



Multiple sources of boron in urban surface waters and groundwaters

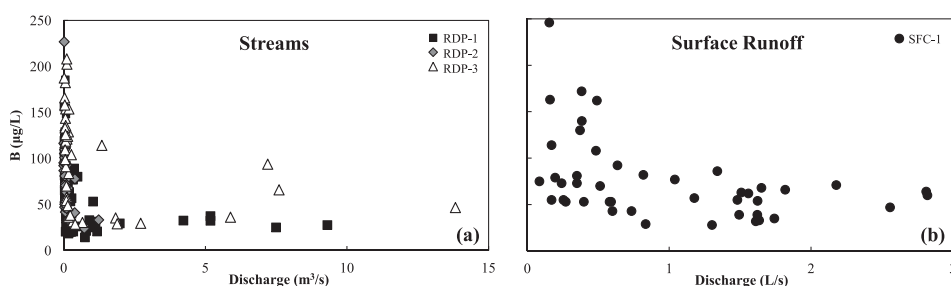
Elizabeth A. Hasenmueller*, Robert E. Criss

Department of Earth and Planetary Sciences, Washington University, Campus Box 1169, 1 Brookings Drive, St. Louis, MO 63130-4899, USA

HIGHLIGHTS

- ▶ Boron sources and loads differ between urban and rural watersheds.
- ▶ Wastewaters are not the major boron source in small St. Louis, MO watersheds.
- ▶ Municipal drinking water used for lawn irrigation can be high in boron.
- ▶ Lawn irrigation practices can considerably alter urban water chemistry.

GRAPHICAL ABSTRACT



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ABSTRACT

Previous studies attribute abnormal boron (B) levels in streams and groundwaters to wastewater and fertilizer inputs. This study shows that municipal drinking water used for lawn irrigation contributes substantial non-point loads of B and other chemicals (S-species, Li, and Cu) to surface waters and shallow groundwaters in the St. Louis, Missouri, area. Background levels and potential B sources were characterized by analysis of lawn and street runoff, streams, rivers, springs, local rainfall, wastewater influent and effluent, and fertilizers. Urban surface waters and groundwaters are highly enriched in B (to 250 µg/L) compared to background levels found in rain and pristine, carbonate-hosted streams and springs (<25 µg/L), but have similar concentrations (150 to 259 µg/L) compared to municipal drinking waters derived from the Missouri River. Other data including B/SO₄²⁻-S and B/Li ratios confirm major contributions from this source. Moreover, sequential samples of runoff collected during storms show that B concentrations decrease with increased discharge, proving that elevated B levels are not primarily derived from combined sewer overflows (CSOs) during flooding. Instead, non-point source B exhibits complex behavior depending on land use. In urban settings B is rapidly mobilized from lawns during “first flush” events, likely representing surficial salt residues from drinking water used to irrigate lawns, and is also associated with the baseflow fraction, likely derived from the shallow groundwater reservoir that over time accumulates B from drinking water that percolates into the subsurface. The opposite occurs in small rural watersheds, where B is leached from soils by recent rainfall and covaries with the event water fraction.

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1. Introduction

Sources of anthropogenic contamination in natural waters are often difficult to decipher because many sources may contribute to loads of any given element. B makes an ideal tracer of contamination

sources because it behaves conservatively, is highly soluble, exhibits isotopic variability, and is found in low concentrations in most natural waters (Barth, 1998). B concentrations in surface waters vary widely, but in most cases the concentration of B in a particular aquatic environment is dominated by anthropogenic contributions (Neal et al., 1998; Wyness et al., 2003). Thus, several workers have used the concentrations and/or isotope ratios of B to trace municipal, agricultural, industrial, and landfill leachate contamination (Davidson and Bassett,

* Corresponding author. Tel.: +1 314 935 7475; fax: +1 314 935 7361.

E-mail address: eahasnm@wustl.edu (E.A. Hasenmueller).

1993; Vengosh et al., 1994; Bassett et al., 1995; Leenhouts et al., 1998; Neal et al., 2010).

Natural loads of B in surface waters and groundwaters are predominantly derived from weathering of B-bearing minerals in host rock and soil, with the highest observed concentrations resulting from leaching of B-bearing salt deposits (Christ and Harder, 1978). Specifically, B-bearing Neogene evaporite deposits can host groundwaters with B concentrations in excess of 100 mg/L (Waggott, 1969; Harben and Bates, 1984). In coastal areas, rain containing sea salt from ocean spray provides another natural B source, but such inputs decline with distance from the coast (Jahiruddin et al., 1998). The United States has few B-bearing lithologies, so most natural, unpolluted waters have low average B concentrations of 10–20 µg/L (Drever, 1997; Langmuir, 1997; Lemarchand et al., 2002).

Elevated B levels in surface waters most commonly occur in industrial and urban areas. Among many possible sources, wastewaters enriched in B from bleaching agents and fertilizers that contain B as a micronutrient are considered to be the largest contributor of anthropogenic B to riverine and groundwater environments (Waggott, 1969; Barth, 1998; Chetelat and Gaillardet, 2005; Neal et al., 2010). Other, typically minor, sources of anthropogenic B include herbicides and insecticides, glass manufacturing wastes, antifreeze, landfill and coal mine leachates, fly ash, petroleum products, slag, sewage sludge, manure, and compost (Waggott, 1969; Davidson and Bassett, 1993; Hebblethwaite and Emberson, 1993; Vengosh et al., 1994; Bassett et al., 1995; Barth, 1998; Hogan and Blum, 2003; Bayless et al., 2004; Chetelat and Gaillardet, 2005).

Domestic and some industrial wastewater effluents are extremely enriched in B, with concentrations varying from several hundred µg/L to several mg/L (Barth, 2000; Fox et al., 2000). By far the most common reason for this enrichment is the presence of sodium perborate that used as a bleaching agent in detergents and cleaning products that are ubiquitously discharged into domestic wastewater, which are then received by sewage treatment plants that remove little or no B during conventional processing (Waggott, 1969; Stueber and Criss, 2005; this study). Previous authors have asserted that almost the entire anthropogenic B load is released into urban environments through treated or untreated wastewater (e.g., Vengosh et al., 1994; Bassett et al., 1995; Barth, 1998; Chetelat and Gaillardet, 2005; Neal et al., 2010). For example, Vengosh et al. (1994) used B isotopes to determine that the Coastal Plain aquifer of Israel was contaminated with treated sewage effluent, and Chetelat and Gaillardet (2005) concluded that the high B concentrations of the Seine River near Paris were a result of wastewater discharge. Nevertheless, Neal et al. (2010) found that B concentrations have substantially declined in European wastewater effluent discharges due to lower B levels in detergents and thus have decreased in river systems. However, reductions in the B flux are smaller because of indirect inputs that are not regionally diffuse.

Fertilizers can also be a major source of anthropogenic B due to their widespread, heavy application. B is an essential micronutrient for plants and consequently is included in many fertilizers at levels ranging from 0.01 to 0.06 wt.% (Table 1), most commonly in the form of borax (Bohn et al., 2001; Brady and Weil, 2008). However, available studies show that fertilizers typically contribute only small amounts of B to surface waters. For example, Trauth and Xanthopoulos (1997) and Stueber and Criss (2005) respectively measured average B concentrations of 25–60 µg/L and 52 µg/L in agricultural runoff, and Chetelat and Gaillardet (2005) observed agricultural inputs of less than 30 µg/L in the headwaters of the Seine River. In contrast, Wyness et al. (2003) found that rivers draining high intensity agricultural areas of southeastern England can have average B concentrations of up to 387 µg/L, which they argued was due to the relatively low rainfall and high evapotranspiration in this region, fostering a low dilution potential. Surface waters had an average B concentration of 54 µg/L in proximal areas of low intensity agriculture (Wyness et al., 2003).

2. Regional hydrogeologic setting

East-central Missouri is a temperate, humid region of abundant rainfall, rolling topography, large rivers, and diverse land use practices that include agricultural regions, large forested tracts, and urban and suburban areas (Fig. 1). The area is predominantly underlain by Paleozoic carbonate rocks, so karst features are common though not ubiquitous. Hydrologic investigations benefit from long term monitoring at several National Oceanic and Atmospheric Administration (NOAA) weather stations and from an extremely dense network of US Geological Survey (USGS) gaging stations on large and small watersheds.

The average rainfall in the area is 97 cm/year (NOAA, 2012) and the evapotranspiration rate is 71 cm/year (Vandike, 1995). Over the long term, average monthly rainfall is rather steady in this region (8.4 ± 2.8 cm/month; NOAA, 2012), but regional runoff is more variable, being about 4.5 times higher during March, April, and May than it is during August, September, and October (USGS, 2012a). Despite the wet climate of this area, lawn irrigation accounts for up to 60% of water use in St. Louis households, averaging 443 L per home per day (City of St. Louis Water Division, 2012). This irrigation rate is similar to that in dry areas such as Utah, where Aurasteh et al. (1984) found that homeowners used 61% of their total water supply for irrigation. Much of this water is wasted because application rates greatly exceed seasonal evapotranspiration (e.g., Haley et al., 2007). The municipal drinking water in the St. Louis area used for irrigation is drawn from the Missouri, Mississippi, and Meramec Rivers, but most has the chemical and isotopic character of the Missouri River, which is observed in treated wastewaters for the area (Table 2). The largest drinking water treatment plants are on the Missouri and Mississippi Rivers, and the intake for the Mississippi plant draws Missouri-type water due to slow river mixing below the confluence point (Fig. 1).

3. Study sites

A monitoring network for urban surface waters in the St. Louis region was implemented and operated from 2009 to 2012. It was designed to determine and quantify sources of anthropogenic pollutants from point and non-point sources as well as to define temporal variations of water quality parameters. B measurements were included because contributions to streams from combined sewer overflows (CSOs), which constitute the combination of stormwater runoff and wastewater that overflows from the sewer system directly into surface waters during heavy rains, have become a major concern in the St. Louis area. Six sites were continuously monitored, and additional samples of surface waters, groundwaters, and potential B end-member sources were collected throughout east-central Missouri.

The continuously monitored sites were located in the River des Peres watershed, a large (295 km²), highly degraded watershed draining the City of St. Louis and the eastern part of St. Louis County. The River des Peres extends approximately 30 km through the metropolitan area before discharging into the Mississippi River, and its basin has a high average population density (1,990 people/km²; US Census, 2010) and high urban land coverage (>90%; USGS, 2012b; Fig. 1). The geology of the basin consists predominantly of Mississippian limestones in the southwest and Pennsylvanian shales in the northeast, overlain by Quaternary loess soils (Lutzen and Rockaway, 1989; Harrison, 1997); all of these lithologies are B-poor. Three sites were selected along the Upper River des Peres to capture the variations in B concentrations in flowing streams, and three small catchments in the River des Peres basin were monitored to define the character of suburban runoff (Fig. 1, inset).

Of the River des Peres stream sites, the most upstream site (RDP-1) monitored a cement-walled channel that drains an area of 2.8 km², so rapid changes in discharge occur during storms. There is

Table 1

Average values for various water quality parameters for surface waters, groundwaters, and potential B end-members.

Sample ^a	Description	Sample Number	SpC (µS/cm)	pH	B (µg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	Cl (mg/L)	K (mg/L)	Si (mg/L)	NO ₃ ⁻ -N (mg/L)	PO ₄ ³⁻ -P (mg/L)	SO ₄ ²⁻ -S (mg/L)	Al (µg/L)	Cu (µg/L)	Fe (µg/L)	Li (µg/L)	Zn (µg/L)
Rainwater	Precipitation	10	54	4.78	24	6.7	0.5	0.9	0.6	0.4	0.2	0.0	0.01	1.9	37	13.9	5.3	0.2	28.5
SFC-Coal	Surface runoff	2	523	7.82	21	41.7	13.8	8.0	12.0	4.5	5.7	-	0.50	2.5	420	8.0	49.2	0.7	83.9
SFC-1	Surface runoff	126	406	8.30	89	37.3	7.6	26.0	55.1	6.5	3.5	0.5	0.23	10.9	87	2.8	19.3	3.1	16.6
SFC-2	Surface runoff	25	178	7.55	58	20.8	4.3	5.5	5.6	12.8	3.1	0.1	0.54	2.8	200	6.9	23.1	2.2	41.0
SFC-3	Surface runoff	1	110	7.38	37	12.9	2.1	12.0	2.8	3.9	2.8	0.2	0.26	2.4	228	3.3	20.3	1.8	10.2
SFC-3, road salt-rich melt water	Surface runoff	1	36,000	7.38	57	71.3	15.7	13,500	13,900	152.5	1.8	0.0	0.46	17.6	116	351.8	54	68.5	36.4
Street runoff	Surface runoff	1	-	-	88	31.9	9.0	32.6	32.6	2.8	6.1	-	0.07	26.8	226	22.2	42.4	35.2	206.0
Monroe Co., IL agricultural runoff ^b	Surface runoff	43	-	-	52	26.1	6.3	2.7	17.4	24.0	-	11.5	3.70	1.1	-	6.3	-	-	9.9
RDP-1	Surface water	40	1,570	8.21	88	93.4	25.3	217.2	287.5	6.4	5.1	1.1	0.07	31.1	22	5.4	29.0	11.7	28.0
RDP-2	Surface water	34	1,484	8.08	92	91.9	24.6	202.6	298.5	9.1	4.8	1.2	0.09	29.9	13	5.4	31.4	11.8	20.1
RDP-3	Surface water	29	1,383	8.21	129	73.2	19.6	231.4	273.1	6.5	4.0	0.7	0.03	28.4	22	5.4	24.8	13.2	28.9
Missouri River	Surface water	1	715	8.23	189	58.2	19.9	65.2	11.0	8.9	3.8	0.2	0.34	53.5	20	4.4	31.4	116.4	37.7
Mississippi River	Surface water	1	523	8.42	220	50.0	20.4	23.2	28.0	3.6	2.0	2.9	0.26	12.7	25	2.9	21.0	9.5	12.4
Missouri River at Howard Bend ^c	Surface water	28	545	8.00	110	52.1	16.3	35.8	18.0	5.9	7.2	1.5	0.09	34.8	0.08	-	0.06	-	-
Mississippi River at Chain of Rocks ^{c,d}	Surface water	28	541	8.06	100	54.4	16.6	36.8	20.5	5.9	7.1	1.6	0.09	36.2	0.02	-	0.03	-	-
Streams	Surface water	9	483	7.90	43	63.0	11.7	34.2	24.4	3.5	4.1	1.0	0.11	9.7	26	2.4	19.7	1.9	12.4
Lake	Surface water	1	104	9.66	28	9.6	2.0	0.4	0.5	2.1	0.8	0.3	0.05	1.3	73	1.8	37.0	BDL ^e	2.7
Golf course pond	Surface water	1	546	9.10	133	24.4	16.7	57.4	12.0	9.8	3.3	1.5	1.65	44.6	5	2.3	2.3	42.8	14.6
Springs	Groundwater	59	748	7.49	42	93.7	17.6	44.6	53.6	2.5	6.8	2.0	0.08	13.0	40	1.3	32.5	6.8	16.8
Tap water	Drinking water	15	558	9.74	259	20.1	16.4	65.6	16.0	8.1	3.1	0.5	0.04	58.5	0.39	96.7	10.5	104.9	26.4
Howard Bend ^c	Drinking water	28	417	9.51	150	24.0	13.7	34.4	23.0	5.7	6.2	1.5	0.01	38.1	0.01	-	0.004	-	-
Chain of Rocks ^c	Drinking water	28	412	9.18	100	22.8	15.1	34.4	23.7	5.8	6.0	1.7	0.01	37.3	0.01	-	0.003	-	-
DCSD effluent	Wastewater	3	797	8.15	146	54.3	17.0	73.5	72.0	11.7	5.2	11.4	1.06	24.6	12	3.1	19.6	8.9	44.1
MSD influent	Wastewater	7	932	-	247	47.5	22.2	125.3	39.4	19.6	4.8	1.0	1.70	58.0	673	15.3	343.0	70.1	734.3
MSD effluent	Wastewater	7	810	-	285	40.3	20.4	113.1	87.9	18.4	5.0	12.4	1.26	48.1	66	10.1	81.8	73.3	367.0
Monroe Co., IL effluent ^b	Wastewater	7	-	-	430	66.6	21.7	94.0	129.0	15.8	-	9.9	2.48	25.0	-	8.3	-	-	73.0
Mulching leachate	Organic leachate	3	2,036	7.02	375	176.2	47.6	31.6	38.8	137.4	19.8	1.2	14.33	12.1	119	15.8	266.4	53.7	181.8
Wood ash (in wt.%) ^f	Wood ash	1	-	-	0.058	32.3	0.7	0.3	4.8	3.6	0.0	-	0.33	0.3	0.08	0.006	0.02	0.01	0.035
Scott's Turf Builder with Halts (in wt.%) ^f	Fertilizer	1	-	-	0.06 ^g	BDL ^e	0.025	BDL ^e	0.333	1.8	0.002	0.533 ^h	0.01	9.69	BDL ^e	BDL ^e	0.0004	0.0002	0.0005
Miracle Grow, Miracid (in wt.%) ^f	Fertilizer	1	-	-	0.06	BDL ^e	0.004	BDL ^e	0.083	4.7	0.001	0.033	2.31	0.20	BDL ^e	0.033	0.0124	0.0002	0.0390
Agricultural products (in wt.%) ^{f,i}	Fertilizer	9	-	-	0.01	1.56	0.569	-	-	7.0 ^j	-	4.623 ^k	7.63 ^l	1.80	-	0.075	0.3333	-	0.3553
Detection limit					0.002	0.06	0.02	0.2	0.1	0.03	0.1	0.02	0.06	0.04	0.02	0.09	0.09	0.09	0.09

^a All samples collected in Missouri unless otherwise noted.^b Stueber and Criss (2005).^c Criss et al. (2001).^d Samples have the chemical signature of the Missouri River due to slow river mixing.^e Below detection limit.^f All wood ash and fertilizer values in weight percent.^g Label guarantee is 0.02wt%.^h Urea interference with NO₃⁻-N analysis.ⁱ Averages of nine fertilizers analyzed by the Oregon Department of Agriculture (2010).^j Soluble potash (K₂O).^k Total N.^l Phosphate (P₂O₅).

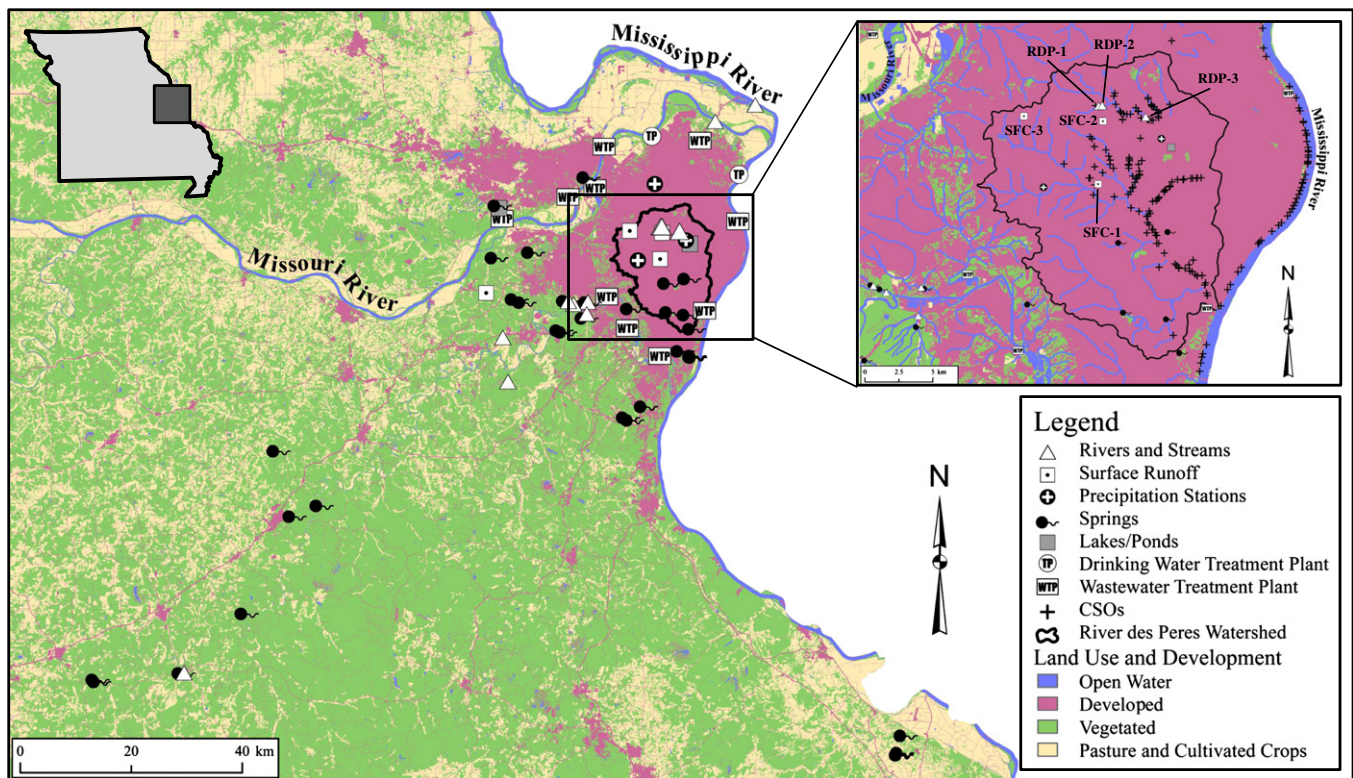


Fig. 1. Sampling sites on a land use map of east-central Missouri. The inset shows an enlarged view of the delineated watershed boundary for the River des Peres. Also shown are the surface runoff (SFC-1, SFC-2, and SFC-3) and stream (RDP-1, RDP-2, and RDP-3) sampling sites within the River des Peres watershed. Land use/land area data are from the 2006 National Land Cover Database (USGS, 2012b).

one CSO upstream of the site (Metropolitan St. Louis Sewer District; MSD, 2012). The next site (RDP-2) was located only 320 m downstream of RDP-1 and occupied a more natural, but erosionally entrenched, channel that allows the stream to communicate with local groundwater; the banks are partly vegetated and no CSOs are located between RDP-1 and RDP-2. Runoff between these sites includes intermittent contributions from a golf course and a mulching operation. The mulching operation produces small volumes of leachate that discharge directly into the stream channel; the discharge ranges from zero to 30 L/s following large storm events. The final site (RDP-3), located 4.4 km downstream of RDP-2, has a drainage area of 23.2 km². There are 11 CSOs upstream of this site (MSD, 2012); and most of the upstream reaches are channelized, but the stream bed at this location is unlined.

The three small (<2 ha), suburban catchments contribute lawn and street runoff to the western River des Peres watershed. The sites, SFC-1, SFC-2, and SFC-3, were selected to characterize surface runoff from a grassy field and parking lot at a church, residential lawns, and streets, respectively. Samples were collected at storm sewer inlets; detailed site descriptions are available in Hasenmueller (2011).

In addition to these six intensively monitored sites in the River des Peres watershed, a total of 49 other features in east-central Missouri were sampled on multiple occasions to document variations in B concentrations and include streams, rivers, springs, and lakes (Fig. 1). These samples represent a broad range of catchment size and land development and were collected under a range of hydrologic conditions including both low and high flow. Springs sampled for this study have mean discharges ranging from about 0.0001 to 4.1 m³/s, which represent effective catchment areas that vary from <10 to 430 km² (Vineyard and Feder, 1982). In addition to the Mississippi and Missouri Rivers, smaller rural and suburban streams were also sampled; they have catchment areas of 10 to 45 km² and corresponding mean discharges of about 0.07 to 0.4 m³/s (USGS,

2012a). Numerous additional samples were collected to characterize potential B end-member sources, including meteoric precipitation, snow melt runoff contaminated by road salt, wood ash and organic-rich leachates, wastewater influent and effluent, fertilizers and agricultural runoff, and treated drinking water.

4. Materials and methods

Biweekly water samples were collected from the Upper River des Peres (i.e., RDP-1, RDP-2, and RDP-3) and analyzed for a suite of parameters; numerous additional samples were collected during storm perturbations by automatic sampling devices for these sites and the surface runoff sites (i.e., SFC-1, SFC-2, and SFC-3). Water chemistry analyses consisted of (1) field measurements of temperature, specific conductivity (SpC), dissolved oxygen (DO), pH, and turbidity with handheld meters, (2) in situ measurements of water quality and stage, and (3) laboratory analyses of major and trace elements, major ions, nutrients, total suspended solids (TSS), and H and O isotopes.

Automatic sampling devices (i.e., ISCO models 6712 and 3700) were used to collect physical samples for the six sites in the River des Peres watershed. In addition to the ISCO autosampler units, in situ continuous monitoring devices were deployed at these sites. At the stream sites (i.e., RDP-1, RDP-2, and RDP-3), YSI 6600V2 sondes continuously measured (5-minute data intervals) a suite of water quality parameters, including temperature, SpC, DO, pH, turbidity, Cl, NH₃-N, NH₄⁺-N, and NO₃⁻-N. Discharge for RDP-1 was determined using an ultrasonic stage sensor; discharge data for RDP-3 was provided by USGS gaging station 07010097 located only 0.75 km upstream. At the surface runoff sites (i.e., SFC-1, SFC-2, and SFC-3), YSI Level Scouts continuously measured (1- to 2-minute data intervals) water level and temperature of storm runoff. Discharge at these locations was determined from monitored stages using well-known empirical relationships (e.g., Fetter, 2001).

Table 2
Chemical analyses for individual wastewater influent and effluent samples.

Site ^a	DC1-E	DC2-E	DC2-E	CWC-I	CWC-E	MOR-I	MOR-E	GGC-I	GGC-E	FEN-I	FEN-E	LMER-I	LMER-E	LEM-I	LEM-E	BP-I	BP-E	DL ^b
SpC (µS/cm)	795	773	822	883	818	968	873	956	781	746	661	813	675	831	762	1,328	1,099	–
Turbidity (NTU)	9	4	4	114	6	151	25	247	5	141	2	142	9	377	9	433	13	0.01
TSS (mg/L)	35	–	10	120	0	182	26	272	32	148	2	170	12	384	18	208	24	0.01
δ ² H (‰)	–62	–50	–60	–81	–82	–78	–79	–82	–80	–40	–40	–40	–40	–74	–74	–81	–85	–
δ ¹⁸ O (‰)	–9.3	–7.2	–8.8	–10.3	–10.6	–10.6	–11.0	–10.4	–10.4	–5.7	–5.7	–5.8	–5.7	–9.5	–9.6	–10.8	–12.7	–
Major (mg/L)																		
Ca	65.3	46.1	51.6	45.3	34.9	45.0	41.7	49.4	43.0	32.6	35.5	52.2	44.0	55.6	42.9	52.3	40.4	0.06
Mg	18.2	16.0	16.9	21.9	20.6	21.6	21.6	21.0	20.1	20.4	20.8	18.6	17.8	21.1	19.9	30.4	22.1	0.02
HCO ₃ ^{–c}	269	217	255	299	200	271	273	370	240	331	210	308	168	285	232	448	216	–
Na	50.5	76.9	93.0	108.0	113.8	114.1	121.5	147.1	123.7	68.6	74.4	69.6	66.4	102.3	99.4	267.2	192.5	0.2
Cl	54	68	94	30	74	44	77	27	84	10	95	10	89	50	51	105	145	0.1
K	6.1	14.4	14.6	19.2	20.0	20.2	22.6	25.0	22.8	15.9	15.8	13.2	13.0	17.3	15.4	26.7	19.1	0.1
Si	4.3	5.9	5.3	5.5	5.3	5.6	5.7	5.3	4.9	3.3	3.3	3.6	3.5	5.0	4.8	5.0	7.7	0.03
NH ₄ ⁺ –N	0.44	0.27	0.59	34.00	10.40	33.20	8.30	37.10	0.40	20.10	1.23	21.60	0.71	16.90	4.37	4.65	0.99	0.02
NO ₃ [–] –N	3.2	16.8	14.2	3.0	3.1	0.0	11.7	0.2	20.6	0.8	19.7	0.8	9.9	1.6	3.8	0.8	18	0.1
PO ₄ ^{3–} –P	0.26	1.73	1.26	1.50	0.96	1.76	1.40	1.44	0.96	1.99	1.88	1.77	1.25	1.82	1.38	1.86	1.19	0.02
SO ₄ ^{2–} –S	19.0	29.7	25.1	56.3	56.6	61.1	49.3	70.7	55.5	15.9	16.0	34.8	25.9	53.2	52.2	114.0	81.2	0.06
Minor (µg/L)																		
Al	25.1	6.9	4.8	426.3	48.0	327.8	98.7	822.3	50.4	348.7	34.0	939.4	67.1	1,722.6	56.7	124.0	103.4	0.04
B	51	240	147	228	347	274	355	340	341	209	231	191	216	249	260	238	246	0.002
Cd	0.24	0.04	0.26	0.85	0.16	0.44	0.13	0.69	0.35	0.18	0.13	0.31	0.14	0.97	0.09	0.88	1.55	0.006
Co	0.31	0.24	0.60	0.86	0.74	1.11	0.77	0.97	0.65	0.70	0.60	0.73	0.49	3.57	1.31	1.88	0.61	0.003
Cr	0.6	1.2	0.7	8.2	1.7	4.5	2.4	2.9	0.1	2.6	0.2	4.2	0.4	7.0	0.1	2.2	5.2	0.04
Cu	3.0	2.8	3.5	16.8	6.8	17.6	16.4	14.4	8.2	17.6	8.5	7.9	11.4	10.8	6.6	22.1	12.9	0.02
Fe	25.1	13.8	20.0	285.4	40.8	630.9	251.5	309.3	37.6	65.3	26.9	91.8	52.5	481.8	50.5	539.6	113.0	0.09
Li	3.6	15.0	8.0	90.2	99.5	87.1	94.3	83.2	88.7	15.0	30.5	18.6	20.7	54.3	80.5	142.3	99.0	0.09
Mn	22.9	20.2	9.6	190.8	144.4	292.4	205.5	378.8	54.1	107.4	31.2	132.6	36.7	772.9	201.7	77.2	208.8	0.006
Mo	2.4	3.6	2.4	5.2	4.3	0.7	4.6	3.7	6.0	2.6	2.7	1.7	5.8	3.2	4.7	10.0	7.5	0.006
Ni	4.4	3.5	3.9	12.1	8.9	12.8	12.2	11.3	10.4	10.4	8.8	13.5	10.1	12.8	11.0	19.0	15.1	0.01
Pb	0.2	0.1	0.2	12.1	1.3	2.3	0.8	16.9	2.8	4.3	1.1	1.7	1.0	15.1	0.6	1.9	1.1	0.003
Zn	32.8	38.5	61.1	430.1	312.1	674.4	216.1	1,933.9	224.2	519.3	349.6	244.7	964.9	551.7	166.1	786.2	336	0.09

^a Wastewater influent (I) and effluent (E) samples from the DCSD (Duckett Creek Plant 1, DC1 and Duckett Creek Plant 2, DC2) and MSD (Coldwater Creek, CWC; Missouri River, MOR; Grand Glaize Creek, GGC; Fenton, FEN; Lower Meramec, LMER; Lemay, LEM; and Bissell Point, BP) wastewater treatment plants. One DC1 sample was collected on July 17, 2010, DC1 and DC2 samples were collected on March 17, 2011, and all MSD samples were collected on October 17, 2011.

^b Detection limit.

^c Calculated using Geochemist's workbench 8.0.

Samples for major and trace elemental compositions were field-filtered and field-acidified. Concentrations for the major elements and B were measured using a Perkin-Elmer Optima 7300DV ICP-OES in accordance with the techniques outlined in US Environmental Protection Agency (USEPA) Method 200.7 (USEPA, 1990). The trace elemental composition was measured with a Perkin-Elmer ELAN DRC II ICP-MS using USEPA Method 200.8 (USEPA, 1994). ICP-OES and ICP-MS instrument operation and data processing were performed with WinLab32™ and ELAN® software packages, respectively. Blanks, reference standards (Sigma-Aldrich TraceCERT® and Perkin-Elmer Pure Plus), and duplicate and triplicate samples were also analyzed to check the precision and accuracy of analytical procedures; laboratory accuracy was $\pm 5\%$. Detection limits for relevant elements are listed in Tables 1 and 2.

Subsamples for major ions, including Cl, $\text{NH}_4^+ - \text{N}$, $\text{NO}_3^- - \text{N}$, and total P as PO_4^{3-} , were collected in pre-cleaned high density polyethylene (HDPE; i.e., Cl, $\text{NH}_4^+ - \text{N}$, $\text{NO}_3^- - \text{N}$) or glass (i.e., total P) bottles. Samples for TSS were also collected in HDPE bottles. The Cl, $\text{NH}_4^+ - \text{N}$, $\text{NO}_3^- - \text{N}$, and total P concentrations were determined using USEPA-approved techniques (Hach, 2005a,b,c,d,e).

Samples for H and O isotopic analyses were collected in clean, air-tight glass bottles. Isotopic measurements for untreated waters were made with a Thermo Finnigan MAT 252 IR-MS. The data are reported in the conventional manner, as $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values that represent ‰ deviations from standard mean ocean water (V-SMOW). The $\delta^2\text{H}$ values were determined by reacting 1.0 μL of water with metallic Cr at 800 °C to produce H_2 gas prior to analysis; precision is $\pm 1.0\%$. The $\delta^{18}\text{O}$ values of sample waters were determined by equilibrating 0.5 mL of the water sample with a 0.3% CO_2/He gas mixture at 1 bar for 16–24 h at 26.5 °C and analyzing the CO_2 gas; precision is $\pm 0.1\%$. Every run included several standards and duplicates and triplicates of samples to check the precision and accuracy of analytical procedures.

The complete set of analytical data collected during this project is too large for tabulation here, but selected data and statistical summaries of B concentrations in various waters and B end-members are presented in Tables 1 and 2. The entire analytical dataset, including ranges of B concentrations for sources and end-members, can be found in Hasenmueller (2011).

B data collected in this study were augmented by archived data maintained by the USGS for a number of regional sites. Composite samples collected by the Howard Bend and Chain of Rocks Water Treatment Plants provide data for the Missouri River and treated water from the two plants (Criss et al., 2001). Because the periods of record and analytical methods differ among the databases, mixing of datasets is avoided whenever possible, and data sources are specified in the tables.

5. Results and discussion

5.1. Concentrations of B in water

The B contents of local waters were systematically quantified by analysis of a suite of rainfall, runoff, urban and rural stream, river, lake/pond, shallow groundwater, and end-member samples (Tables 1 and 2). The average B concentration is only 25 $\mu\text{g}/\text{L}$ for unpolluted watersheds in central Missouri with minimal agricultural and urban development, close to the global average of 10–20 $\mu\text{g}/\text{L}$ (Drever, 1997; Langmuir, 1997; Lemarchand et al., 2002). USGS measurements of rural surface waters and shallow groundwaters typically have B contents of 20 $\mu\text{g}/\text{L}$ or less (USGS, 2012a), confirming the naturally low concentrations in Missouri waters. However, their data show that B can reach several hundred $\mu\text{g}/\text{L}$ near urban and agricultural areas. The USGS statewide average, including both rural and urban areas, is only 40 $\mu\text{g}/\text{L}$.

This study's robust database of surface water and groundwater samples collected from the suburban and urban areas of St. Louis exhibits higher B concentrations of up to almost 250 $\mu\text{g}/\text{L}$ in the River

des Peres watershed. In contrast, in suburban streams, B concentrations were up to 90 $\mu\text{g}/\text{L}$. A suburban lake was slightly above regional background levels (28 $\mu\text{g}/\text{L}$), while a golf course pond in an urban area had elevated B (133 $\mu\text{g}/\text{L}$; Table 1). Shallow groundwaters in the St. Louis metropolitan area likewise had higher B levels (up to 150 $\mu\text{g}/\text{L}$) than their rural counterparts, indicating anthropogenic inputs.

Correlations between B, SpC, and other ions help define likely sources. Winston and Criss (2004) and Stueber and Criss (2005) examined B contents in rural and agricultural waters and showed a negative correlation between B and SpC, leading to the conclusion that B was associated with the event water due to leaching of soils by recent, acidic rainfall. In contrast, in the metropolitan area monitored in this study, the B concentration is positively correlated to SpC in both the streams (Fig. 2) and the suburban runoff. The same behavior is exhibited by the major ions including Ca, Mg, K, and Na (Fig. 2), which are principally associated with baseflow (Winston and Criss, 2004). The likely explanation is that rainfall rapidly mobilizes residual salt crusts on lawns and displaces shallow groundwater that has slowly accumulated B from downward percolation of drinking water and soil leaching (see Section 5.4.). This result suggests that B in the metropolitan area is associated with soil water that over time recharges baseflow. Correlations with discharge, discussed in the following sections, test this hypothesis.

5.2. B versus discharge in watersheds with varying land use

In small rural watersheds, B concentration tends to be positively correlated with discharge. For example, Winston and Criss (2004) found that the B levels for Bluegrass Spring, a perennial karst spring 40 km west of St. Louis, were invariably low (14–33 $\mu\text{g}/\text{L}$) but positively correlated with discharge and negatively correlated to SpC and major ions. They suggested that B is associated with the event water component and its path and is mobilized by pulses of acidic soil water in forested areas. Subsequent measurements of Bluegrass Spring for this study are somewhat higher with a B concentration of about 37 $\mu\text{g}/\text{L}$ during average flow conditions (8.5 L/s).

Stueber and Criss (2005) also found a positive correlation between discharge and B in springs and streams in a rural part of Illinois. Surface runoff into a sinkhole from a large agricultural field planted in corn and soybeans had an average B concentration of 52 $\mu\text{g}/\text{L}$,

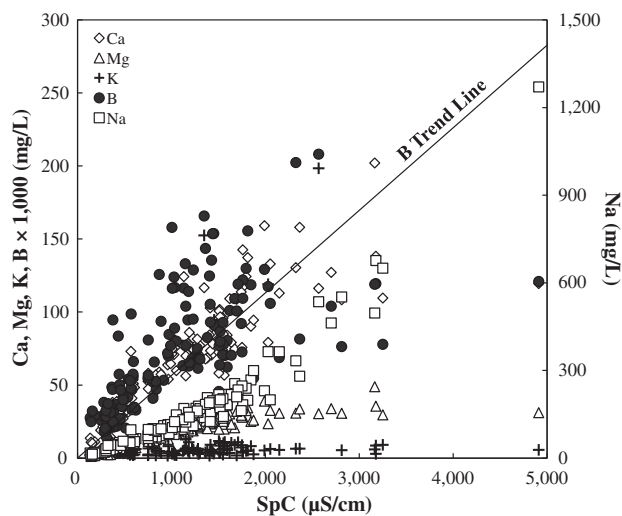


Fig. 2. Graph depicting the positive correlations of B ($\times 1,000$ in mg/L) and major, baseflow-associated ions (Ca, Mg, K, and Na; all in mg/L) with SpC ($\mu\text{S}/\text{cm}$) for individual samples of surface streams in the St. Louis metropolitan area. Table 1 gives average values for these sites.

which was higher than the mean B level of 23 µg/L for two nearby springs and 30 µg/L for local streams. The B concentration at a spring that receives runoff from the sinkhole covaried with discharge and during high flow events could reach up to 45 µg/L. This result confirms the derivation of B from field runoff and, ultimately, probably agricultural fertilizers (Stueber and Criss, 2005).

In contrast to the overall low concentrations of B and its positive correlation with discharge observed in the aforementioned studies, B levels were generally high and negatively correlated with discharge in the urban systems monitored in this study. The River des Peres has the highest average B levels of all the surface streams and groundwater samples, and average concentrations are 88 µg/L at RDP-1, 92 µg/L at RDP-2, and 129 µg/L at RDP-3 (see Table 1). These B concentrations exhibit an inverse relationship with discharge for both the River des Peres channel and one of the suburban runoff sites (Fig. 3). Clearly, concentrations are highest during low flow and become diluted following rainfall and during flood perturbations. Wyness et al. (2003) similarly found that B concentrations in English rivers were highest under low flow conditions and became diluted with increasing flow. However, whereas Wyness et al. (2003) concluded that B was derived from wastewater as well as large-scale agricultural non-point sources, Neal et al. (2010) concluded that there may be other types of B non-point sources involved in urban settings, which are identified in this study.

The negative correlation of B with discharge is confirmed by a detailed series of samples collected during a discharge event on April 2–3, 2010 (Fig. 4). The pre-storm B concentration was approximately 80 µg/L at the RDP-1 and RDP-2 stations and 154 µg/L downstream at RDP-3. All stations experienced B dilution, culminating at minima of 24 µg/L at RDP-1 and RDP-2 and of 30 µg/L at RDP-3, approximately coincident with peak flooding. The dilution trend demonstrates the low contribution of B from rainfall and confirms that elevated B concentrations originate from baseflow.

Time series data for the suburban runoff sites show higher B concentrations and dilution with increased flow similar to the trends in the stream channel. However, unlike the stream, flow at these sites occurs only intermittently and immediately following rainfall, but average B concentrations are high at both SFC-1 (89 µg/L) and SFC-2 (58 µg/L). Nevertheless, the location comprised of predominately street runoff (SFC-3) had a somewhat lower average B value of 37 µg/L. The highest B levels, including an extraordinarily high value of 246 µg/L at SFC-1, occur during “initial flushing” at the onset of overland flow and then become progressively diluted (Fig. 5).

In short, during periods of high discharge, the lowest B concentrations occur in streams and runoff in the St. Louis metropolitan area, while the highest B concentrations occur in small rural watersheds. The striking difference between these behaviors suggests that B is more complex than most other ions, which can be assigned either to a baseflow or event water group. Instead, B is principally associated

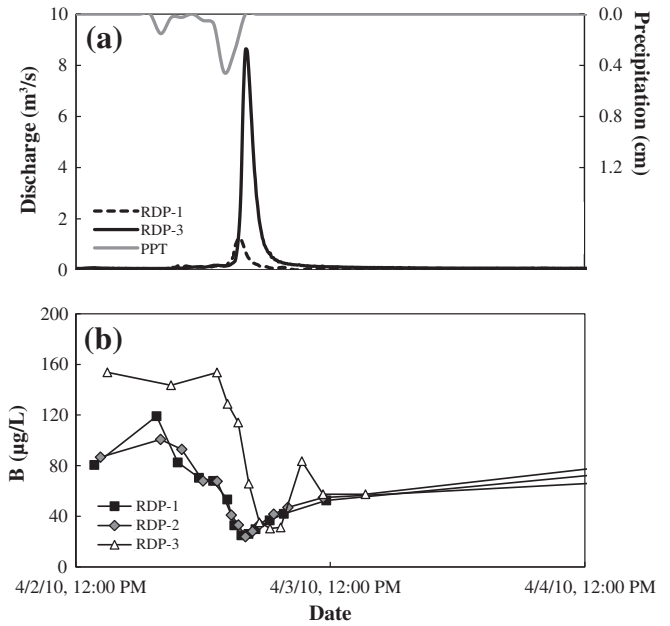


Fig. 4. Response of the River des Peres to a storm on April 2–3, 2010 that delivered 1.07 cm of rainfall. (a) Graph of discharge (m³/s) estimated at RDP-1 and measured by the USGS gaging station near RDP-3 compared to hourly precipitation (cm) at Lambert-St. Louis International Airport (NOAA, 2012; left inverted scale). Peak discharge at RDP-1 occurs 35 min before peak discharge at RDP-3. (b) Dilution of B concentrations (µg/L) in the River des Peres (RDP-1, RDP-2, and RDP-3) during high flows.

with baseflow and the “first flush” in the metropolitan area and with event water in small rural watersheds.

5.3. Soils, leaching acidity, and first flush effects

Mobilization of B is highly dependent on soil pH (Yermiyahu et al., 1995), with B most easily leached from acid soil types. Both Palmer et al. (1987) and Peak et al. (2003) concluded that B is readily leached and likely moves with the flow of soil water. Winston and Criss (2004) and Stueber and Criss (2005) confirm B mobility in rural soils and documented that B concentrations rise as the component of acidic event water increases. Moreover, the B concentration observed in these studies was associated with a “family” of ions including Al, Cu, Fe, and Pb whose concentrations increased with discharge. In contrast, urban St. Louis watersheds have the opposite correlation of B with event water, and B is associated with the major ions including Ca, Mg, K, and Na (Fig. 2) that undergo dilution as streamflow increases. In this case, larger B loads occur in the baseflow component because municipal waters used for lawn

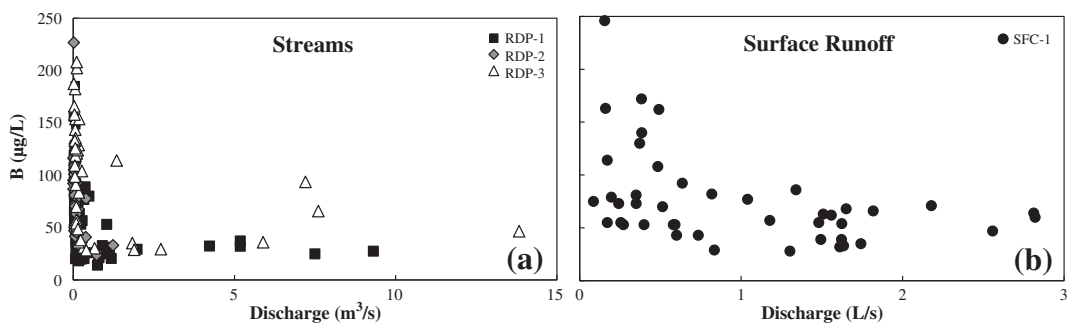


Fig. 3. Inverse relationship between B concentration (µg/L) and discharge (m³/s) for the (a) Upper River des Peres (RDP-1, RDP-2, and RDP-3) sites and (b) suburban runoff site SFC-1. For (a), baseflow B concentrations for the Upper River des Peres are clearly higher than event water concentrations. Similarly, in (b) the B concentrations in suburban surface runoff are initially high but become diluted with increased discharge; possible B sources in these small watersheds include residual salts from lawn irrigation water or lawn fertilizers but not CSOs or sewer leaks.

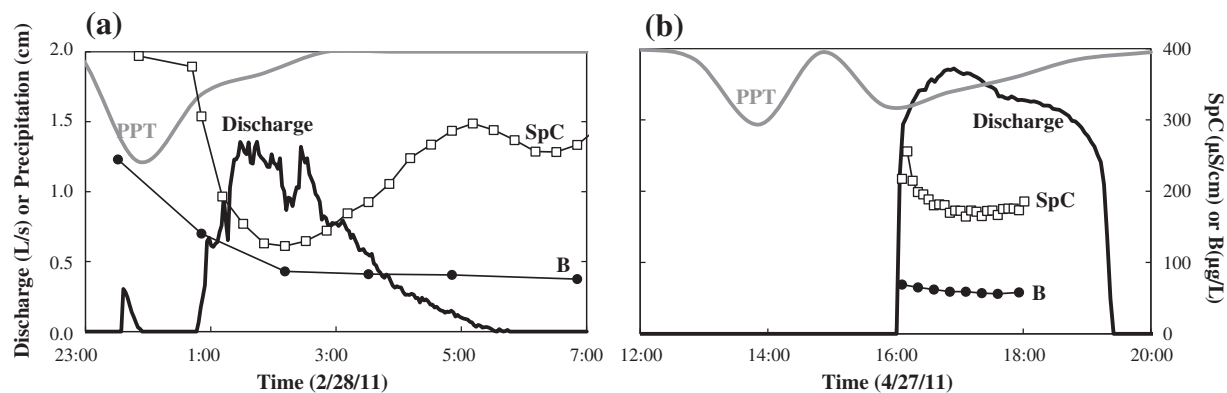


Fig. 5. Examples of typical surface runoff responses at the (a) SFC-1 parking lot and field (February 28, 2011) and (b) SFC-2 residential neighborhood (April 27, 2011). Discharge (L/s) for the drainage area, hourly precipitation (cm) records from Lambert-St. Louis International Airport (NOAA, 2012; scale is inverted; i.e., 2.0 cm is equal to 0.0 cm), SpC ($\mu\text{S}/\text{cm}$), and B ($\mu\text{g}/\text{L}$) are shown. Total rainfall amounts were similar: (a) 1.40 cm and (b) 1.65 cm. The first SpC measurement in (a) is off-scale at 611 $\mu\text{S}/\text{cm}$ and is associated with a small discharge peak from parking lot runoff.

irrigation have percolated downward into shallow, local groundwater and/or thin crusts of B-salts that have accumulated on urban lawns from fertilizers and irrigation waters are rapidly moved into streams and shallow groundwater during “first flush” events at the onset of rainfall. It is important to note that the residential areas that were monitored for surface runoff have no perennial flow and therefore do not have a baseflow component.

This “first flushing” effect, whereby soluble material is accumulated during the pre-storm period and then transported into the stream during the beginning of rainfall, has been noted in many other rivers, streams, and springs (Edwards, 1973; Walling and Foster, 1975; Gupta and Saul, 1996; Lee and Bang, 2000; Lee et al., 2002; Winston and Criss, 2004). Many high discharge events observed in this study, including the April 2010 event on the River des Peres, provide typical examples of this type of transient spike in SpC and several other ions including Ca, Mg, Na, Cl, Si S-species. This flushing effect coincides with the arrival of the event water and is expectedly associated with a transient pulse of high ion concentrations. These concentration spikes are a result of event water and displaced baseflow rapidly mobilizing ions from the ground surface and soils. However, it was not possible to measure the large changes in the concentrations of many elements, including B, on a continuous basis because of the very rapid delivery rate of this transient spike in urban environments. Thus, detailed temporal information is not available.

5.4. B sources and end-members

The initial findings of ubiquitously high B concentrations in waters of the St. Louis metropolitan area, interpreted in a manner consistent with available literature, would suggest that CSOs and sewage leaks were major sources. Detailed examination of correlations and trends did not support this interpretation. A systematic search was therefore made to quantify possible sources of B and to evaluate their relative significance.

5.4.1. Atmospheric deposition

Previous studies found that the major global sources of atmospheric B are volcanic emissions and sea salt aerosol production, but in urban areas, atmospheric concentrations of B can be elevated by coal burning (Fogg and Duce, 1985). In continental areas away from the coasts, B concentrations in rainfall range from 0.8 to 94 $\mu\text{g}/\text{L}$, with a mean of 15 $\mu\text{g}/\text{L}$ (Fogg and Duce, 1985). The average B concentration measured in rain for the St. Louis area is well within this range at 24 $\mu\text{g}/\text{L}$ (Table 1). This value was consistently lower than that for urban waters and the Missouri River but close to the average B concentrations found in rural surface waters and groundwaters. At

these concentrations, St. Louis rainfall would contribute an average annual load of 0.24 kg/ha of B to the land surface. Thus, meteoric deposition cannot alone explain the anomalously high B levels in St. Louis streams. Moreover, two surface runoff samples collected only 10 km east and generally downwind of a large coal-fired power plant in Labadie, Missouri, had B values of 21 $\mu\text{g}/\text{L}$ (SFC-Coal; Table 1), suggesting that B contributions from coal fly ash to surface waters and groundwaters are probably no more than two times larger than natural levels in this area. The evident difference between this result and earlier studies may be due to implementation and improvement of scrubbers and electrostatic precipitators at power plants in recent years.

5.4.2. Road salt contamination

Road salt contamination during winter is a chronic problem in many urban areas (Buttle and Labadia, 1999; Williams et al., 2000; Howard and Maier, 2007), including St. Louis (Hasenmueller, 2011). Street runoff was collected from the SFC-3 monitoring site during a winter snow melt event to test whether road salt is a significant B source. Runoff collected immediately following snow melt was highly enriched in Na and Cl from road salting activities, and SpC was 36,000 $\mu\text{S}/\text{cm}$, corresponding to extraordinarily high Na and Cl concentrations of about 13,500 mg/L and 13,900 mg/L, respectively (Table 1). The B concentration, however, was only slightly elevated (57 $\mu\text{g}/\text{L}$) considering that the SpC level was almost 30 times higher than the mean SpC for the River des Peres watershed, and Na and Cl levels were more than 50 times higher. If this B/Cl ratio is multiplied by the average Cl concentration of local surface streams, the indicated B concentration contributed by road salt to local streams is <0.5 $\mu\text{g}/\text{L}$. Thus, road salt contamination does not cause the high B levels in urban streams such as the River des Peres.

5.4.3. Organic-rich leachates

Organic-rich leachate from a mulching operation located 30 m from RDP-2 showed elevated levels of B (301–492 $\mu\text{g}/\text{L}$). However, the maximum flow of this leachate into the River des Peres was less than 0.03 m^3/s (30 L/s) and therefore could only minimally contribute B to RDP-2, which has peak discharges exceeding 9 m^3/s . Furthermore, significant leachate runoff occurs only when it is diluted with recent rainfall. Moreover, the average B concentration for the site upstream of the mulching facility (RDP-1) was 88 $\mu\text{g}/\text{L}$ during low flow conditions and is similar to that of the site downstream of this facility (RDP-2; 92 $\mu\text{g}/\text{L}$), demonstrating the minimal effect of this operation on the B concentration in Upper River des Peres. The leachate also had substantially different relationships between B and SO_4^{2-} – S, Li, and Zn (Fig. 6a–c), with the leachate having lower

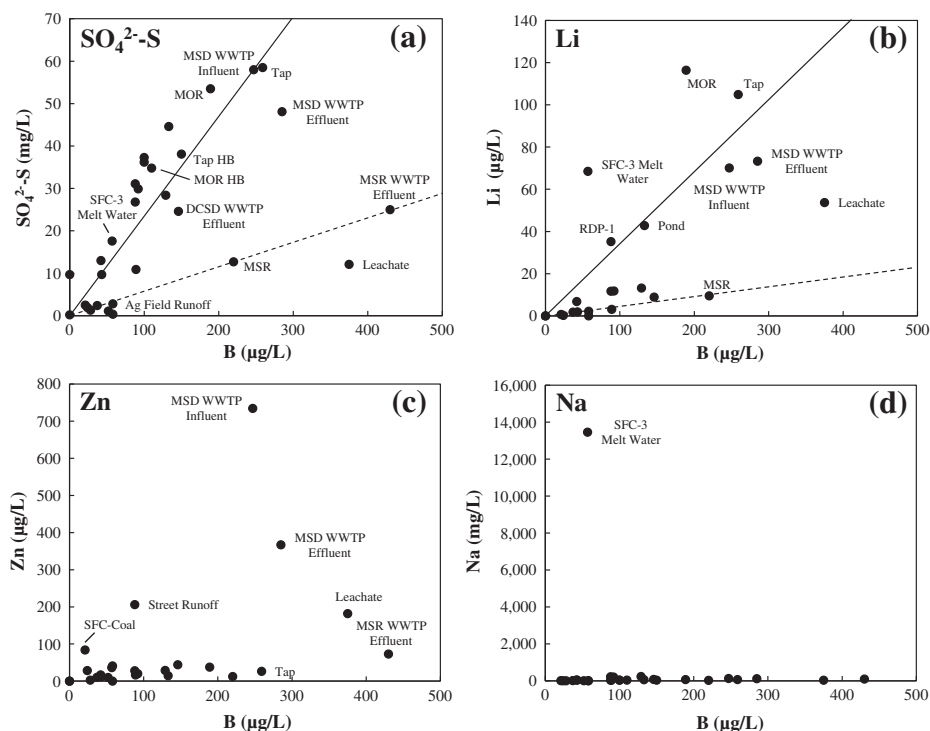


Fig. 6. Relationship between average values of B ($\mu\text{g/L}$) and (a) $\text{SO}_4^{2-}\text{-S}$ (mg/L); (b) Li ($\mu\text{g/L}$); (c) Zn ($\mu\text{g/L}$); and (d) Na (mg/L) for surface waters, groundwaters, and B end-members (Table 1). In (a) there is a distinct relationship between waters with a Missouri River (MOR) signature (solid line) and those with a Mississippi River (MSR) signature (dotted line). Measurements of the municipal drinking water (Tap) made in this study and by the Howard Bend Treatment Plant (HB) are shown. The characteristic differences between the Missouri and Mississippi Rivers seen in (a) are also observed in (b), which shows a B versus Li plot. In (c) wastewaters, street runoff, coal fly ash fall out surface runoff (SFC-Coal), and organic-rich mulching leachates (Leachate) are shown to be high in Zn, but this signature is not imparted on local waters. (d) Demonstrates that the SFC-3 melt waters that come in contact with road salt are responsible for the high Na and Cl contents in the local streams but are not the source of the high B concentrations.

average $\text{SO}_4^{2-}\text{-S}$ values and higher average Li and Zn values than the RDP-2 monitoring station.

5.4.4. Wastewaters

Elevated B levels were found in municipal wastewaters. Two treatment plants operated by the Duckett Creek Sanitary District (DCSD) in St. Charles, Missouri, had an average B concentration of 146 $\mu\text{g/L}$ for the plant effluent, while the seven treatment plants operated by the Metropolitan St. Louis Sewer District (MSD) that serve St. Louis and the surrounding metropolitan area had an average value of 247 $\mu\text{g/L}$ for the influent and 285 $\mu\text{g/L}$ for the effluent (Table 1). Both these values are lower than the average B value of effluent samples collected by Stueber and Criss (2005) from Monroe County, Illinois (430 $\mu\text{g/L}$; Table 1). St. Louis wastewater samples were collected from the entry points of the main sewer lines that carry influent into the seven wastewater treatment facilities (Table 2). Additional samples from both the St. Charles and St. Louis treatment plants were collected from the post-treatment plant effluent lines and permitted comparison of influent and effluent concentrations, revealing any changes due to the sewage treatment processes (Table 2). The B concentrations in water samples from the wastewater treatment plant effluent were consistent with the B concentrations in the influent (Tables 1 and 2). B concentrations in both the influent and effluent were surprisingly similar to the concentrations in municipal water samples from the Missouri River collected in this study, which indicates that B loads in the drinking water also contribute to the B load in wastewaters. Al, Fe, and Zn are all elevated in wastewater influent but are reduced in the treated water, while Li is high in both compared to local surface waters and groundwaters (Tables 1 and 2).

Na and Cl concentrations in water samples from the combined sewer lines were comparable with those in treatment plant effluents

but are elevated considerably above the Na and Cl levels in municipal drinking water (Tables 1 and 2). Thus, appreciable amounts of Na and Cl have been added during the use of the supply water, for instance from water softeners, and additional contributions of Na and Cl come from the treatment process, such as sterilization, chlorination, and flocculation. Still, the Na and Cl concentrations in the wastewaters are lower than in some urban surface waters and groundwaters. For example, the River des Peres has on average twice the Na and Cl concentrations of the wastewaters, mostly originating from road salt.

While wastewaters have high B concentrations, no effluents from these treatment plants are discharged into the small streams sampled in this study, including the River des Peres watershed; instead, they are discharged into the Mississippi, Missouri, and Meramec Rivers and Coldwater Creek (Fig. 1). Thus, the only possible sources of wastewater in the River des Peres are CSOs and sewer leaks. There are CSOs located upstream of the River des Peres sampling sites (Fig. 1, inset); however, CSOs debauch during high flow conditions when B concentrations would be highly diluted with stormwater. Further, no CSOs, leaky pipes, or septic systems are located in the small drainage areas of the suburban surface runoff sites. Thus, wastewaters are not responsible for the high B concentrations in the suburban runoff sites and are probably not the major source of the high B concentrations in the River des Peres.

5.4.5. Fertilizers

In rural areas, agricultural fertilizers can be significant sources of B, so it was tested whether lawn fertilizers could be a large B source in urban runoff, streams, and shallow groundwaters. Analyses of several commercially available lawn and garden fertilizers, along with the average of agricultural fertilizers analyses by the Oregon Department of Agriculture (2010; Table 1), reveal that only small

or modest increases of B in surface runoff can normally occur when the dilution factor of fertilizer with rainfall is considered. Leenhouts et al. (1998) reached a similar conclusion when examining the B isotope ratios of irrigation waters recharging groundwater in Avra Valley, Arizona. Here, higher B concentrations were attributed to the use of wastewaters for irrigation rather than to fertilizers used on the fields.

Fertilizer application and intensity are more variable in urban areas than in agricultural landscapes, as lawns occupy discrete portions of the landscape and application rates vary with the preferences of multiple land managers. However, application rates of B-containing lawn fertilizers are likely to be similar to or lower than agricultural application rates (Gold et al., 1990; Liu et al., 1997). Survey data collected by Law et al. (2004) for Baltimore, Maryland, estimated a mean annual fertilizer application rate of 97.6 kg/ha with a standard deviation of 88.3 kg/ha for urban golf courses. This application rate, which is probably far higher than the average for the whole metropolitan area, can be used to estimate an upper limit for the average B load from fertilizers in the urban areas of this study. If one assumes an application rate of 97.6 kg/ha and that the fertilizer with the highest B concentration is used (0.06wt.%; Table 1), then loads up to 0.06 kg/ha can be contributed annually, which is much less than B loads contributed by ordinary rainfall. Furthermore, discussions with the relevant property owners indicate that no lawn fertilizers have been applied for many years at the three surface runoff sampling sites in the River des Peres watershed. Of course, the application rates throughout the study area cannot be similarly quantified.

5.4.6. Lawn irrigation

The average B concentration of tap water from several locations in River des Peres watershed is 259 µg/L, one of the highest concentrations for measured waters (Table 1). This concentration is twice as high as the average of measurements made by the Chain of Rocks and Howard Bend Treatment Plants during 1995–2000 (Table 1), probably because the samples for this study were collected in late September and October 2011. In particular, the Missouri River is

normally dominated by contributions from the upper basin during summer and fall. Because this interval overlaps the time when lawn irrigation is most common, this high B concentration may better represent the B in water applied to lawns than the lower, annualized B concentration. As mentioned above, lawn irrigation can be a substantial portion of household water use (on average 443 L/day per 0.1 ha household lot), so municipal waters can potentially contribute up to 0.42 kg/ha of B annually. This load of B is larger than that delivered by normal rainfall and dwarfs possible contributions from lawn fertilizers.

Derivation of major B loads in St. Louis watersheds from municipal irrigation water is strongly supported by the relationships between B and $\text{SO}_4^{2-} - \text{S}$, Li, Zn, and Na (Fig. 6a–d). Fig. 6a shows that the Missouri River and derivative municipal drinking waters and wastewaters have a similar trend in B and $\text{SO}_4^{2-} - \text{S}$ contents to that exhibited by surface runoff, streams, and shallow groundwaters in the metropolitan area, demonstrating that local waters have developed a chemical signature similar to the Missouri River. Analogously, data collected by Stueber and Criss (2005) show that wastewaters from the Waterloo Treatment Plant in Illinois inherit their B/ $\text{SO}_4^{2-} - \text{S}$ ratio from the Mississippi River, which provides the municipal water source in that area (Fig. 6a). A similar relationship can be observed between B and Li (Fig. 6b), where municipal waters derived from the Missouri River have a distinct trend. In addition to contributions of $\text{SO}_4^{2-} - \text{S}$ and Li, municipal drinking water used for lawn irrigation also contributes substantial non-point loads of Cu (Table 1). Fig. 6c shows that while there are generally high concentrations of Zn in wastewaters, leachates, and street runoff, Zn remains low in the tap water, surface water, and groundwater samples, indicating that wastewaters are an unlikely source of B in local waters. Finally, Fig. 6d illustrates that the B concentration in melt water is slightly elevated (57 µg/L), but the Na level is more than 50 times higher than regional surface waters, groundwaters, and municipal waters (see Section 5.4.2 for more detail).

During the year, the amount of B entering the River des Peres increases in the late summer when lawn irrigation is most prevalent.

Table 3
B concentrations along the Missouri River (USGS, 2012a).

Station	State	USGS gaging station number	River kilometer	Number of B samples	Sampling dates	Discharge (m ³ /s)	Average B (µg/L)
Toston	MT	06054500	3,695	31	1991–1995	158	108
Fort Benton	MT	06090800	3,336	29	1970–1972 1980–1982	216	76
Virgelle	MT	06109500	3,274	1	1991	236	80
Landusky	MT	06115200	3,093	26	1976–1978	255	91
Wolf Point	MT	06177000	2,738	68	1961–1973	276	102
Culbertson	MT	06185500	2,608	150	1965–1974 1996–2007	285	104
Forsyth ^a	MT	06295000	–	118	1953–1954 1974–1982 2000–2001	297	141
Williston	ND	06330000	2,270	169	1950–1965 1974–1982	576	132
Bismarck	ND	06342500	2,115	74	1974–1980 1988–1994 2005–2011	626	138
Schmidt	ND	06349700	2,089	48	1976–1981	–	120
Pierre	SD	06440000	1,716	111	1953–1964 1971–1978 1997–2000	–	129
Yankton	SD	06467500	1,297	93	1956–1959 2000–2008	–	124
Omaha	NE	06610000	991	168	1970–1971 1996–2011	926	107
St. Joseph	MO	06818000	721	17	2007–2011	1,339	95
Sibley	MO	06894100	557	12	2008–2011	–	90
Hermann	MO	06934500	158	202	1969–1972 1996–2011	2,528	75

^a On the Yellowstone River.

The degree of dilution also changes through the seasons; hence the lowest concentrations of B occur during the wettest period of the year in early spring.

5.4.7. B concentrations along the Missouri River

Because municipal waters are derived from the Missouri River, it is important to examine potential B sources and trends in the watershed, and available USGS data define these patterns (Table 3). Concentrations of B in the upper Missouri River are similar to those in the lower Missouri River near Hermann, Missouri. However, a sharp increase in B contents occurs just below the confluence of the Missouri and Yellowstone Rivers (Fig. 7a and b), and B remains high in the reach that includes the large reservoirs in the Dakotas. A dilution trend is observed downstream of these reservoirs, which asymptotically approaches a value of about 55 µg/L (Fig. 7c) and approximates B concentrations for lower basin rivers (cf. Winston and Criss, 2003). The USGS data at Hermann are only half the concentrations measured in this study, likely because analytical methods, sampling times, and intervals are all different (see Table 3).

High B concentrations in the Missouri River are probably principally derived from natural rock weathering of evaporite deposits (Butterwick et al., 1989) and inputs from hydrothermal systems (Thompson, 1969), but agricultural fertilizers could also contribute significant B to the watershed. Wastewater treatment plants along the river must provide additional inputs, but it is estimated that these contribute <2% of the total B load. For example, average effluent discharge from the large Bissell Point and Lemay Wastewater Treatment Plants into the Mississippi River is only 11 m³/s and 15 m³/s, respectively (MSD, 2012), which are very small (<<1%) compared to the average discharge of 5,500 m³/s for the Mississippi River at

St. Louis (USGS, 2012a). Similarly, no more than a few percent of the flow of the Missouri River could represent wastewater effluent.

6. Conclusions

The use of “exotic” water from the Missouri River as a municipal drinking water source in St. Louis, Missouri, provides a unique opportunity to identify the input of municipal waters into shallow groundwater and surface water systems. The regional B concentrations in surface runoff, surface streams and rivers, and springs representative of the shallow groundwater are established by using a large suite of data generated by this study and augmented by data from the Howard Bend and Chain of Rocks Water Treatment Plants and regional USGS data. The database from this study establishes generally low (25 µg/L) background levels of B in east-central Missouri but systematically high concentrations in the surface waters and groundwaters of the St. Louis metropolitan area.

Previous studies have largely attributed high concentrations of B to wastewaters and fertilizer use. However, in this study area, attribution of high B to the “usual suspects” has been proven unlikely by evaluating sample locations in terms of land use, estimated B loads, and correlations of B with other ions and discharge. Here, treated wastewaters are debauched into large rivers or lowermost tributaries and cannot directly affect their upstream tributaries. Moreover, no CSO or sewage inputs are possible at the small, residential runoff sites that were monitored. Wastewater contributions are also unlikely to be the dominant B source in local streams, where CSO inputs would only occur during heavy storms when their B load would be highly diluted by ordinary stormwater runoff. Fertilizer contributions were found to be minor sources due to the trace amounts of B they contain; other studies have confirmed that B concentrations in agricultural field runoff are rather small.

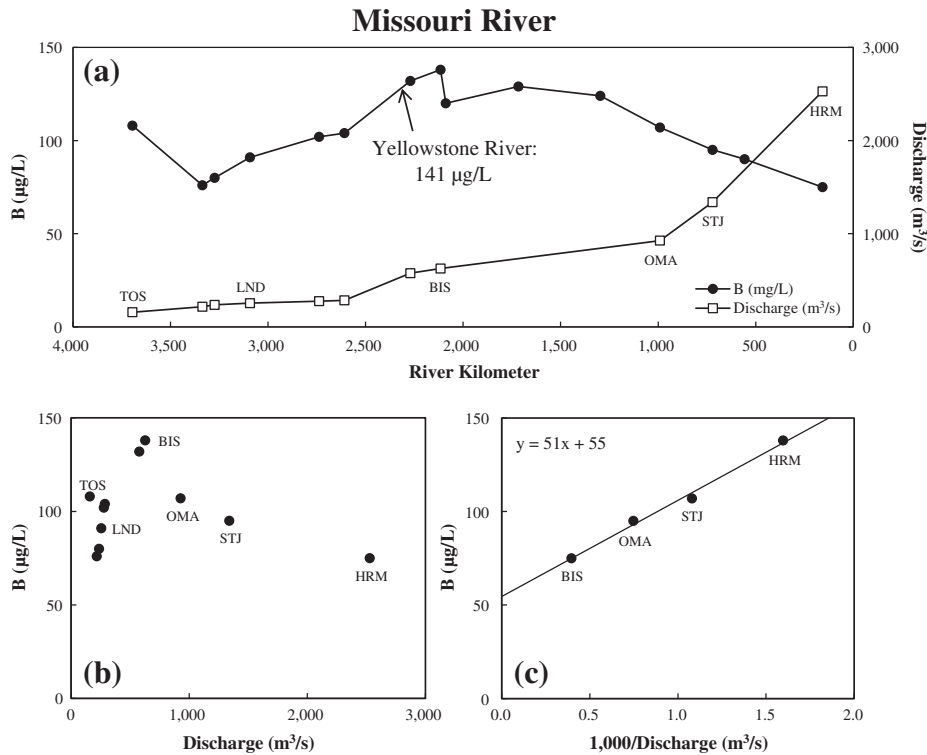


Fig. 7. (a) Discharge (m³/s) and B concentrations (µg/L; USGS, 2012a; Table 3) along the Missouri River. Selected stations from Table 3 are labeled on the diagram and include Toston, Montana (TOS); Landusky, Montana (LND); Bismark, North Dakota (BIS); Omaha, Nebraska (OMA); St. Joseph, Missouri (STJ); and Hermann, Missouri (HRM). The B concentrations are highest just below the Yellowstone River and in the large Dakota reservoirs and become progressively diluted downstream. (b) B concentrations plotted against discharge using values from (a). This figure shows the complex relationship between the two parameters and demonstrates that B levels increase in the upper basin despite increasing discharge, possibly because of contributions of hydrothermal waters from the Yellowstone River (Butterwick et al., 1989) or agricultural inputs. However, in the lower basin, B concentrations decrease with increased discharge. In (c) B concentrations are plotted against 1,000/Discharge for the four lowermost gaging stations (Table 3) and show that a coherent B-dilution trend occurs downstream of kilometer 1,500 (below the lowest major reservoir), which projects to 55 µg/L.

Systematic consideration of these and other possible sources reveals that lawn irrigation waters, mostly derived from municipal tap waters sourced from the Missouri River, provide the major B load. Most municipal drinking waters in this area inherit the high B concentrations of the Missouri River and may have an average concentration of more than 250 µg/L. Urban lawn irrigation in the area comprises up to 60% of the annual household water use, so municipal drinking water contributes large loads of non-point source B to surface waters and shallow groundwaters. The highest levels of B were observed during low flow conditions when applications of irrigation water are necessary and streamflow is maintained by release of shallow groundwater. B likely accumulates as residual salts on irrigated lawns, in soils, and in soil water, and some percolates downward to the water table. The salts are rapidly flushed out during precipitation events, with the first runoff having the highest B concentrations.

Urban irrigation and possibly the use of urban lawn fertilizers play a substantial role in replacing and/or changing the chemical character of the shallow groundwater in the St. Louis metropolitan area, as shown by the enhanced B signature of local surface streams and springs. Using B as tracer, this study demonstrates that urban irrigation waters impact surface waters and groundwaters more than previously thought and can be an important source of B in some urban settings. Contributions of municipal drinking water used for lawn irrigation are likely substantial in other urban areas and may be traceable if the chemical signature of municipal waters differs enough from the local water, as is the case in St. Louis.

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