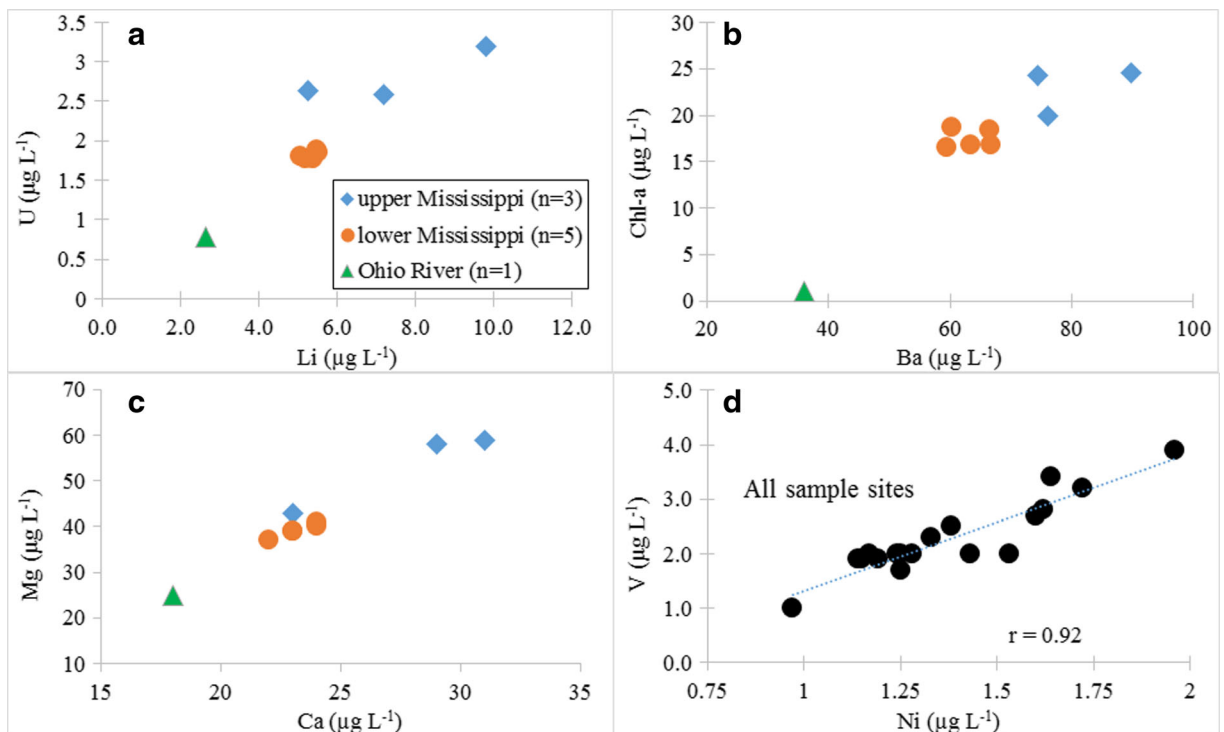
**Table 4** Maximum contaminant levels, mean metal and Chl-a concentrations, and pH in the Mississippi River system during the summer of 2012

Element	MCL	SRM 1643e Certified	SRM 1643e Found	Arkansas	Tennessee	Ohio	Mississippi	Illinois	Missouri
Al	50–200 <sup>a</sup>	141.8 ± 8.6	137.3 ± 0.8	13.5 ± 7.3	4.9 ± 1.2	19.0 ± 4.6	21.2 ± 3.0	23.5 ± 8.6	27.6 ± 2.9
Ba	2000	544.2 ± 5.8	505.0 ± 4.6	79 ± 10	26 ± 2	47 ± 4	52 ± 1	71 ± 2	98 ± 2
Be	4	13.98 ± 0.17	13.78 ± 0.09	0.129 ± 0.001	0.127 ± 0.002	0.128 ± 0.001	0.133 ± 0.002	0.128 ± 0.001	0.127 ± 0.002
Cd	5	6.568 ± 0.073	7.06 ± 0.07	0.56 ± 0.01	0.56 ± 0.01	0.58 ± 0.01	0.57 ± 0.01	0.6 ± 0.1	0.58 ± 0.01
Co	NA	27.06 ± 0.32	24.86 ± 0.17	0.52 ± 0.03	0.47 ± 0.05	0.48 ± 0.02	0.49 ± 0.03	0.74 ± 0.04	0.48 ± 0.01
Cr	100	20.40 ± 0.24	19.06 ± 0.24	0.21 ± 0.02	0.20 ± 0.01	0.27 ± 0.04	0.24 ± 0.01	0.22 ± 0.01	0.22 ± 0.01
Cs	NA	NA	0.73 ± 0.10	0.15 ± 0.01	0.21 ± 0.08	0.15 ± 0.01	0.14 ± 0.01	0.14 ± 0.01	0.15 ± 0.01
Cu	1300	22.76 ± 0.31	19.91 ± 0.06	4.5 ± 2.6	1.2 ± 0.52	1.5 ± 0.3	2.1 ± 0.4	1.9 ± 0.1	1.62 ± 0.06
Fe	300 <sup>a</sup>	98.1 ± 1.4	93.0 ± 1.0	28.9 ± 29.4	3.6 ± 0.47	10.9 ± 1.5	18.2 ± 2.3	19 ± 7	22.0 ± 1.5
Mg	NA	8037 ± 98	7671 ± 93	9.3 ± 1.4	5.0 ± 0.5	15.2 ± 2.4	17.2 ± 0.01	33 ± 1	25.5 ± 0.4
Mn	50 <sup>a</sup>	38.97 ± 0.45	35.59 ± 0.21	23.4 ± 2.9	10 ± 12	1.8 ± 0.1	8.1 ± 9.5	4.3 ± 2.1	4.0 ± 0.6
Ni	NA	62.41 ± 0.69	56.08 ± 0.46	1.19 ± 0.16	0.44 ± 0.14	1.2 ± 0.1	1.55 ± 0.07	2.81 ± 0.07	1.53 ± 0.03
Pb	15	19.63 ± 0.21	19.32 ± 0.37	0.33 ± 0.15	0.24 ± 0.04	0.35 ± 0.09	0.31 ± 0.03	0.32 ± 0.04	0.26 ± 0.02
Rb	NA	14.14 ± 0.18	14.39 ± 0.12	2.51 ± 0.04	2.3 ± 0.1	2.0 ± 0.1	1.91 ± 0.02	2.49 ± 0.03	2.91 ± 0.03
Sr	NA	323.1 ± 3.6	305.6 ± 4.8	323 ± 32	72 ± 4	236 ± 14	101 ± 1	230 ± 8	505 ± 4
Tl	0.5	7.445 ± 0.096	7.86 ± 0.09	0.24 ± 0.01	0.24 ± 0.01	0.26 ± 0.01	0.24 ± 0.01	0.24 ± 0.01	0.25 ± 0.01
V	NA	36.86 ± 0.59	35.92 ± 0.36	2.7 ± 0.6	1.0 ± 0.1	1.0 ± 0.1	3.4 ± 0.1	6.7 ± 0.1	4.9 ± 0.1
Zn	500 <sup>a</sup>	78.5 ± 2.2	69.4 ± 1.2	1.3 ± 1.4	1.7 ± 1.2	0.78 ± 0.37	1.6 ± 1.4	0.64 ± 0.23	0.34 ± 0.14
pH	6.5–8.5	NA	NA	8.01 ± 0.59	7.39 ± 0.23	7.85 ± 0.22	7.69 ± 0.16	8.05 ± 0.03	8.21 ± 0.06
Chl-a	NA	NA	NA	22.7 ± 3.3	14.6 ± 9.9	13.2 ± 12.4	16.8 ± 2.1	48.8 ± 4.9	43.6 ± 7.7

All concentrations are  $\mu\text{g L}^{-1} \pm 1 \text{ SD}$ , except Mg which is  $\text{mg L}^{-1} \pm 1 \text{ SD}$

MCL maximum contaminant level (US EPA), NA not available, SD standard deviation

<sup>a</sup> National secondary drinking water regulation



**Fig. 4** Select relationships between trace elements and between chlorophyll-a (Chl-a) and Ba in the Mississippi and Ohio rivers. Bivariate plots for **a** Li vs U, **b** Ba vs Chl-a, **c** Ca vs Mg, and **d** Ni vs V; data from 2013

TORCs targeted for analysis, 18 were detected above the method reporting limits at one or more sites within the Mississippi River system. Concentrations were highest in the Illinois River and near urban centers (e.g., Memphis, St. Louis) and lowest near Natchez, Mississippi, the furthest downriver site, likely reflecting dilution and losses from degradation and photolysis. PCA analysis of the combined elemental and anthropogenic compound data shows that the rivers can be distinguished based on their different compositional patterns of metals and TORCs (Fig. 5). The score and loading plots show that Chl-a and atrazine are positively correlated with each other (arrows pointing in the same general direction) and relatively high in concentration in the Illinois, Missouri, and Yazoo rivers. This is not surprising given that both fertilizers and herbicides are commonly found in agricultural runoff. Others have found that periphyton biomass ( $\text{mg m}^{-2}$  chlorophyll-a) increased significantly along correlated gradients of nitrate and atrazine at the watershed scale (Dalton et al. 2015). The results for atrazine are discussed further below. Samples from the upper portion of the main stem of the Mississippi River

grouped together in the center of the plot, reflecting similar concentrations (fingerprints). In contrast, the Mississippi River near Memphis had relatively high concentrations of several PPCPs, likely influenced by the city's WWTPs.

We estimated the mass loadings of TORCs at select sites in the Mississippi River system during the summer of 2013 using measured concentrations and USGS stream flow data (<http://waterdata.usgs.gov/nwis/rt>). Loadings were calculated for compounds determined above the limit of quantitation and when flow data were available at or near the sampling sites. Whereas the concentrations of TORCs were relatively low in the Ohio River, it delivered most TORCs to the Mississippi River because of its high flow volume ( $\sim 7.1 \times 10^8 \text{ m}^3 \text{ day}^{-1}$ ) compared to the Illinois ( $\sim 0.38 \times 10^8 \text{ m}^3 \text{ day}^{-1}$ ), Missouri ( $\sim 1.2 \times 10^8 \text{ m}^3 \text{ day}^{-1}$ ), and Upper Mississippi rivers ( $\sim 3.7 \times 10^8 \text{ m}^3 \text{ day}^{-1}$ ). For example, the concentration of atrazine in the Ohio River was  $250 \text{ ng L}^{-1}$ , second lowest among study sites, but its  $177 \text{ kg day}^{-1}$  loading was the highest. The river site with the highest overall load of TORCs was at Natchez, Mississippi where the flow was greatest ( $\sim 2.4 \times 10^9 \text{ m}^3 \text{ day}^{-1}$ ). It should be noted that we did not

**Table 5** Concentrations (ng L<sup>-1</sup>) and loadings (kg day<sup>-1</sup>, in parenthesis) of trace organic compounds in the Mississippi River and tributaries in 2013 compared to surface waters from other areas

Compound	This study: river and nearest city; data listed from north (left) to south (right)										Literature values		
	Illinois	Upper Miss.	Missouri	Ohio	Miss.	Arkansas	Yazoo	Miss.	Range	Location	Reference		
	Grafton, IL	Grafton, IL	St. Louis, MO	St. Gen., MO	Hartford, IL	Cairo, IL	Memphis, TN	Rosedale, MS	Vicksburg, MS	Natchez, MS			
Atenolol	30 (1.2)	<20	<21	<19	<20	<19	25	<21	<19	<16	ND-414	Mankyung R., South Korea	Kim et al. (2009)
Atrazine	673 (26)	326	462 (170)	408	464 (55)	250 (177)	242	263 (23)	521 (9.4)	273 (667)	ND-433.9	Suquia River Basin, Argentina	Bonansea et al. (2013)
Caffeine	15 (0.59)	10	47 (17)	12	28 (3.3)	13 (9.4)	202	8.3 (0.73)	15 (0.28)	12 (29)	38.8	Tennessee River, TN	Conley et al. (2008)
Carbamazepine	11 (0.43)	<4.5	<5.1	<4.1	4.2 (0.5)	<2.6	6	4.0 (0.35)	<3.5	<2.8	<10-373	Han River, Korea	Choi et al. (2008)
Clofibric acid	<4.2	<3.9	<3.5	<3.2	<3.1	<2.9	<3.1	<3.7	<3.9	<3.2	24-185	Madrid, Spain	Valcárcel et al. (2011)
DEET	58 (2.3)	16	48 (18)	15	17 (2)	13 (9.1)	540	13 (1.2)	23 (0.41)	7.2 (18)	30-24,000	South Wales, UK	Kasprzyk-Hordern et al. (2008)
Dexamethasone	<6	<5.2	<6.3	<6.3	<5.1	<3.2	<4.6	<5.3	4.7 (0.09)	<4.1	<0.01-0.06	Danube River, Hungary	Tölgyesi et al. (2010)
Diphenhydramine	<19	<23	<12	<22	<19	<17	<14.5	<39	<11	<55	7.7-1441	Rivers in Nebraska	Bartelt-Hunt et al. (2009)
Diltiazem	<8	<8.3	<7.25	<8.1	<7.7	<6.1	<6.5	<9.2	<6.3	<8.4	<5-13	Han River, Korea	Choi et al. (2008)

Table 5 (continued)

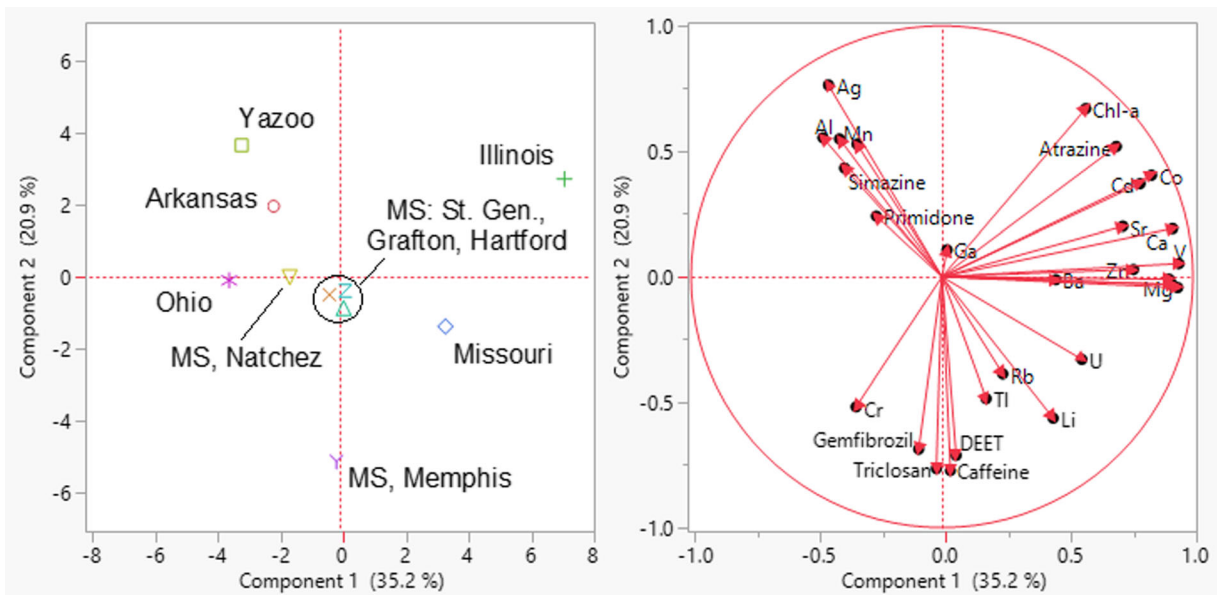
Compound	This study: river and nearest city; data listed from north (left) to south (right)										Literature values			Reference
	Illinois	Upper Miss.	Missouri	Ohio	Miss.	Arkansas	Yazoo	Miss.	Range	Location				
	Grafton, IL	Grafton, IL	St. Louis, MO	St. Gen., MO	Hartford, IL	Cairo, IL	Memphis, TN	Rosedale, MS	Vicksburg, MS	Natchez, MS				
Fluoxetine	<12	<13	<8.4	<12	<11	<8.5	<12	<11	<23	<20	ND-66.1	Madrid, Spain		Fernández et al. (2010)
Gemfibrozil	<2.4	<2.1	3.2 (1.2)	<2.5	2.5 (0.30)	<2	16	2.7 (0.24)	<2.1	<2	1113-5192	Madrid, Spain		Valcárcel et al. (2011)
Ibuprofen	<2.2	<2.2	8.3 (3.1)	<2.1	<3.5	<1.7	47	<2.1	2.8 (0.05)	<1.9	<0.3-100	South Wales, UK		Kasprzyk-Hordern et al. (2008)
Meprobamate	<9.4	<7.6	<7.7	<7.6	<6.8	<4.4	<6.1	<4.9	8.1 (15)	<6.2	3569-16,866	Madrid, Spain		Valcárcel et al. (2011)
Naproxen	<15	<14	31 (11)	<13	<11	<10	37	<13	<14	<11	<5.0-7.0	Cape Cod, MASS, USA		Standley et al. (2008)
PFHxA	5 (0.19)	<5	<5.5	<5	<6	<4	<5	<5	<6	<4	<0.13-5.3	Pearl River, China		So et al. (2007)
PFOA	6.2 (0.24)	4	2.5 (0.93)	3	<1.6	13 (8.9)	6	4.2 (0.37)	<2.3	6.2 (15)	7.4-44	Northeast Spain		Flores et al. (2013)
PFOS	<11	<10	<5	<6.5	<2.6	<14	11	<10	<14	<11	20-348	Northeast Spain		Flores et al. (2013)
Primidone	12 (0.46)	<7	15 (5.5)	<7	<6.3	16 (11)	12	64 (5.6)	<6.8	14 (35)	6-62	Unspecified rivers (USA)		Guo and Krasner (2009)
Propylparaben	<20	<21	<17	<16	<17	<14	<16	<18	<19	<17	ND-52.1	Mogi Guacu River, Brazil		Galinaro et al. (2015)
Simazine	15 (0.57)	4	7.4 (2.7)	6	6.3 (0.76)	18 (13)	12	14 (1.2)	23 (0.42)	24 (58)	ND-3180	Axios River, Greece		Papadopoulou-Mourkidou (2002)

**Table 5** (continued)

Compound	This study: river and nearest city; data listed from north (left) to south (right)										Literature values						
	Illinois	Upper Miss. IL	St. Louis, MO	St. Gen., MO	Missouri IL	Hartford, IL	Ohio IL	Cairo, IL	Miss. TN	Memphis, TN	Arkansas MS	Rosedale, MS	Vicksburg, MS	Natchez, MS	Miss. MS	Range	Location
TCPP	231 (8.9)	<100	<103	<95	<76	<61	169	<110	<130	<65	2.4–150	Han River, Korea	Yoon et al. (2010)				
Testosterone	<15	<15	<16.5	<13	<12	<8.3	<9.6	<12	<11	<9.1	ND–1.2	Danshui River, China	Liu et al. (2011)				
Triclocarban	<7.1	<6.7	<6.3	<6.1	2.3 (0.28)	<5.7	<5.9	<5	<7.3	<6.1	33–5600	Black River, Maryland	Halden & Paul (2004)				
Triclosan	<2.4	3	3.4 (1.2)	<2.6	2.6 (0.31)	<2.7	11	3.1 (0.27)	<2.5	<2.5	ND–87.4	Mankyung R., South Korea	Kim et al. (2009)				
Trimethoprim	<10	<13	<11	<11	<8.9	<6.8	<9.05	<9.9	<9	<9.1	2.41–7.00	Tennessee River, TN	Conley et al. (2008)				
											<10–26	Han River, Korea	Choi et al. (2008)				

Loadings were estimated for data above the limit of quantitation using USGS stream flow data; for columns without loadings, flow data was unavailable  
 ND no data





**Fig. 5** PCA score plot (*left*) and loading plot (*right*) of 2013 data. Compounds were included in the analysis if their concentrations were above method reporting limit (MRL) for multiple sites; among those sites, the MRL value was used for data <MRL. *MS* Mississippi River

account for any degradation or photolysis loss of these TORCs during the flow so these are conservative estimates.

Perfluorinated compounds (PFCs) are widely used industrial surfactants and lubricants that have been measured in surface waters around the world (Prevedouros et al. 2006; Yang et al. 2011). PFCs are of concern because they bioaccumulate and have adverse effects on biota and humans (Nakata et al. 2006; Pan et al. 2010). We targeted perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and perfluorohexanoic acid (PFHxA), three of the more common PFCs detected in water. PFOA was detected above the reporting limit at 8 of the 10 sampling sites, while PFOS was detected above the reporting limit only in the Mississippi River near Memphis (11 ng L<sup>-1</sup>), and PFHxA was detected above the reporting limit only in the Illinois River near Grafton (5 ng L<sup>-1</sup>). The concentration of PFOA was highest in the Ohio River (13 ng L<sup>-1</sup>). Concentrations of PFOA and PFOS were slightly lower than surface waters in northeast Spain (Flores et al. 2013), while the concentration of PFHxA was comparable to the Pearl River in China (So et al. 2007). Overall, concentrations of PFOA and PFOS in the Mississippi River system were below the US EPA drinking water health advisory level of 70 ng L<sup>-1</sup> (US EPA 2016).

Tris(2-chloropropyl) phosphate (TCPP) is a common flame retardant that is a potential carcinogen (Malm 1998). Wastewater treatment plants are sources of TCPP in surface waters (Fries and Püttmann 2001; Kolpin et al. 2002). The highest concentration of TCPP in this study was in the Illinois River downstream of Grafton, Illinois (231 ng L<sup>-1</sup>) and in the Mississippi River downstream of Memphis, Tennessee (169 ng L<sup>-1</sup>). These concentrations are similar to the Han River in Korea and the Ruhr River in western Germany, both of which have multiple WWTP discharges that flow into them (Andresen et al. 2004). The concentrations of TCPP in the Mississippi River near Memphis (<1 km downstream of a WWTP) were also comparable to concentrations reported for several wastewater effluent discharge in the USA (Anumol et al. 2015).

Atrazine is a commonly used triazine herbicide that is used to prevent pre- and post-emergence of broadleaf weeds in crops. It was first registered in 1958 by Ciba-Geigy and has since been used extensively for weed control in the USA. It has also been identified as a possible carcinogen and endocrine disruptor (Donna et al. 1980; Ribaud and Bouzahr 1994; Eldridge et al. 1999; Rusiecki et al. 2004). The US Environmental Protection Agency (EPA) maximum contaminant level for atrazine is 3 µg L<sup>-1</sup> in drinking water and 1500 µg L<sup>-1</sup> for aquatic life criteria (US EPA 2003).

We detected atrazine at all sample sites, with the highest concentrations found in the Illinois and Yazoo rivers (673 and 521 ng L<sup>-1</sup>, respectively). These concentrations are similar to those found two decades earlier at similar locations, suggesting that atrazine use in these areas has not diminished (Pereira et al. 1995). Another herbicide, simazine, was also detected at all sampling locations but at lower concentrations ranging from 4 to 24 ng L<sup>-1</sup>. Like Pereira et al. (1995), we found that the Ohio River Basin was the source of >50% of the simazine in the Mississippi River.

*N,N*-diethyl-*m*-toluamide (DEET) is the most common active ingredient found in insect repellents and is also used as a resin solvent and a surface plasticizer. Its environmental release and ecological risk have been reported elsewhere (Frances 2007; Aronson et al. 2012). In this study, DEET ranged from 7 ng L<sup>-1</sup> near Natchez, Mississippi, to 540 ng L<sup>-1</sup> near Memphis, Tennessee. A previous study detected DEET in 26 of 30 samples (maximum 200 ng L<sup>-1</sup>) along the length of the Mississippi River (Pereira et al. 1995); increased use of DEET insecticides, particularly in developed areas, could certainly have raised the upper level since that prior study.

Caffeine has been used as an anthropogenic marker for wastewater contamination (Buerge et al. 2003). We detected it at all sample sites, with the highest concentrations near Memphis, Tennessee (202 ng L<sup>-1</sup>) and the lowest near Natchez, Mississippi (8 ng L<sup>-1</sup>). The analgesics ibuprofen and naproxen were highest near Memphis (47 and 37 ng L<sup>-1</sup>, respectively), as was the pharmaceutical gemfibrozil (16 ng L<sup>-1</sup>). The high concentrations at Memphis are likely due to the WWTP discharges upstream of the sampling location.

## Conclusions

Several major rivers in the MRB can be distinguished from each other based on trace metal and organic contaminant profiles, reflecting different soil characteristics and industry within the sub-basins, and the presence and proximity of WWTPs. Generally, the Illinois River had relatively high concentrations of heavy metals and the Ohio River had low concentrations of these elements. For those rivers with intense agriculture in their watersheds (Illinois, Missouri, Arkansas, and Yazoo), there were relatively high concentrations of Chl-*a* and atrazine. Eighteen anthropogenic TORCs were detected in

the water, including PPCPs and EDCs, with the highest concentrations occurring near urban centers. The concentrations of TORCs were generally similar or lower than that reported for rivers in Europe and Asia. Determining the temporal variability of these chemicals within the MRB and understanding their ecological impact requires further monitoring and toxicological studies. This study provides a baseline for trace metals and organics in the MRB and can serve as a guideline for monitoring and regulatory agencies in the region. Future monitoring programs could focus on heavy metals and anthropogenic TORCs, including ratios of these contaminants to bulk parameters. This is particularly important for the Lower Mississippi River which currently lacks routine and long-term water quality monitoring.

**Acknowledgements** This study was partly funded by an award from the US National Science Foundation (Division of Environmental Biology) (Award #1049911). The team acknowledges Agilent Technologies for their equipment and technical support for the analyses of trace organic contaminants at the University of Arizona. We would like to thank Jason Payne, Justin Millar, Bram Stone, and Alexa Lampkin for all their help with sampling.

## References

- Andresen, J., Grundmann, A., & Bester, K. (2004). Organophosphorus flame retardants and plasticisers in surface waters. *Science of the Total Environment*, 332, 155–166.
- Anumol, T., & Snyder, S. A. (2015). Rapid analysis of trace organic compounds in water by automated online solid-phase extraction coupled to liquid chromatography–tandem mass spectrometry. *Talanta*, 132, 77–86.
- Anumol, T., Wu, S., Marques dos Santos, M., Daniels, K. D., & Snyder, S. A. (2015). Rapid direct injection LC-MS/MS method for analysis of prioritized indicator compounds in wastewater effluent. *Environmental Science: Water Resource Technology*, 1, 632–643.
- Aronson, D., Weeks, J., Meylan, B., Guiney, P. D., & Howard, P. H. (2012). Environmental release, environmental concentrations, and ecological risk of *N,N*-diethyl-*m*-toluamide (DEET). *Integrated Environmental Assessment and Management*, 8, 135–166.
- Bartelt-Hunt, S. L., Snow, D. D., Damon, T., Shockley, J., & Hoagland, K. (2009). The occurrence of illicit and therapeutic pharmaceuticals in wastewater effluent and surface waters in Nebraska. *Environmental Pollution*, 157(3), 786–791.
- Bonansea, R. I., Amé, M. V., & Wunderlin, D. A. (2013). Determination of priority pesticides in water samples combining SPE and SPME coupled to GC-MS. A case study: Suquia River basin (Argentina). *Chemosphere*, 90(6), 1860–1869.
- Boyd, G. R., Palmeri, J. M., Zhang, S., & Grimm, D. A. (2004). Pharmaceuticals and personal care products (PPCPs) and

- endocrine disrupting chemicals (EDCs) in stormwater canals and Bayou St. John in New Orleans, Louisiana, USA. *Science of the Total Environment*, 333(1), 137–148.
- Brown, A. V., Brown, K. B., Jackson, D. C., & Pierson, W. K. (2005). Lower Mississippi River and its tributaries. In A. C. Benke & C. E. Cushing (Eds.), *Rivers of North America* (pp. 231–281). Amsterdam: Elsevier.
- Buck S, Denton G, Dodds W, Fisher J, Flemer D, Hart D, Parker A, Porter S, Rector S, & Steinman A (2000) Nutrient criteria technical guidance manual: rivers and streams. US Environmental Protection Agency, EPA-822-B00-002
- Buerge, I.J., Poiger, T., Müller, M.D., Buser, H.-R. (2003). Caffeine, an anthropogenic marker for wastewater contamination of surface waters. *Environmental Science & Technology*, 37(4), 691–700.
- Busetti, F., & Heitz, A. (2011). Determination of human and veterinary antibiotics in indirect potable reuse systems. *International Journal of Environmental Analytical Chemistry*, 91, 989–1012.
- Choi, K., Kim, Y., Park, J., Park, C. K., Kim, M., Kim, H. S., & Kim, P. (2008). Seasonal variations of several pharmaceutical residues in surface water and sewage treatment plants of Han River, Korea. *Science of the Total Environment*, 405(1), 120–128.
- Conley, J. M., Symes, S. J., Kindelberger, S. A., & Richards, S. M. (2008). Rapid liquid chromatography–tandem mass spectrometry method for the determination of a broad mixture of pharmaceuticals in surface water. *Journal of Chromatography A*, 1185(2), 206–215.
- Cwiertny, D. M., Snyder, S. A., Schlenk, D., & Kolodziej, E. P. (2014). Environmental designer drugs: when transformation may not eliminate risk. *Environmental Science & Technology*, 48, 11737–11745.
- Dalton, R. L., Boutin, D., & Pick, F. R. (2015). Determining in situ periphyton community responses to nutrient and atrazine gradients via pigment analysis. *Science of the Total Environment*, 515, 70–82.
- Daughton, C. G., & Ternes, T. A. (1999). Pharmaceuticals and personal care products in the environment: agents of subtle change? *Environmental Health Perspectives*, 107, 907.
- Desbrow, C., Routledge, E., Brighty, G., Sumpter, J., & Waldock, M. (1998). Identification of estrogenic chemicals in STW effluent. 1. Chemical fractionation and in vitro biological screening. *Environmental Science & Technology*, 32, 1549–1558.
- Donna, A., Betta, P., Gagliardi, F., Ghiazza, G., Gallareto, M., & Gabutto, V. (1980). Preliminary experimental contribution to the study of possible carcinogenic activity of two herbicides containing atrazine-simazine and trifluralin as active principles. *Pathologica*, 73, 707–721.
- Dsikowitzky, L., Heruwati, E., Ariyani, F., Irianto, H. E., & Schwarzbauer, J. (2014). Exceptionally high concentrations of the insect repellent N, N-diethyl-m-toluamide (DEET) in surface waters from Jakarta, Indonesia. *Environmental Chemistry Letters*, 12(3), 407–411.
- Edwards, D., & Daniel, T. (1993). Runoff quality impacts of swine manure applied to fescue plots. *Transactions of the ASAE*, 36, 81–86.
- Edwards, D., Daniel, T., Murdock, J., & Moore, P. (1996). Quality of runoff from four northwest Arkansas pasture fields treated with organic and inorganic fertilizer. *Transactions of the ASAE*, 39, 1689–1696.
- Eghball, B., & Power, J.F. (1999). Phosphorus-and nitrogen-based manure and compost applications corn production and soil phosphorus. *Soil Science Society of America Journal*, 63(4), 895–901.
- Eldridge, J. C., Wetzel, L. T., Stevens, J. T., & Simpkins, J. W. (1999). The mammary tumor response in triazine-treated female rats: a threshold-mediated interaction with strain and species-specific reproductive senescence. *Steroids*, 64, 672–678.
- Fernández, C., González-Doncel, M., Pro, J., Carbonell, G., & Tarazona, J. V. (2010). Occurrence of pharmaceutically active compounds in surface waters of the Henares-Jarama-Tajo River system (Madrid, Spain) and a potential risk characterization. *Science of the Total Environment*, 408(3), 543–551.
- Fischer, C., Schmidt, C., Bauer, A., Gaupp, R., & Heide, K. (2009). Mineralogical and geochemical alteration of low-grade metamorphic black slates due to oxidative weathering. *Chemie der Erde-Geochemistry*, 69, 127–142.
- Flores, C., Ventura, F., Martin-Alonso, J., & Caixach, J. (2013). Occurrence of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in NE Spanish surface waters and their removal in a drinking water treatment plant that combines conventional and advanced treatments in parallel lines. *Science of the Total Environment*, 461, 618–626.
- Frances, S. P. (2007). Efficacy and safety of repellents containing DEET. In M. Debboun, S. P. Frances, & D. Strickman (Eds.), *Insect repellents: principles, methods, and uses* (pp. 311–326). New York: CRC Press.
- Fries, E., & Püttmann, W. (2001). Occurrence of organophosphate esters in surface water and ground water in Germany. *Journal of Environmental Monitoring*, 3, 621–626.
- Galinaro, C. A., Pereira, F. M., & Vieira, E. M. (2015). Determination of parabens in surface water from Mogi Guaçu River (São Paulo, Brazil) using dispersive liquid-liquid microextraction based on low density solvent and LC-DAD. *Journal of the Brazilian Chemical Society*, 26(11), 2205–2213.
- Gannon, J. E., & Stemberger, R. S. (1978). Zooplankton (especially crustaceans and rotifers) as indicators of water quality. *Transactions of the American Microscopical Society*, 97, 16–35.
- Garbarino, J. R., Hayes, H. C., Roth, D. A., Antweiler, R. C., Brinton, T. I., & Taylor, H. E. (1996). Heavy metals in the Mississippi River. *US Geological Survey, Circular*, 53–72.
- Guo, Y. C., & Krasner, S. W. (2009). Occurrence of primidone, carbamazepine, caffeine, and precursors for N-nitrosodimethylamine in drinking water sources impacted by wastewater. *JAWRA Journal of the American Water Resources Association*, 45(1), 58–67.
- Halden, R. U., & Paull, D. H. (2004). Analysis of triclocarban in aquatic samples by liquid chromatography electrospray ionization mass spectrometry. *Environmental Science & Technology*, 38(18), 4849–4855.
- Harding, L.W., & Perry, E.S. (1997). Long-term increase of phytoplankton biomass in Chesapeake Bay, 1950-1994. *Marine Ecology Progress Series*, 150, 39–52.
- Henry, W. M., & Knapp, K. T. (1980). Compound forms of fossil fuel fly ash emissions. *Environmental Science & Technology*, 14, 450–456.

- Hernando, M. D., Mezcuca, M., Fernández-Alba, A., & Barceló, D. (2006). Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. *Talanta*, *69*, 334–342.
- Hope, B. K. (1997). An assessment of the global impact of anthropogenic vanadium. *Biogeochemistry*, *37*, 1–13.
- Huser, B., Köhler, S., Wilander, A., Johansson, K., & Fölster, J. (2011). Temporal and spatial trends for trace metals in streams and rivers across Sweden (1996–2009). *Biogeosciences*, *8*, 1813–1823.
- Jackson, C. R., Millar, J. J., Payne, J. T., & Ochs, C. A. (2014). Free-living and particle-associated bacterioplankton in large rivers of the Mississippi River basin demonstrate biogeographic patterns. *Applied and Environmental Microbiology*, *80*, 7186–7195.
- Kasprzyk-Hordern, B., Dinsdale, R. M., & Guwy, A. J. (2008). The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK. *Water Research*, *42*(13), 3498–3518.
- Kim, J. W., Jang, H. S., Kim, J. G., Ishibashi, H., Hirano, M., Nasu, K., & Arizono, K. (2009). Occurrence of pharmaceutical and personal care products (PPCPs) in surface water from Mankyung River, South Korea. *Journal of Health Science*, *55*(2), 249–258.
- Koczura, R., Mokracka, J., Jabłońska, L., Gozdecka, E., Kubek, M., & Kaznowski, A. (2012). Antimicrobial resistance of integron-harboring *Escherichia coli* isolates from clinical samples, wastewater treatment plant and river water. *Science of the Total Environment*, *414*, 680–685.
- Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B., & Buxton, H. T. (2002). Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance. *Environmental Science & Technology*, *36*, 1202–1211.
- Levins, I., & Gosk, E. (2008). Trace elements in groundwater as indicators of anthropogenic impact. *Environmental Geology*, *55*, 285–290.
- Lindsay, W. (1984). Soil and plant relationships associated with iron deficiency with emphasis on nutrient interactions. *Journal of Plant Nutrition*, *7*, 489–500.
- Liu, S., Ying, G. G., Zhao, J. L., Chen, F., Yuxton, B., Zhou, L. J., & Lai, H. J. (2011). Trace analysis of 28 steroids in surface water, wastewater and sludge samples by rapid resolution liquid chromatography–electrospray ionization tandem mass spectrometry. *Journal of Chromatography A*, *1218*(10), 1367–1378.
- Loomis, W., & Durst, R. (1992). Chemistry and biology of boron. *BioFactors*, *3*, 229–239.
- Malm, O. (1998). Gold mining as a source of mercury exposure in the Brazilian Amazon. *Environmental Research*, *77*, 73–78.
- Mast RF, Ruch RR, Meents WF (1973) Vanadium in Devonian, Silurian, and Ordovician crude oils of Illinois. Illinois State Geological Survey, Circular 483
- Michael, I., Rizzo, L., McArdell, C., Manaia, C., Merlin, C., Schwartz, T., Dagot, C., & Fatta-Kassinos, D. (2013). Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: a review. *Water Research*, *47*, 957–995.
- Millar, J. J., Payne, J. T., Ochs, C. A., & Jackson, C. R. (2015). Particle-associated and cell-free extracellular enzyme activity in relation to nutrient status of large tributaries of the Lower Mississippi River. *Biogeochemistry*, *124*, 255–271.
- Mozaffari, M., & Sims, J. (1994). Phosphorus availability and sorption in an Atlantic Coastal Plain watershed dominated by animal-based agriculture. *Soil Science*, *157*, 97–107.
- Nakata, H., Kannan, K., Nasu, T., Cho, H. S., Sinclair, E., & Takemura, A. (2006). Perfluorinated contaminants in sediments and aquatic organisms collected from shallow water and tidal flat areas of the Ariake Sea, Japan: environmental fate of perfluorooctane sulfonate in aquatic ecosystems. *Environmental Science & Technology*, *40*, 4916–4921.
- Office of Air Quality, U.S. Environmental Protection Agency (2008) National Emission Inventory (NEI) data
- Pan, Y. Y., Shi, Y. L., Wang, Y. W., Cai, Y. Q., & Jiang, G. B. (2010). Investigation of perfluorinated compounds (PFCs) in mollusks from coastal waters in the Bohai Sea of China. *Journal of Environmental Monitoring*, *12*, 508–513.
- Papadopoulou-Mourkidou, E. (2002). *Quality of surface waters of Macedonia-Thrace, Northern Greece, quality control program, final report*. Thessaloniki: Ministry of Agriculture.
- Pereira, W. E., Moody, J. A., Hostettler, F. D., Rostad, C. E., & Leiker, T. J. (1995). Concentrations and mass transport of pesticides and organic contaminants in the Mississippi River and some of its tributaries, 1987–89 and 1991–92. *US Geological Survey, Open-File Report*, 94-376, 169.
- Prevedouros, K., Cousins, I. T., Buck, R. C., & Korzeniowski, S. H. (2006). Sources, fate and transport of perfluorocarboxylates. *Environmental Science & Technology*, *40*, 32–44.
- Purdom, C., Hardiman, P., Bye, V., Eno, N., Tyler, C., & Sumpter, J. (1994). Estrogenic effects of effluents from sewage treatment works. *Chemistry and Ecology*, *8*, 275–285.
- Rabalais NN, Turner RE, & Wiseman Jr WJ (2002) Gulf of Mexico hypoxia, AKA “The dead zone”. Annual Review of ecology and Systeematics, 235–263
- Rabotyagov, S., Kling, C., Gassman, P., Rabalais, N., & Turner, R. (2014). The economics of dead zones: causes, impacts, policy challenges, and a model of the Gulf of Mexico hypoxic zone. *Review of Environmental Economics and Policy*, *8*, 58–79.
- Ribaudou, M., & Bouzaher, A. (1994). *Atrazine: environmental characteristics and economics of management*. Economic Research Service: US Department of Agriculture.
- Richardson, B. J., Lam, P. K., & Martin, M. (2005). Emerging chemicals of concern: pharmaceuticals and personal care products (PPCPs) in Asia, with particular reference to Southern China. *Marine Pollution Bulletin*, *50*, 913–920.
- Royer, T.V., David, M.B., Gentry, L.E., Mitchell, C.A., Starks, K.M., Heatherly, T., et al. (2008). Assessment of chlorophyll-a as a criterion for establishing nutrient standards in the streams and rivers of Illinois. *Journal of Environmental Quality*, *37*(2), 437–447.
- Rusiecki, J. A., De Roos, A., Lee, W. J., Dosemeci, M., Lubin, J. H., Hoppin, J. A., Blair, A., & Alavanja, M. C. (2004). Cancer incidence among pesticide applicators exposed to atrazine in the Agricultural Health Study. *Journal of the National Cancer Institute*, *96*, 1375–1382.
- Shiller, A. M. (1997). Dissolved trace elements in the Mississippi River: seasonal, interannual, and decadal variability. *Geochimica et Cosmochimica Acta*, *61*, 4321–4330.



- Shiller, A. M., & Boyle, E. A. (1985). Dissolved zinc in rivers. *Nature*, *317*, 49–52.
- Shiller, A. M., & Boyle, E. A. (1987). Variability of dissolved trace metals in the Mississippi River. *Geochimica et Cosmochimica Acta*, *51*, 3273–3277.
- Smith, D. B., Cannon, W. F., Woodruff, L. G., Solano Federico, Ellefsen, K. J. (2014). Geochemical and mineralogical maps for soils of the conterminous United States: U.S. Geological Survey Open-File Report 2014-1082. doi:10.3133/ofr20141082.
- Snyder, S. A. (2014). Emerging chemical contaminants: looking for better harmony. *Journal American Water Work Association*, *106*, 38–52.
- Snyder, S. A., Westerhoff, P., Yoon, Y., & Sedlak, D. L. (2003). Pharmaceuticals, personal care products, and endocrine disruptors in water: implications for the water industry. *Environmental Engineering Science*, *20*, 449–469.
- So, M. K., Miyake, Y., Yeung, W. Y., Ho, Y. M., Taniyasu, S., Rostkowski, P., & Yamashita, N. (2007). Perfluorinated compounds in the Pearl river and Yangtze river of China. *Chemosphere*, *68*(11), 2085–2095.
- Standley, L. J., Rudel, R. A., Swartz, C. H., Attfield, K. R., Christian, J., Erickson, M., & Brody, J. G. (2008). Wastewater-contaminated groundwater as a source of endogenous hormones and pharmaceuticals to surface water ecosystems. *Environmental Toxicology and Chemistry*, *27*(12), 2457–2468.
- Temes, T. A., Joss, A., & Siegrist, H. (2004). Peer reviewed: scrutinizing pharmaceuticals and personal care products in wastewater treatment. *Environmental Science & Technology*, *38*, 392A–399A.
- Tölgyesi, Á., Verebey, Z., Sharma, V. K., Kovacsics, L., & Fekete, J. (2010). Simultaneous determination of corticosteroids, androgens, and progesterone in river water by liquid chromatography–tandem mass spectrometry. *Chemosphere*, *78*(8), 972–979.
- Turner, R. E., & Rabalais, N. N. (2003). Linking landscape and water quality in the Mississippi River basin for 200 years. *Bioscience*, *53*, 563–572.
- US EPA. (2003). *Ambient aquatic life water quality criteria for atrazine*. Washington DC: U.S. Environmental Protection Agency, Office of Water EPA-822-R-03-023.
- US EPA. (2016). *PFOA & PFOS drinking water health advisories fact sheet*. Washington DC: U.S. Environmental Protection Agency, Office of Water EPA-800-F-16-003.
- Valcárcel, Y., Alonso, S. G., Rodríguez-Gil, J. L., Maroto, R. R., Gil, A., & Catalá, M. (2011). Analysis of the presence of cardiovascular and analgesic/anti-inflammatory/antipyretic pharmaceuticals in river-and drinking-water of the Madrid region in Spain. *Chemosphere*, *82*(7), 1062–1071.
- Wetzel, R., & Likens, G. (2000). *Limnological analysis* (3rd edn). Philadelphia: WB Saunders Co., p. 357.
- Wilhelm, C., & Wild, A. (1984). The variability of the photosynthetic unit in chlorella I. The effect of vanadium on photosynthesis, productivity, P-700 and cytochrome f in undiluted and homocontinuous cultures of chlorella. *Journal of Plant Physiology*, *115*, 115–124.
- Wilson, B. A., Smith, V. H., deNoyelles, F., & Larive, C. K. (2003). Effects of three pharmaceutical and personal care products on natural freshwater algal assemblages. *Environmental Science & Technology*, *37*, 1713–1719.
- Yang, L., Zhu, L., & Liu, Z. (2011). Occurrence and partition of perfluorinated compounds in water and sediment from Liao River and Taihu Lake, China. *Chemosphere*, *83*, 806–814.
- Yoon, Y., Ryu, J., Oh, J., Choi, B., & Snyder, S. A. (2010). Occurrence of endocrine disrupting compounds, pharmaceuticals, and personal care products in the Han River (Seoul, South Korea). *Science of the Total Environment*, *408*(3), 636–643.