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Evaluation of chemical indicators for tracking and apportionment of phosphorus sources to Table Rock Lake in Southwest Missouri, USA

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ABSTRACT

This work evaluated the suitability of selected chemical species as indicators for tracking and apportionment of point and non-point phosphorus sources within the Table Rock Lake watershed in Southwest Missouri, USA. The species were evaluated with respect to their uniqueness to specific source types, their ability to be detected in both sources and receiving waters, and the consistency of their concentration ratios to phosphorus. Four sampling events were conducted at 15 sample locations in one year to collect water samples for measuring the concentrations of total and dissolved phosphorus, seven anions, and 19 major and trace elements. Current analytical methods were sensitive enough for quantification of most of the chemical species in both sources and the receiving waterbody. Due to the high seasonal variation of phosphorus concentrations in source samples, no chemical species had consistent concentration ratios to phosphorus across source types. However, several chemicals were found to be unique to specific sources; bromide ion can be used as a unique indicator for the effluent of the largest wastewater treatment plant in the watershed.

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1. Introduction

Phosphorus contamination of surface waters from point and non-point sources remains an environmental problem of great concern. Excess loading of phosphorus to surface waters can cause eutrophication (Tchobanoglous and Schroeder, 1985; Effler et al., 2002). Previous studies revealed that phosphorus is the limiting nutrient in Table Rock Lake, the target water body of this study (Thorpe et al., 2004).

Tracking and apportionment of phosphorus sources are challenging due to the large number of potential sources and the significance of non-point sources. Previous studies have modeled contributions of non-point loads in watersheds using export coefficients for land use types, topography, and geology (McFarland and Hauck, 2001) or mass balance models (Pieterse et al., 2003).

Receptor modeling is an alternative source apportionment approach, in which concentrations of multiple species are monitored at a receptor location and then apportioned among

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different sources by comparing the chemical compositions of different sources. This approach is based on chemical mass balances and on specific pollution source categories having unique ratios of certain chemical species (i.e., source profiles). By measuring the concentrations of n species at a location in the surface water (c_i) and knowing the concentrations of species in the source water (a_{ij}) of m source types, the fraction of the total water flux coming from each source (s_j) can be calculated (Eq. (1)) and does not need to be known beforehand.

$$c_i = \sum_{j=1}^m f_{ij} a_{ij} s_j \quad (1)$$

Modification factors (f_{ij}) are often included in this approach to account for retardation or degradation of the species during transport. Key steps in receptor modeling are establishing the profiles of specific source types and verifying that downwind or downstream locations have air or water compositions that reflect mixtures of the source profiles.

Source apportionment using receptor modeling requires an appropriate set of identifying indicator species. The term species is used here to refer to both chemical and biological constituents; this paper focuses on inorganic chemical species, and a previous paper examined the use of bacteriophages (Dryden et al., 2006). The use of *Escherichia coli* measurements at Higgins Lake to identify failing septic systems as the source of phosphorus is an example of the use of a biological indicator for source tracking of phosphorus inputs (Minnerick, 2001), and recent work demonstrated the use of a large suite of organic chemicals as indicators for inputs from wastewater treatment plants (Glassmeyer et al., 2005).

Receptor modeling is widely used in the air quality field (Watson, 1984), but it is rarely used for water quality modeling because the signatures of pollutant sources tend to change during transport. In particular, the transport of phosphorus from sources to locations in a surface water is controlled by the distribution of phosphorus between the dissolved phase and suspended solids and by the biogeochemical processes of phytoplankton growth and decay, which cycle phosphorus through organic and inorganic species (Schlesinger, 1997). However, receptor modeling can still complement land use-based water quality modeling.

This study examined the source profiles of various phosphorus sources within the Table Rock Lake watershed through field sampling and laboratory analysis of a suite of chemical species. Samples were collected from potential sources and at locations in the receiving water that are most likely to be impacted by a single type of source to determine whether or not the source profiles were apparent in the receiving water. Useful indicator species must (1) be present in the receiving waters at detectable concentrations, (2) have unique source profiles, (3) have ratios to one another (especially to phosphorus) for a given source that are constant and reproducible, (4) be transported directly from the source to the receiving body or have known retardation factors, and (5) not degrade or have known degradation rates. In this work, the usefulness of the selected species was evaluated with respect to the first three of these requirements. The latter two

requirements are important and can be evaluated in subsequent work.

2. Materials and methods

2.1. System description

Table Rock Lake on the Missouri–Arkansas border (Fig. 1) was created by a dam on the White River built by the US Army Corps of Engineers in 1958. The lake has a surface area of approximately 43,100 acres and the watershed upstream of the dam encompasses 4020 square miles. The major flows into the lake are the James River from the north, the Kings River and Long Creek from the south, and the White River from the southwest. The lake volume is approximately 3.3 million m^3 and the average hydraulic residence time is 0.8 year (Green et al., 2003). Land use in the watershed has been changing rapidly with population growth and increasing agricultural activities, especially animal-feeding operations (AFOs). In 2002, the Missouri Clean Water Commission placed Table Rock Lake on the Missouri list of impaired waters because of high phosphorus concentrations.

The lake is impacted by a variety of sources, including point sources (e.g., municipal wastewater treatment plants) and non-point sources, such as confined animal feeding operations, poultry litter applied to farm fields, and storm-water runoff. There are also over 20,000 septic systems near Table Rock Lake (Table Rock Lake Water Quality, Inc., 2003). Due to their widespread distribution, septic systems may be viewed as a non-point source. For properly functioning septic systems, phosphorus will be retained within the soils of the leach field; however, at many locations along Table Rock Lake, effluent from malfunctioning septic systems can flow directly into the lake. The failure of septic systems is attributed to the highly fractured karst geology of much of the watershed and to thin soils that provide little retention of phosphate in the leach field (Midwest Environmental Consultants, 2001).

2.2. Sampling site selection

Fifteen sampling sites (Fig. 1) were selected and classified into five main types: (1) source sites (S1, S2, S3A, S3B, and S3C), (2) surface water sites likely to be predominantly impacted by specific source types (A1, A2, A3, and A5), (3) control sites upstream of source sites (C1, and C2), (4) drinking water supplies (D1, D2, and D3), and (5) one undeveloped lake site (B). A GIS (geographic information system)-based multi-criteria decision analysis was applied to identify potential sampling locations. The details of the GIS analysis are presented in a separate publication (Angenent et al., 2006). Briefly, suitability surfaces (i.e., maps) were generated to identify sites on the lake that would be most likely to have measurable impacts from four specific source types (large wastewater treatment plant, small wastewater treatment plant, septic systems, and concentrated animal feeding operations) and a site with minimal impact from any sources. Geospatial data included in the analysis were topography, lake surface, land cover, soil type and depth, road density, and locations of permitted water discharges.

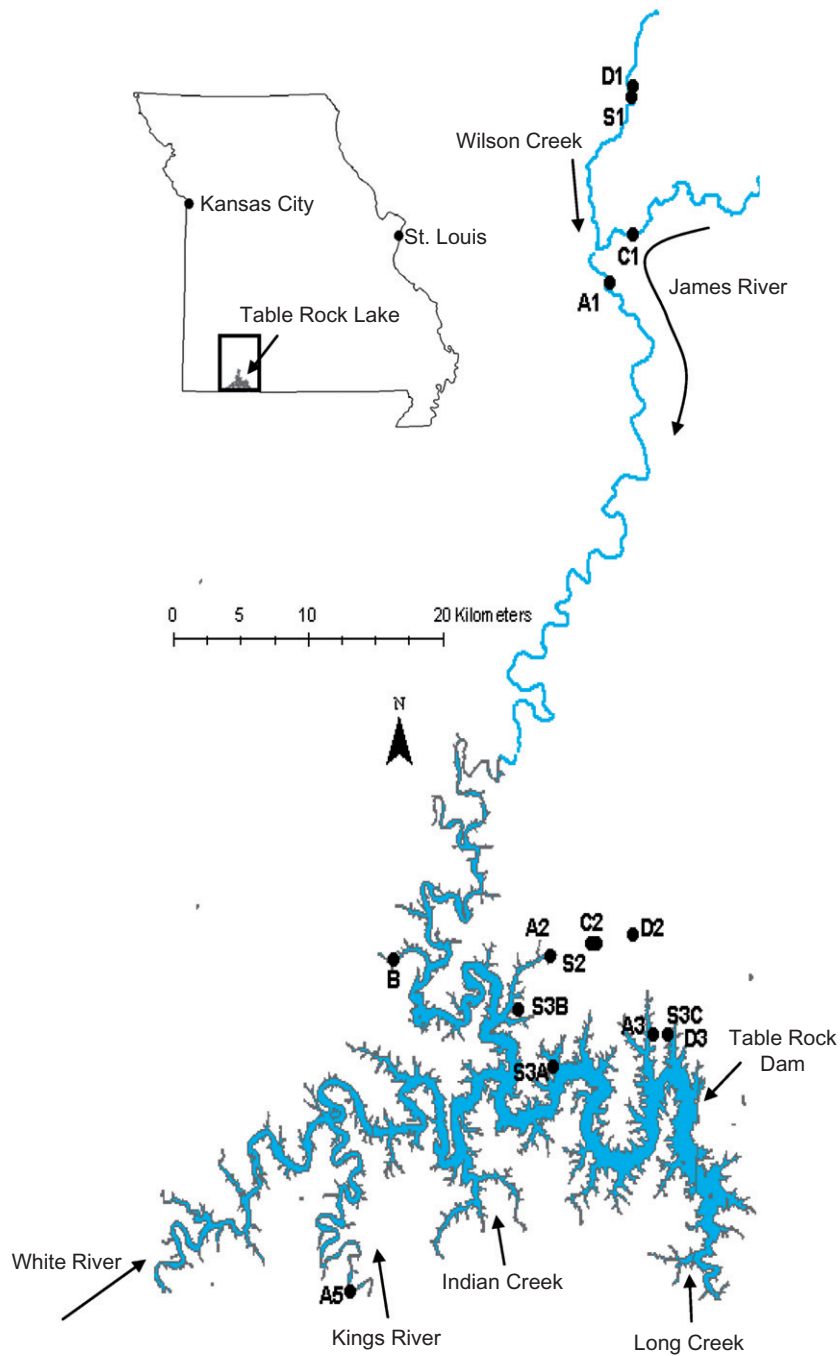


Fig. 1 – Sampling sites in the Table Rock Lake watershed, Missouri, USA.

Site S1 is the effluent of the Springfield Southwest Wastewater Treatment Plant, which discharges into Wilson Creek, which in turn flows into the James River, the major northern tributary to Table Rock Lake. The flow of Wilson Creek is dominated by the treatment plant effluent. The average daily discharge from the Springfield Southwest WWTP is approximately 35 million gallons per day (MGD). Although the plant has processes for phosphorus removal, this WWTP is still a large point source of phosphorus due to its large discharge volume. Site A1 is on the James River downstream of the confluence with Wilson Creek, which carries the flow of S1.

Site C1 is on the James River upstream of this confluence. Site D1 is Springfield tap water, which was sampled at public locations (e.g., restaurants and city offices).

Site S2 is the effluent of the Branson West Wastewater Treatment Plant (0.75 MGD capacity), which discharges into Aunts Creek. Site A2 is on the lake about 100 m west of the mouth of Aunts Creek. Site C2 is on Aunts Creek upstream of the discharge point of S2. Site D2 is Branson West tap water, which was sampled at public locations. Sites S3A, S3B, and S3C are effluents of septic tanks around Table Rock Lake. S3A and S3B are single compartment septic tanks. S3C is a holding

tank in a step system that sits between several individual septic systems and the drainfield. Site A3 is on the lake near Indian Point, a region surrounded by a high density of septic systems. Site D3, sampled at a kitchen tap, is well water that supplies a small resort that discharges to septic system S3C. Site A5 is on the Kings River arm of the lake, which is likely to be impacted by runoff from animal feeding operations and wastewater from Berryville, Arkansas. Site B is a relatively less developed lake site surrounded primarily by a wilderness area.

2.3. Sample collection and analysis

Sampling was conducted once per season (April, July, October 2004, and January 2005) for one year. The different sampling campaigns included a range of hydrologic conditions. The April, July, and January sampling periods were dry, but the region received 1.4" of rain during the week of the October sampling. The April sampling campaign was conducted when the lake was just below normal pool and the inflows were affected by moderate precipitation in the preceding week. The July sampling campaign was conducted when the reservoir level was high and the preceding week had included high inflows, which were largely the result of releases from Beaver Reservoir upstream and not from recent precipitation. The October sampling campaign was conducted during a week of heavy precipitation and was also preceded by high precipitation; however, the lake inflows in the preceding week were low and the lake level was also low. The January sampling campaign had the highest streamflows, reservoir inflows, and lake levels of the four sampling campaigns.

The lake sites (A2, A3, A5, and B) were sampled from a boat using a portable sampler (Masterflex[®] E/STM, Cole-Parmer, USA) with Teflon[®] tubing from a depth of 3–6 feet. Additional water samples were collected for sites B and A3 from deeper water (15–20 feet) in April, July, and October 2004.

Samples for each analytical technique were collected in triplicate. Field blanks were collected during each sampling campaign. All bottles used were acid washed. Phosphorus samples were stored in glass bottles. All other samples were stored in HDPE bottles. Raw water was collected for analysis of total phosphorus (TP) and total trace elements. Water was filtered using 0.45 μm membrane filters for analysis of dissolved reactive phosphorus, major anions, major elements, and dissolved trace elements. Samples for analysis of major and trace elements were acidified to pH < 2 by addition of concentrated trace metal grade HNO₃. Samples were kept cold in ice chests immediately after sampling and were stored in the laboratory at 4 °C prior to analysis.

All chemical species were analyzed according to Standard Methods for the Examination of Water and Wastewater (American Public Health Association, 1999). The dissolved concentrations of seven anions (F⁻, Cl⁻, Br⁻, SO₄²⁻, PO₄³⁻, NO₃⁻, NO₂⁻) were determined by ion chromatography (Dionex DX-600, USA) by Standard Method 4110. Dissolved concentrations of Na, K, Mg, and Ca were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Varian Liberty II, USA) according to Standard Method 3120. Dissolved and total trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) (Finnigan Ele-

ment 1, Thermo Electron Corporation) according to Standard Method 3125. For measurement of total phosphorus (TP), water samples were first digested by the persulfate digestion method and then analyzed colorimetrically using the ascorbic acid method (Lambda 2S spectrometer, Perkin Elmer, USA) according to Standard Method 4500-P. A quartz spectroscopy cell with a 10 cm light path was used to provide a method detection limit of 1 ppb. Chemicals used in analysis were purchased from Fisher Scientific, USA. Ultrapure water (>18.2 MΩ-cm) was supplied by a laboratory purification system (Millipore, USA). Standard operating procedures for each technique included quality assurance and quality control protocols.

2.4. Data treatment

The significance of differences in concentrations was evaluated using t-tests. The significance of differences in the concentrations of species among sources was evaluated using a two-sample t-test. The significance of differences among upstream, downstream, and source concentrations was examined using paired t-tests. In addition to the absolute concentrations of species, indicator ratios (IR) with respect to TP were also determined; the IR (Eq. (2)) expresses the ratio of the concentration (C) of chemical species *i* to the TP concentration in source *j* during sampling time *k*.

$$IR_{i,j,k} = C_{i,j,k} / TP_{j,k}. \quad (2)$$

3. Results and discussion

3.1. Distribution pattern of phosphorus

Table 1 lists the concentrations of selected species. TP concentrations for the source sites are also shown in Fig. 2a. Because the relative standard deviations of triplicate or duplicate samples were generally small, all values reported in this paper are mean values unless otherwise indicated. The concentrations in the septic system effluents were significantly higher (greater than 99.9% confidence level) than those in the centralized treatment plant effluents. There were no statistically significant differences among the septic system effluents. The effluent from the large wastewater treatment plant (WWTP) had lower TP concentrations than did the effluent from the smaller WWTP; although this difference was not significant at greater than 90% confidence, when the S2 sample from April 2004 is not included, the difference is statistically significant (>98% confidence).

By comparing the TP concentrations of three related sites (source, downstream, and upstream), the trend of S1 > A1 > C1 in all four seasons on the James River indicates that the WWTP effluent contributes measurable phosphorus pollution to the upper James River (Fig. 3a). The effluent concentration (S1) is significantly greater (95% confidence level) than the downstream concentration (A1), which in turn is significantly greater (95% confidence level) than the upstream concentration (C1). The impact of S1 on the James River is not surprising because the discharge volume of S1 (average of 35 MGD = 54

Table 1 – Concentrations of phosphorus and potential indicators

Species	Time	S1	A1	C1	D1	S2	A2	C2	D2	A3	D3	A5	B	S3A	S3B	S3C
TP (ppb)	4/2004	111	32	17	9	1240	21	10	4	6	9	54	25	2.4 ppm	9.6 ppm	7.4 ppm
	7/2004	113	80	34	6	111	14	—	4	6	7	59	11	5.2 ppm	11.2 ppm	6.3 ppm
	10/2004	94	95	73	3	60	13	13	4	6	9	52	12	1.3 ppm	13.0 ppm	7.5 ppm
	1/2005	135	38	35	3	318	15	—	6	6	9	20	82	6.1 ppm	8.3 ppm	1.2 ppm
Br ⁻ (ppm)	4/2004	38.6	4.26	0	0	0	0.53	0	0	0.51	0	0	0.73	1.41	0	0
	7/2004	30.4	5.28	0	0	0	0.16	—	0	0.21	0	0	0.39	0.11	0	0
	10/2004	24.1	4.93	0	0	0	0.34	0	0	0.16	0	0	0.83	0	0.70	0.64
	1/2005	26.0	1.03	0	0	0	0.38	—	0	0.28	0	0	—	0	0	0
F ⁻ (ppm)	4/2004	0.78	0.36	0.05	1.19	0.16	0.07	0.07	0.09	0.06	0.10	0.04	0.06	10.9	0.72	0.50
	7/2004	0.36	0.17	0.03	0.10	0.11	0.03	—	0.02	0.03	0	0.02	0.03	0	0	0.00
	10/2004	0.39	0.16	0.05	0.17	0.07	0.04	0.03	0.09	0.06	0	0.02	0.03	0	0	0.00
	1/2005	0.32	0.11	0.10	0.19	0.20	0.07	—	0.14	0.06	0.12	0.04	0.05	0	17.4	0.34
SO ₄ ²⁻ (ppm)	4/2004	98.6	24.1	12.0	10.3	51.4	9.7	9.3	11.5	9.2	20.0	8.0	9.8	8.70	14.0	16.4
	7/2004	63.7	33.3	10.7	10.3	85.5	6.7	—	10.5	7.4	15.7	4.9	7.0	16.6	1.4	35.8
	10/2004	72.0	30.0	12.5	10.1	82.7	7.2	13.2	10.0	7.0	14.9	8.2	8.8	84.1	3.0	9.1
	1/2005	60.0	11.8	8.2	11.0	39.4	7.3	—	11.5	33.3	16.0	6.4	6.6	36.2	6.0	20.4
Cu (ppb)	4/2004	3.2	2.1	2.6	49.3	1.1	0.53	0.06	6.9	0.24	60.0	0.27	0.50	4.2	37	6.9
	7/2004	1.6	2.3	2.1	11.2	1.5	0.62	—	57.2	0.72	55.8	0.96	0.63	31	20	57.2
	10/2004	1.1	1.8	1.9	3.9	1.5	0.18	0.28	90.5	0.31	63.4	0.43	0.21	7.0	60	90.5
	1/2005	3.2	1.7	1.9	5.2	2.6	0.82	—	15.6	0.64	10.4	0.49	0.96	26.4	53.1	15.6

Values reported are the means of triplicate samples. The relative standard deviation of measurements was almost always below 5%.
— No data available.

cubic feet per second (cfs)) is significant relative to the flow rate of the James River. The average flow rate at the nearest US Geological Survey gauging station (Boaz, MO, No. 07052250) downstream of A1 was 629 cfs during the study period, and the daily flow rate at the time of sampling varied from 122 to 1460 cfs depending on the sampling season. The average flow rate at the nearest upstream gauging station (Springfield, MO, No. 07050700) had an average flow rate of 629 cfs and a range of 35–520 cfs. The magnitude of the difference in TP concentrations between the downstream (A1) and upstream (C1) sites depended upon the river flow rate. In January 2005, the difference was very small (3 ppb) because the proportion of river flow contributed by the WWTP was the lowest (flow at Boaz of 812–1460 cfs). For the season (October 2004) with the highest proportion of river flow from the WWTP (flow at Boaz of 212–422 cfs), A1 had the same total phosphorus concentration as S1 and the difference between A1 and C1 was 22 ppb.

In contrast, the impact of the smaller WWTP (S2) was not observable at the downstream site (A2) (Fig. 3b). A2 is a lake site connected to the main water body of Table Rock Lake, where the TP concentrations were generally very low (around several ppb). S2 has a much smaller discharge volume (design capacity of 0.75 MGD) than S1 and its phosphorus input can be diluted by water from the rest of the lake.

A similar situation was observed for the three septic systems. Although the three septic systems had high concentrations of TP, the sampling location on the lake (A3) that was identified as being most likely to be impacted by septic system effluent did not have elevated phosphorus concentrations relative to the background lake location. In

fact the concentrations at A3 were the lowest measured in the study, and were significantly lower (90% confidence) than at the background site. Although each septic system will discharge water at a flow rate on the order of only 60 gal/person-d, the large number of septic systems (more than 20,000) in the watershed and the high phosphorus concentrations of phosphorous in the effluent could provide substantial phosphorus to the lake if they do not retain phosphorus in the leach field. At site A3 the phosphorus either did not reach the lake because it was captured in the drainfield or the inputs were rapidly mixed and diluted with relatively clean water from the rest of the lake; site A3 is closer to the main body of the lake than the other sampling sites and would be more influenced by overall lake mixing.

3.2. Evaluation of potential indicators

3.2.1. Detectability of investigated species

Current analytical methods were sensitive enough for quantification of almost all investigated species in sources, receiving waters, and drinking water supplies. However, mercury was often difficult to quantify by ICP-MS and potassium by ICP. Nitrite was almost never detected.

3.2.2. Uniqueness of source profile

The ideal indicator is a chemical species or a unique combination of several species that are only present in a certain source or present at much higher concentrations than in other types of sources. By examining the distribution patterns of individual chemical species among sites, bromide, fluoride, sulfate, and copper had distinctive patterns as

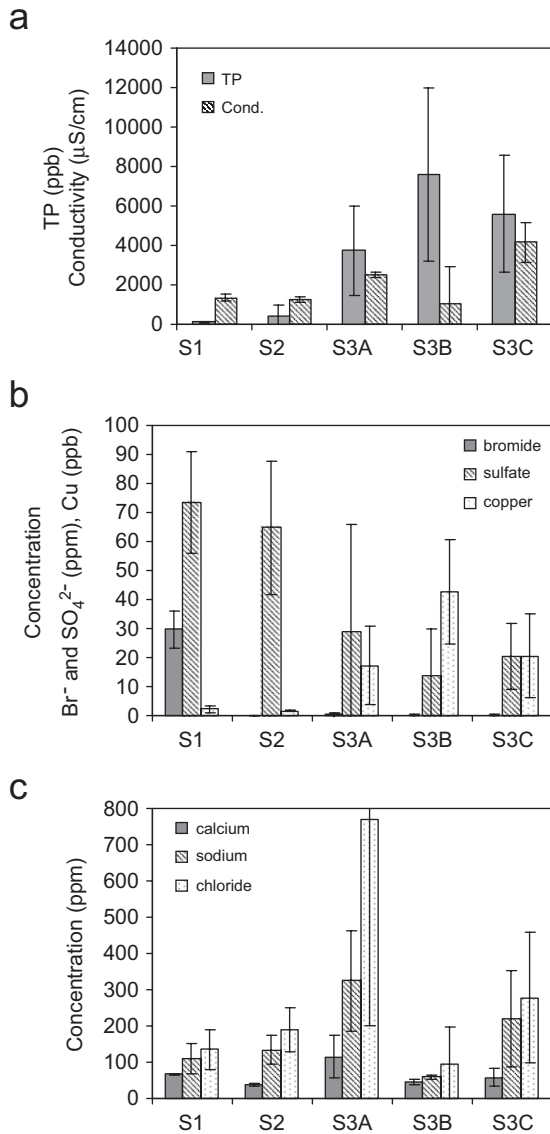


Fig. 2 – Concentration profiles of wastewater treatment plant (S1 and S2) and septic tank effluents (S3A, S3B, and S3C) for (a) TP and conductivity, (b) species that are characteristic of specific sources, and (c) selected species that are not characteristic of sources. The height of the bar is the average concentration and the error bars are the standard deviation associated with the four sampling seasons.

described below and illustrated in Fig. 2b. The other species investigated, such as those shown in Fig. 2c, did not show a distinctive distribution pattern and are not ideal indicators for tracking phosphorus sources to Table Rock Lake.

3.2.2.1. Bromide ion (Br^-). Br^- is an ideal indicator for the effluent of Springfield WWTP (S1) (Table 1). High concentrations of Br^- were present in S1 all year, ranging from 24.1 to 38.6 ppm, and these concentrations were significantly greater (at 99% confidence level) than in the other sources. Since the upstream site (C1) did not have detectable Br^- , relatively high concentrations of Br^- downstream (A1) were derived exclusively from A1 (Fig. 3a). The three lake sites A2, A3 and B had

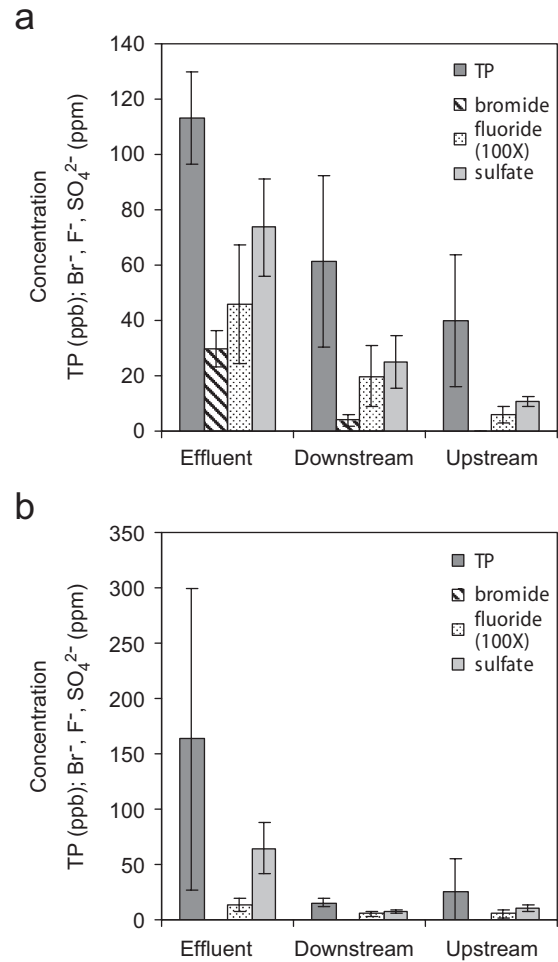


Fig. 3 – Concentrations of TP and selected indicator species in effluent, upstream, and downstream samples associated with (a) a large (S1) and (b) a small (S2) wastewater treatment plant. Concentrations shown are the average values for the four sampling seasons, and the error bars are equal to one standard deviation.

consistently low concentrations of Br^- (around 0.2–0.8 ppm) and concentrations decreased with distance from S1 ($B > A2, A3$); the difference between B and A2 and A3 is significant at the 99% level, however differences between A2 and A3 were not significant. A5 did not have detectable Br^- concentrations because this site is close to where the Kings River flows into the lake and is far from the entrance of the James River into the lake (Fig. 1). Thus S1 is the main Br^- source for all lake sites. Br^- was below the detection limit in S2, the three drinking water supplies, C2, and A5. Br^- was only occasionally detected in the three septic tanks and at low concentrations. The source of Br^- in S1 is not known; bromine is used as a disinfectant in swimming pools and cooling towers and is discharged into wastewater in the form of Br^- .

3.2.2.2. Fluoride (F^-). F^- concentrations of most sites were low (Tables 1 and 2), and high concentrations were occasionally observed only in a few samples (D1 April 2004, D2 January 2005, S3A April 2004, and S3B Jan 2005). Concentrations of F^-

Table 2 – Mean and relative standard deviation (RSD in %) of selected parameters and indicator ratios (IR) of concentrations of specific species to the concentration of TP

		S1	S2	S3A	S3B	S3C
TP (ppb)	Mean	113	432	3750	7600	5588
	RSD (%)	14.8	127.2	60.5	57.4	53.2
Conductivity ($\mu\text{S}/\text{cm}$)	Mean	1342	1256	2491	1067	4155
	RSD (%)	11.8	12.9	4.9	171.3	23.8
Cu (ppb)	Mean	2.3	1.6	17.2	42.6	20.5
	RSD (%)	48.1	8.5	78.8	42.5	71.0
Br^- (ppm)	Mean	0.2662	0.0000	0.0002	0.0001	0.0000
	RSD (%)	24.0	NA	190.6	200.0	200.0
F^- (ppm)	Mean	0.0042	0.0007	0.0018	0.0000	0.0001
	RSD (%)	48.8	64.5	121.4	200.0	153.1
SO_4^{2-} (ppm)	Mean	0.665	0.577	0.018	0.002	0.007
	RSD (%)	30.0	108.0	171.4	86.3	110.9
IR-Cu (ppb/ppb)	Mean	0.020	0.012	0.004	0.015	0.004
	RSD (%)	41.2	89.1	42.9	145.8	32.8
IR- Br^- (ppm/ppb)	Mean	0.26616	ND	0.00015	0.00013	0.00002
	RSD (%)	24.0	ND	190.6	200.0	200.0
IR- F^- (ppm/ppb)	Mean	0.00416	0.00074	0.00185	0.00002	0.00009
	RSD (%)	48.8	64.5	121.4	200.0	153.1
IR- SO_4^{2-} (ppm/ppb)	Mean	0.665	0.577	0.018	0.002	0.007
	RSD (%)	30.0	108.0	171.4	86.3	110.9

were higher at S1 than at the other sites because of fluoride addition at the two Springfield water treatment plants to a concentration of approximately 1 mg/L. The concentrations in S1 were significantly higher than in S2 (90% confidence level). Fluoride is a potentially useful indicator for distinguishing the inputs of wastewater from plants treating fluoridated water from a public supply from the inputs from plants treating water from non-fluoridated sources. While the concentrations in S1 and S2 were greater than in the septic systems, the differences cannot be established as significant because of a few high F^- measurements in the septic systems. The influence of F^- in S1 was apparent downstream at site A1 (Fig. 3a), and F^- might be a useful indicator for S1 at this site. Sites C1, A2, C2, A3, A5, and B had consistently low concentrations of F^- that may reflect background concentrations.

3.2.2.3. Sulfate (SO_4^{2-}). Seasonal variation of SO_4^{2-} was low (Tables 1 and 2). The effluents of the two WWTPs (S1 and S2) had the highest concentrations of SO_4^{2-} (50–100 ppm, Fig. 2b), which were significantly higher (99.9% confidence level) than in the septic systems. The three septic tanks had lower SO_4^{2-} concentrations than the two WWTPs, probably because SO_4^{2-} was reduced to insoluble sulfide and other sulfur compounds under the anaerobic conditions in the septic tanks. A1 had higher SO_4^{2-} concentrations than C1 due to the input of S1. The indicator ratio of SO_4^{2-} to TP was significantly higher (95% confidence level) downstream than upstream. In contrast, the effect of S2 on A2 was not apparent because of the dilution with the lake (Fig. 3).

3.2.2.4. Copper (Cu). Cu can potentially be used as an indicator for septic system effluent as shown in Table 1 and Fig. 2b. The septic tanks had significantly (99.9% confidence

level) higher Cu concentrations than the effluents of the WWTPs had. The three drinking water supplies had the highest Cu concentrations, which is probably from the pipe in the water distribution system. A large portion of Cu was probably removed by centralized wastewater treatment processes but not by processes in septic systems.

3.2.3. Consistent concentration ratio of potential indicator to phosphorus

The ability of a species to be a consistent and reproducible indicator for phosphorus sources was evaluated using the indicator ratio (IR) (Eq. (2)). For a specific source, the best indicators will be those with consistent indicator ratios over time. There are a total of four IRs (four sampling events) for each chemical species and site, and the relative standard deviation (RSD) of these four IRs for each species was used to evaluate the consistency of IR over the year (Table 2). Because of its consistent composition, S1 had several species with RSDs of IRs less than 50%: Sr, Ba, V, Cu, Ca, Mg, Na, F^- , Cl^- , SO_4^{2-} , and Br^- . Particularly, Br^- had an IR RSD of 24% and can be a useful indicator for S1. S3A had Cu and PO_4^{3-} with IR RSDs less than 50%. S3C had the following species with IR RSDs less than 50%: Cu, Zn, Ca, Mg, Na, Cl^- , and PO_4^{3-} . For S2 and S3B, all species had much higher IR RSDs because their TP concentrations had the greatest variations over the seasons. For all sites the main cause of high variation of IRs was the highly variable phosphorus concentrations in sources over the whole year (Table 2), which is also illustrated by the large error bars in Fig. 2a.

Although IRs for phosphorus were not consistent with respect to sources or season, the concentrations of several chemical species other than phosphorus were relatively constant through the year. The concentrations of these species may be useful for indicating the sources of water

input but not necessarily of phosphorus loadings, which provides a way to determine the proportion of water influx to the receiving waterbody from each source.

4. Application of receptor modeling to source apportionment

The receptor modeling approach can potentially be applied to the source apportionment of pollutant loading to surface waters. Successful total maximum daily load (TMDL) plans depend upon accurate apportionment of pollutant loads to all point and non-point sources (EPA, 1986). For systems with source categories that have sufficiently diverse source profiles, the receptor modeling approach can be useful in developing and implementing a TMDL plan. The receptor modeling approach has the advantage of not needing to determine the flux from each individual source.

The receptor modeling approach does have limitations and it may be only marginally useful at Table Rock Lake. The magnitude of the source flow rates must be significant relative to the overall flows of water through the system. The influence of the large WWTP in the receiving water was apparent in the river downstream of the source, but, with the exception of bromide, its influence was not detected elsewhere in the lake. Further work in receptor modeling for lakes would benefit from analysis of other chemical species. Several synthetic organic compounds (e.g., caffeine and pharmaceuticals) may be more useful indicators because they could be entirely unique to specific sources. The analysis of dissolved reactive phosphorus in addition to TP would be valuable because DRP will be transported more easily. The sampling strategy must be designed for a particular water body, with characterization of all source categories; although urban storm water discharge and cultivated agriculture were not major sources in the watershed of this study, they are potentially significant pollution sources in other watersheds.

5. Conclusions

This project evaluated three requirements of potentially useful indicators for source apportionment: detectability, uniqueness, and reproducibility. Requirements with respect to transport and transformation were not evaluated in this work. All of the chemical species studies met the requirement of being detectable in both sources and receiving waters. Several species had concentrations that were significantly different for a large WWTP, small WWTP, and septic systems. Br^- was a unique indicator for the large WWTP, and this source also had the highest F^- concentrations because of the fluoridation of the public water supply. The centralized WWTPs had significantly higher SO_4^{2-} concentrations, while the septic systems were characterized by high Cu concentrations. The influence of the unique concentrations of Br^- , F^- , and SO_4^{2-} were apparent downstream of the large WWTP, and Br^- could be used to track the flow of the effluent throughout the lake. For the septic systems and smaller WWTP, the species that were characteristic of those sources were not observed at elevated concentrations in the surface waters

nearest to their discharge points. No chemical species met the requirement of constant ratios with respect to TP due to the high variation of phosphorus concentrations for the septic systems and the small WWTP; the large WWTP had the most consistent indicator ratios. Some individual species concentrations (not ratios) were relatively constant throughout the whole year and may be used to apportion the contribution of wastewater from various sources.

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