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ORIGINAL ARTICLE

Diurnal variations in, and influences on, concentrations of particulate and dissolved arsenic and metals in the mildly alkaline Wallkill River, New Jersey, USA

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Abstract Diurnal variations in particulate and dissolved As and metal concentrations were observed in mildly alkaline water from a wetlands site on the Wallkill River in northwestern New Jersey. The site, underlain by glacial sediments over dolomite bedrock, is 10 km downstream from a mined area of the Franklin Marble, host to Zn ores, also As and Mn minerals. In mid-September 2005, maxima and minima in dissolved-oxygen-concentration and pH, typically caused by photosynthesis and respiration, occurred at 2000 and 0800 hours. Concentrations of dissolved As (1.52–1.95 μg/L) peaked at dusk (2000 hours), whereas dissolved Mn and Zn concentrations (76.5–96.9 and 8.55–12.8 μg/L, respectively) were lowest at dusk and peaked at 1000 hours. These opposing cycles probably reflect sorption and desorption of As (an anion), and Mn and Zn (cations) as pH varied throughout the 24-h period. Doubly-peaked cycles of B, Cl, SO_4, and nutrients also were observed; these may result from upstream discharges of septic-system effluent. Both recoverable amd particulate Al, Fe, Mn, and Zn concentrations peaked between 0200 and 0600 hours. The particulate metals cycle, with perturbations at 0400 hours, may be influenced by biological activity.

Keywords Diurnal · Arsenic · Metals · Geochemistry · Wallkill River, New Jersey, USA

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Introduction

Diurnal variations in concentrations of As and metals occur in alkaline streams; these variations are substantially different from those found to occur in acidic streams (e.g., Gammons et al. 2005). The variations in dissolved As and metals concentrations in alkaline streams appear to be caused by cycles of sorption and desorption that occur with photosynthesis-driven pH cycles in stream water (Fuller and Davis 1989; Bourg and Bertin 1996; Brick and Moore 1996; Nimick et al. 1998, 2003, 2005; Nagorski et al. 2003; Jones et al. 2004), and also, particularly for Mn and Zn, by diurnal water temperature (*T*) cycles (Shope et al. 2006). Concentrations of metals such as Mn and Zn (as divalent cations) increase during the night and decrease during the day, generally opposing the diurnal T and pH cycles, whereas the cycle for As (as arsenate, an oxyanion) generally follows the pH cycle. Metals cycles that oppose the pH cycle occur because the cations typically desorb from positively charged substrates at low pH, but increasingly sorb as pH increases and the substrate is less protonated. The As anion, however, increasingly desorbs as pH increases. Maxima in dissolved metal concentrations and minima in dissolved As concentrations typically occur at or shortly after dawn (Fuller and Davis 1989; Brick and Moore 1996; Nimick et al. 2003, 2005).

Most diurnal-variation studies have taken place during June through September on alkaline rivers and streams—most in the western USA (e.g., Fuller and Davis 1989; Brick and Moore 1996; Nagorski et al. 2003; Nimick et al. 2003; Parker et al. 2005)—but also in France (Bourg and Bertin 1996). Because such studies involve concentrated field and analytical efforts, they typically extend over time periods that range from 24 h to about 72 h. A recent study of a western USA headwaters stream indicated that, in addition to T cycles, pH, As, and metals cycles persist through winter months into the spring (Nimick et al. 2005). In addition to cycles of dissolved metals and As, cycles in particulate metal concentrations also have been reported (Brick and Moore 1996; Nagorski et al. 2003; Gammons et al. 2005).

Determining the existence of diurnal cycles has real practical application to surface-water studies, because, as pointed out in many of the above-cited studies, the timing of sample collection could affect the evaluation of stream chemistry. The US Geological Survey (USGS) began a cooperative investigation with the New Jersey Department of Environmental Protection (NJDEP) of a northwestern New Jersey watershed where As concentrations in water and sediments of some reaches of the Wallkill River had been found to exceed several New Jersey standards: the Maximum Contaminant Level for drinking water (5 µg/L), the Surface Water Quality Standard (0.017 µg/L), and the soil/sediment Cleanup Criterion (20 mg/kg). [The low Surface Water Quality Standard is a health-based standard calculated for a 1:1,000,000 risk level for a carcinogen (N.J.A.C. 7:9B-1.5(c)2).]

Determining the temporal variability in concentrations of As and associated metals with which As might interact and identifying the processes controlling the variability were of substantial importance to the study. Consequently, at the outset (mid-September 2004), sampling was conducted over a 24-h period using automatic samplers at two sites (WAL-2 and WAL-4; Fig. 1) on the Wallkill River, one a rocky reach near a mined area and the other a downstream wetlands site, to determine whether diurnal variations in recoverable (acid-leachable or ‘‘total’’) As and associated metal concentrations occurred. Filtered samples were collected manually during daylight hours (data in Deluca et al. 2005, p. 651–658).

Diurnal cycles in concentrations of recoverable metals, with nighttime maxima, and a possible cycle in As concentrations occurred at both sites; the coincidence of timing at both sites indicated that recoverable metals cycles were affected by local, similar processes, and that a time-of-travel component to the observations apparently was absent. The analytical data were insufficient to delineate cycles for dissolved metals and other constituents or to determine whether an apparent perturbation in cycles on or about 0400 hours at both sites was a sampling artifact, or an actual geochemical/hydrologic event. Consequently, the study was repeated in mid-September, 2005 at the downstream wetlands site (WAL-4, 01367770) in which sets of filtered and unfiltered samples were collected over 24 h and additional constituents were analyzed. This paper describes the diurnal cycles found in 2005 for selected stream characteristics and chemical constituents, including As and metals, and examines the processes that may cause or affect the observed cycles. To the authors' knowledge, this is the first study of diurnal cycles of As, metals, and other inorganic constituents in a river of the eastern USA; a river where concentrations of As and metals are low and inputs from development may have influenced the chemical cycles in stream water.

Study area

The Wallkill Watershed (540 km^2 in Sussex County) is one of the more rural areas in New Jersey, although suburban development has increased during the past 25 years. Average annual precipitation (1895–1999) has been 117 cm. The headwaters of the Wallkill River originate at man-made Lake Mohawk, created in 1927 from a former wetland. The river drains north through Franklin Pond, an impoundment, and into New York State (Fig. 1).

Bordered by Middle Proterozoic gneiss and granite highlands to the south and to the east and shales to the west (Drake et al. 1996), the river channel lies mostly on valley fill of glacial sands and gravels (Stone et al. 2002), which is underlain by faulted Cambrian and Ordovician dolomites and the Middle Proterozoic Franklin Marble (Fig. 1). Within the Franklin Marble, two ore bodies (one upstream and one downstream from Franklin Pond) were mined for rare Zn minerals; the ore assemblages included As- and Mn-bearing minerals (Palache 1935; Dunn 1995). In addition to elevated As concentrations (22 µg/L) in groundwater discharging to the river, bed sediments in the area of the now-closed Franklin Mine (Fig. 1) contained elevated concentrations of As, Mn, and Zn and traces of the Zn-ore mineral willemite ($(Zn, Mn)_2SiO_4$), also arsenopyrite (FeAsS) and loellingite ($FeAs_2$) (Barringer et al. 2006a). About 10 km farther downstream, the river flows through meadows and wetlands underlain by dolomite; there, As and metal concentrations are lower in river water and bed sediments (Deluca et al. 2005, 2006). The sampling site for the 2005 diurnal study, WAL-4, is in a meadows and wetlands reach within the Wallkill River National Wildlife (Fig. 1). There, the streambed is predominantly sands, silts, and clays. These are composed mainly of quartz, feldspars, calcite, dolomite, kaolinite, with minor amounts of amphiboles and traces of willemite, zircon, apatite, monazite, and fluorite (S. Sutley, USGS, 2006, written communication). The fine-grained materials (<63 µm) are enriched in Al and Fe (4.7 and 1.3%, respectively) relative to Ca and Mg (0.93 and 0.46%, respectively) (Deluca et al. 2006). Sediment grains appear to have Fe hydroxide coatings; undetected by X-ray diffraction, these coatings are probably amorphous. The channel, roughly 10 m wide, contains rooted macrophytes; filamentous algae also were observed.

A piezometer survey indicated that the stream was barely gaining at WAL-4. Although slightly less oxic, the

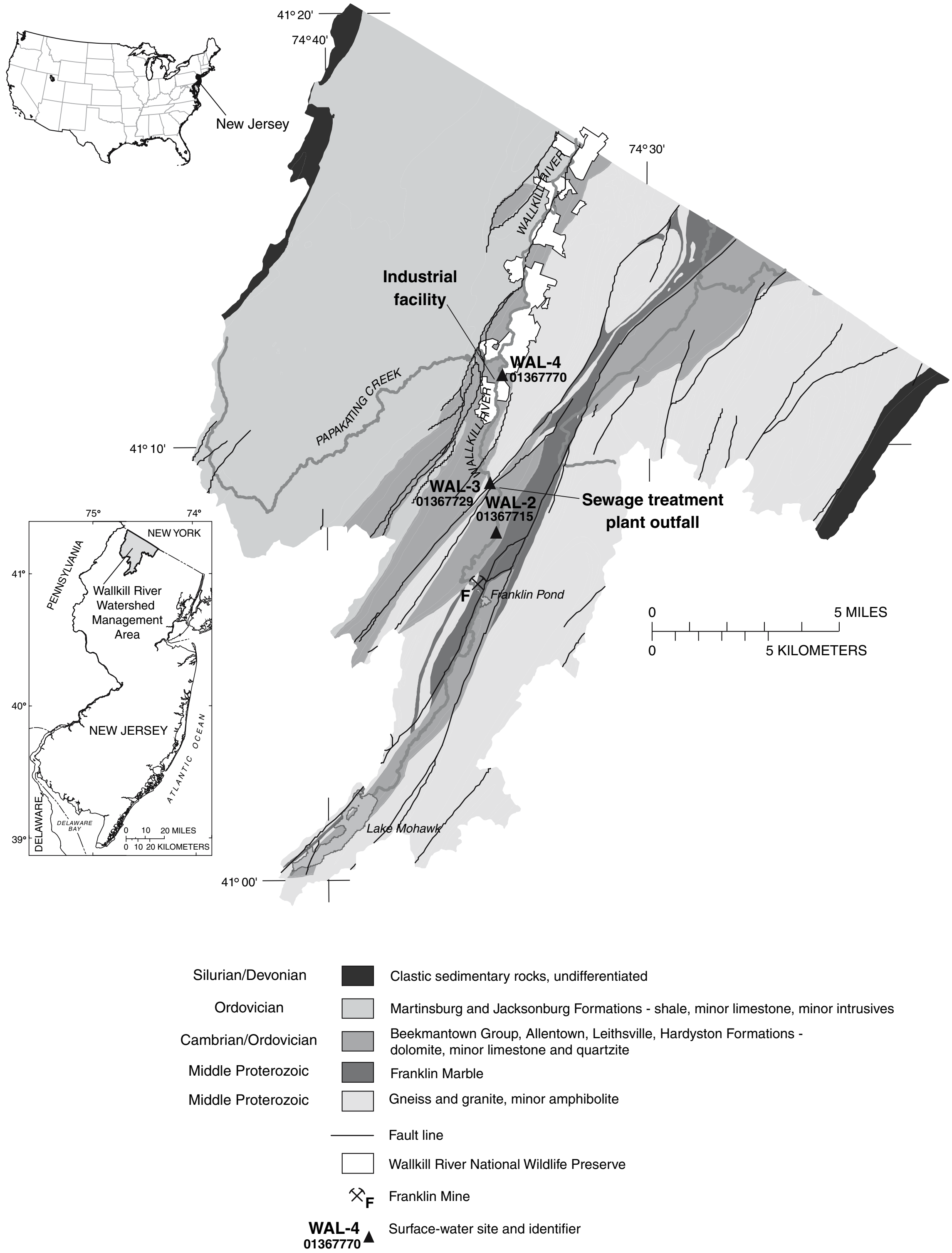


Fig. 1 Bedrock geology of the Wallkill River watershed, New Jersey and locations of the Franklin Mine, local dischargers, and sampling sites WAL-2, WAL-3 and WAL-4

chemistry of the hyporheic-zone water at WAL-4 was about the same as the stream water, indicating local exchange. At upstream sampling sites, however, groundwater discharge to the river in the summer of 2005 generally was colder, less oxic, and of lower pH than the river water (data in Deluca et al. 2006).

A few private homes are present just outside the Wildlife Preserve boundary; several businesses and an industrial operation are located about 0.6–0.8 km west of WAL-4, near the boundary of the Preserve. All are unsewered. The industrial operation is permitted to withdraw and air-strip groundwater contaminated with volatile organic compounds (VOCs), and to discharge the treated water to the wetlands; these withdrawals and discharges are essentially continuous (L. Moore, NJDEP, 2006, personal communication), but their effect on river flow has not been quantified. About 4 km upstream from WAL-4, a municipal sewage treatment plant (STP) discharges treated water (0.092 m^3/s) continuously to the river (E. Hofer, Sussex Co. MUA, 2005, written communication). To date, results of sampling upstream and downstream from the STP outfall (at WAL-2, 01367715; and WAL-3, 01367729; Deluca et al. 2005, 2006) indicated minimal effect on stream water chemistry from this discharge, which, at moderate flow, is about 4% of the river flow—comparable to inputs from a minor tributary. During the summer of 2005, concentrations of solutes increased in the river water (Deluca et al. 2006), although changes in Ca and Mg concentrations generally were small, probably the result of precipitation of a carbonate phase. The largest increase in $NO_2 + NO_3$ (by a factor of 5) occurred in water at WAL-4, The increase at site WAL-3, immediately downstream from the STP, was comparatively minor (Table 1).

Methods

Sample collection and analysis

The 2005 sampling campaign took place during a period of warm weather and base-flow discharge in the river, occurring a year later than the 2004 sampling round in which the presence of diurnal cycles in unfiltered arsenic and metal concentrations was determined using automatic samplers.

During the 2005 sampling campaign, bi-hourly samples were collected from midway in the water column at the centroid of flow using a peristaltic pump on the riverbank. The pump was fitted with an acid-washed Teflon-lined collection tube stepped down to 1-m-long acid-washed thermoplastic elastomer tubing—the latter tubing was changed every three samples. Before each bi-hourly sample was collected, the tubing was flushed with stream water for about 10 min. Samples were collected into 1-L acid-washed, field-rinsed polyethylene bottles for As and metal analysis and 1-L field-rinsed polyethylene bottles for As-species, anion, and nutrient analysis. These were filtered, bottled and preserved immediately in a glove bag in the nearby clean van, using a second peristaltic pump. (In this study the filtrates are operationally defined as ‘‘dissolved.’’) Ultraclean protocols (Horowitz 1994) included changing glove bags and pump tubing between samples. All tubing used in sample preparation was acid-washed. Disposable in-line capsule filters (0.45-μm pore size) were rinsed with de-ionized water and field rinsed with stream water, as were sample bottles unless individual constituent protocols dictated otherwise. Bottles for trace-element samples (except As-species samples) were acid washed prior to use; ultrapure HNO_3 was used to preserve samples for determination of metals. Samples for As-species determination were preserved with 100 μL of EDTA (Garbarino et al. 2002). An equipment blank, using certified analyte-free water, was collected.

At each sample-collection time, measurements of T, DO, pH, and SC were made using a multi-parameter YSI 6920 data sonde and turbidity was measured using a Hach

Table 1 Concentrations of selected constituents, Wallkill River at WAL-3 and WAL-4, April–August 2005

Site name Site number Date Time	WAL-3 01367729 04/19/05 1355	WAL-3 01367729 08/04/05 1300	WAL-4 01367770 04/19/05 1030	WAL-4 01367770 06/08/05 1150	WAL-4 01367770 08/04/05 1700	WAL-4 01367770 08/24/05 1010
Constituent						
T (°C)	16.9	26.8	13.4	22.9	27.1	19.9
pH	8.2	8.3	8.1	7.7	7.8	7.8
DO (mg/L)	11.0	10.4	9.5	8.0	11.1	7.74
Na (mg/L)	40.6	46.9	37.4	43.0	56.5	52.5
NH_3 (mg/L as N)	<0.04	<0.04	0.03	0.061	0.05	0.063
Cl (mg/L)	72.7	101	66.4	79.1	109	102
SO_4 (mg/L)	14.3	19.9	14.5	12.9	20.8	20.1
$NO_2 + NO_3$ (mg/L as N)	0.98	1.18	0.70	0.986	5.09	2.94
PO_4 (mg/L as P)	<0.02	0.070	<0.02	0.025	0.046	0.064
DOC (mg/L)	2.74	–	2.75	3.52	–	3.08
As filtered (μg/L)	1.1	2.3	0.90	2.0	2.5	2.0
B (μg/L)	23	–	20	24.2	–	50.3

2100 P turbidimeter. River stage was read on the staff gage at the site at the time of each sample collection and later converted to discharge, using a rating curve established for the site.

Analyses were carried out at the USGS National Water Quality Laboratory (NWQL), Arvada, CO. Analytical methods, precision, reporting limits, and results for the equipment blank are given in Table 2 (see http://www.water.usgs.gov/pubs/twri/ for method references). All sampling times are reported as local time (EDT).

Geochemical modeling and statistical analysis

Speciation calculations were done for a water sample collected 24 August 2005 (Table 1) and for the diurnal samples, using PHREEQC (version 2.0; Parkhurst and Appelo 1999). Because Na, K, SiO_2, and DOC were not measured in the diurnal samples, K and SiO_2 concentrations from the August sample were used in those calculations and kept constant throughout; a Na:Cl ratio from the August sample was used to estimate Na concentrations in the diurnal samples. The DOC concentration from the August sample also was used and entered as citrate. Values of pe were calculated from diurnal DO concentrations, using the method of Johnsson and Lord (1987).

Because the diurnal data represent a group of time series, use of standard statistical methods is constrained because the data are serially correlated, that is, the observations for a given series are not independent. Rather, for each variable (constituent or characteristic) the value at time $t + 1$ is related to the value at the preceding time t. The time dependence of observations in a time series can be removed by differencing. To remove first-order dependency, adjacent values are subtracted from each other,

Table 2 Analytical methods, precision, and reporting limits for field parameters and dissolved (d) and recoverable [acid-leachable (r)] constituents, and concentrations in equipment blank

Constituent	Method	Precision[a], RPD[b] or RSD[c]	LRL[d]	Blank
Temperature (°C)	Data sonde	0.15°C[a]	NA	NA
DO (mg/L)	Data sonde	2%[a]	NA	NA
pH (units)	Data sonde	0.2 units[a]	NA	NA
SC (µS/cm)	Data sonde	5% + 1 µS/cm[a]	NA	NA
Turbidity (NTU)	Turbidimeter	2%[a]	NA	NA
Alkalinity (mg/L as $CaCO_3$)	titration	1.7%[b]	5	<5
Cl (mg/L)	Ion chromatography	0.9%[b]	0.2	<0.2
SO_4 (mg/L)	Ion chromatography	0.4%[b]	0.18	<0.18
$NO_2 + NO_3$ (mg/L as N)	Colorimetry	1.9%[b]	0.016	<0.016
PO_4 (mg/L as P)	Colorimetry	8.5%[b]	0.006	<0.006
Ca (mg/L)	ICP/AES[e]	0.7%[b]	0.02	<0.02
Mg (mg/L)	ICP/AES[e]	0.9%[b]	0.008	<0.008
NH_3 (mg/L as N)	Colorimetry	11.3%[b]	0.04	0.005
Al (d, r) (µg/L)	ICP/MS[f]	14%[b] 4%[c]	1.6, 2	<1.6, 2.5
As (d, r) (µg/L)	cICP/MS[f]	8.8%[b], 6%[c]	0.12, 0.12	<0.12, <0.12
As (V) (d) (µg/L)	cICP/MS[f]	7.1%[b]	0.8	<0.8
As (III) (d) (µg/L)	cICP/MS[f]	4.4%[b]	0.6	<0.6
B (d) (µg/L)	ICP/AES[e]	0.3%[b]	7.0	<7.0
Fe (d, r) (µg/L)	ICP/AES[e]	19.7%[b], 2%[c]	6, 6	<6, <6
Mn (d, r) (µg/L)	ICP/AES[e]	3.6%[b], 2%[c]	0.6, 0.6	<0.6, <0.6
Zn (d, r) (µg/L)	ICP/AES[e]	5.3%[b], 4%[c]	2, 0.6	–

NA not applicable

[a] Listed as accuracy for T, DO, pH in YSI 6-Series Multiparameter Water Quality Sondes User Manual, rev D, October 2006 and turbidity; in Hach Company Portable Turbidimeter Model 2100 P Instrument and Procedure Manual

[b] RPD = relative percent difference (from replicate sample pair; this study)

[c] RSD = relative standard deviation (USGS NWQL data)

[d] LRL = lower reporting limit, which is 2× the minimum detection limit

[e] ICP/AES = inductively coupled plasma/atomic emission spectrometry

[f] ICP/MS = inductively coupled plasma/mass spectrometry; c = collision cell

resulting in a series of $N - 1$ first-order-independent observations (Box and Jenkins 1976). After conditioning to remove first-order dependency, the resulting series were tested for relational significance at the 0.05 level using linear regression. Depending on the length of the original series, N for the differenced series varied from 12 to 14. Results of the regressions were used to quantify the significance of relations between the cycles illustrated in graphical plots of the time-series. R^2 and t-statistic are reported. The short nature of the various time series in this dataset precluded using classical statistical time-series modeling techniques, however.

Results

A sequential replicate to the 1200-hour sample was collected at 1205. A spike in turbidity and concentrations of recoverable metals occurred at 1200 hours, presumably because of a disturbance upstream. The pulse of particles passed rapidly, but caused large discrepancies in concentrations measured in unfiltered samples from 1200 and 1205 hours. Filtered samples, however, were not affected, and relative percent differences (RPDs) for dissolved constituents are listed in Table 2. For recoverable constituents in unfiltered samples, long-term relative standard deviations (RSDs) from the NWQL are listed.

The standard deviations (SDs) from the mean values for the recoverable and dissolved metals (except dissolved Fe) were substantially greater than the analytical errors indicated by the sequential replicate or those routinely reported by the NWQL. SDs for dissolved As, alkalinity, B, Cl, NH_3 and $NO_2 + NO_3$, turbidity, SC, and % DO saturation measurements also were greater than the expected analytical errors (DO is reported herein as a concentration, not % saturation). Therefore, the measurements are presumed to represent actual variations over time for these characteristics and constituents. Variations in pH were smoothly sinusoidal over time, displaying regular rather than random behavior, and also appear to illustrate a pH cycle over time. Concentrations of PO_4, inorganic As species, and dissolved Fe and Al concentrations were close to or at instrument detection limits, and interpretations of those data are necessarily limited in scope. Results are presented below in three groups to facilitate comparisons among cycles.

Discharge and field parameters

The measurements of field parameters T, DO, pH, SC, and turbidity and the analytical results for samples collected 13–14 September 2005, indicated several distinct sets of chemical cycles were present, and a cycle in stream discharge also may have been present. There was no rain during the 24-h period during which sampling was being conducted at WAL-4 in September 2005; it was predominantly sunny. Discharge (measured as stream stage to 0.01 ft and calculated from a rating curve) increased slightly, from 3.03 to 3.08 m^2/s during the sampling period (Fig. 2a), however. The increase in discharge was out of phase with both turbidity and SC cyclic variations (Fig. 2a).

DO and pH variations were in phase ($R^2 = 0.81$, $t = 6.29$) and represented a set of cycles distinct from turbidity and SC cycles; a low-amplitude T cycle was nearly in phase with those of DO and pH (Fig. 2b). Both DO and pH increased during the afternoon and evening of the first day until about 2000 h, then decreased until 0800–1000 hours (Fig. 2b). Air temperature at WAL-4 on 13–14 September 2005, varied between 13 and 32°C. In WAL-4 water, however, T ranged only from 18.8 to 21.8°C over the 24 h, reaching a maximum at 2200 hours (Fig. 2b).

B, major anions, and nutrients

Concentrations of B, Cl, SO_4, $NO_2 + NO_3$, and NH_3 all exhibited two maxima during the 24-h period—the smaller peak at about 1800 hours the first day, and the larger peak at about 0600 hours the second day (Fig. 3a; Table 3). Concentrations of PO_4 also showed two peaks at about the same times as the other nutrients. It is likely that the increases in anion concentrations were balanced by an increase in Na, which was not measured, as variations in Ca and Mg concentrations did not coincide with those of B and the major anions and nutrients. SC measurements showed two maxima at about the same times as maxima in concentrations of B and the major anions and nutrients (Figs. 2a, 3a). The highest SC measurement occurred at about 0800 hours when the larger peak in B, Cl, SO_4, and nutrient concentrations occurred. Relations among most of these series were significant. The R^2s for change in B and $NO_2 + NO_3$ concentrations with change in Cl concentration were 0.97 and 0.94, respectively ($t = 20.2$ and 13.4, respectively), but $R^2 = 0.52$ and 0.45, respectively for SO_4 and NH_3 with Cl ($t = 3.46$ and 3.03, respectively). The SC and Cl series were significantly related ($R^2 = 0.83$; $t = 7.03$), but the PO_4 and Cl series were not. Relations of the anions and nutrients with As and metals also were not significant with the exception of dissolved Zn with Cl ($R^2 = 0.41$; $t = 2.78$). SC levels and concentrations of B and the major anions and nutrients (except, perhaps, PO_4) represented a set of similar cycles that differed from those of most other dissolved constituents (Fig. 3a, b; dissolved As and Zn shown).

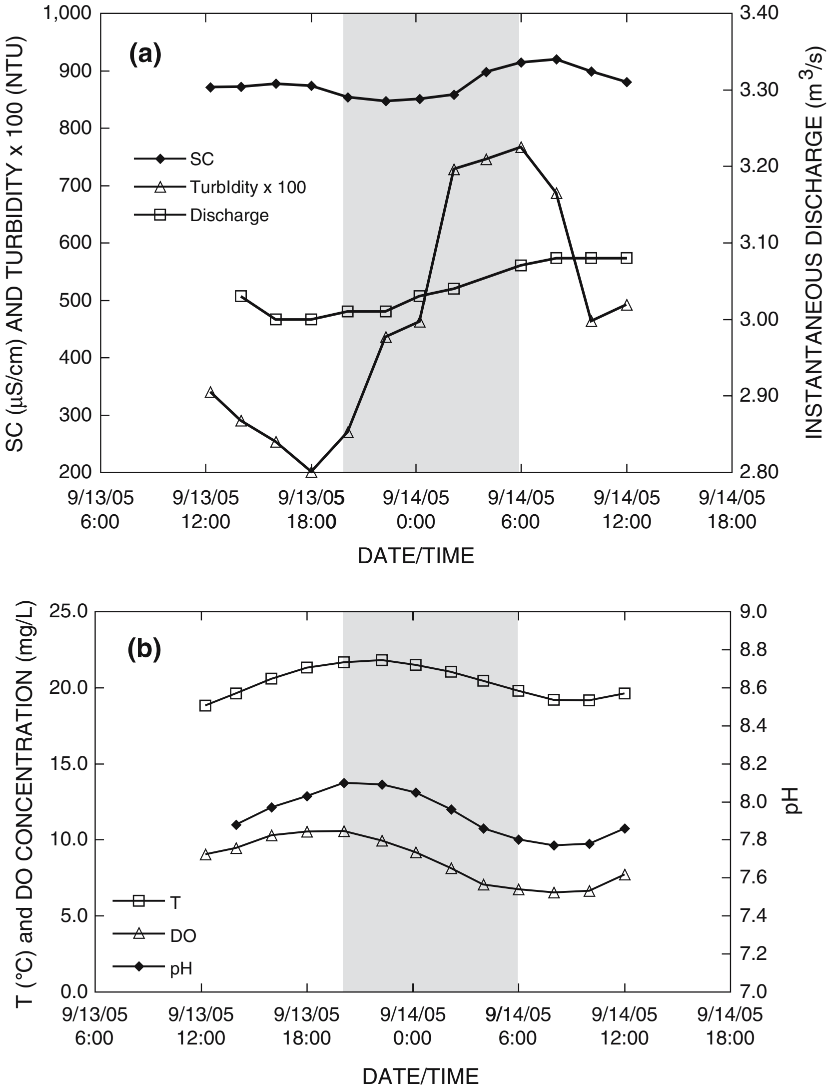


Fig. 2 Diurnal variations in **a** streamflow (instantaneous discharge), turbidity, and SC; and **b** T, pH, and DO concentrations in water at WAL-4, September 2005. (*Shaded area* shows nighttime hours.)

As, metals, and alkalinity

Dissolved As (which could include colloids) constituted from about 85 to 99% of recoverable As, and arsenate [hereafter, As (V)] was the dominant species (Table 3). Concentrations of methylated As species were either less than the LRL or were not detected. The sum of species concentrations did not equal dissolved As concentrations, in part, because arsenite [hereafter, As (III)] and methylated species concentrations were near or at the method detection limits and values are uncertain, but also because any As colloids in filtered samples would be retained in the column during the As species analysis. If perturbations (anomalous spikes) in concentration at 0400 hours are discounted, the cycle for dissolved As, was mostly anti-coincident with the cycle for dissolved Zn (Fig. 3b). The dissolved Mn cycle was similar to that of dissolved Zn, but the perturbation at 0400 hours shown in the As and Zn cycles (Fig. 3b) was not present in the dissolved Mn cycle and the relation between the dissolved Mn and Zn cycles was not significant. Overall, the dissolved cycles for both Mn and Zn were mostly anti-coincident with the dissolved As cycle and with the pH cycle. The Mn minimum coincided with the pH maximum at 2000 hours and the Mn maximum with the pH minimum at 0800 hours (R^2 = 0.87; t = –7.87); but, for change in dissolved Zn with change in pH, R^2 = 0.40 (t = –2.45).

Cycles in concentrations of recoverable and particulate (recoverable–dissolved) metals Al, Fe, Mn, and Zn were coincident, with minima at about 1800 hours and maxima at about 0200 hours. Of the metals, Fe and Al were virtually all (about 88–98%) in particulate form. The amount of Zn present in particulate form varied from about 35 to 65% of the recoverable concentration, but only about 5–30% of the Mn was in particulate form. The recoverable metals cycles coincided with the tur-

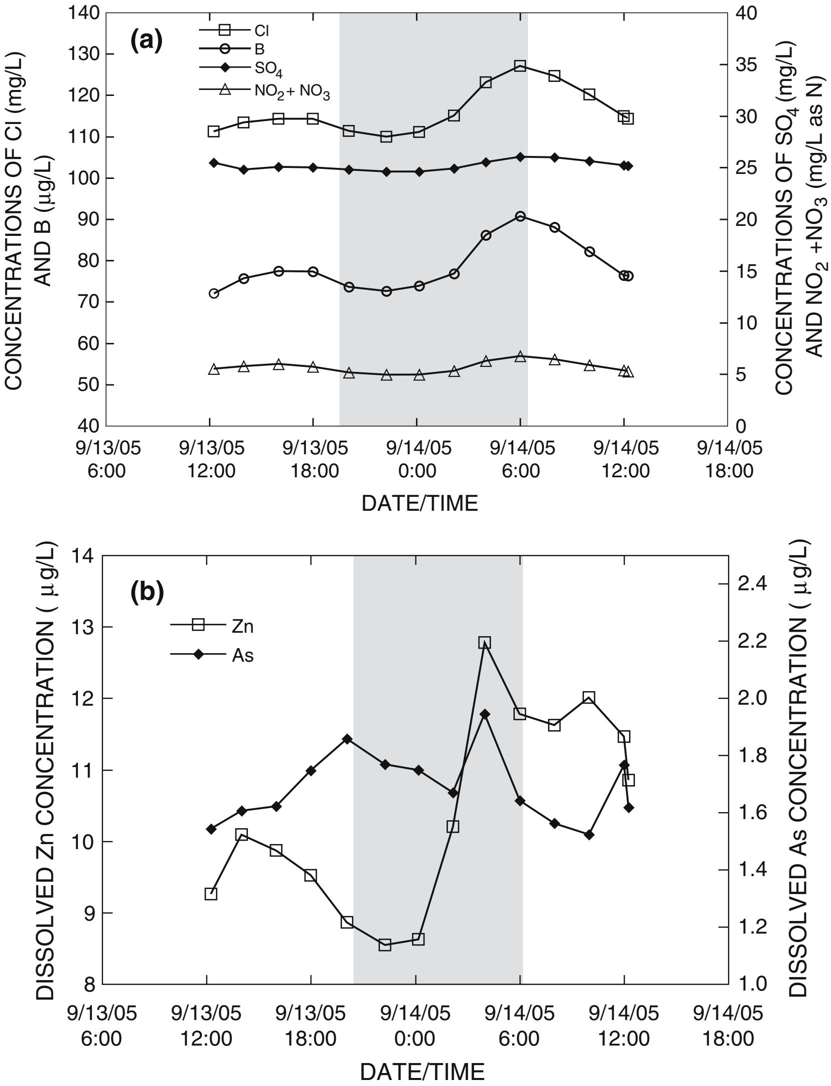


Fig. 3 Diurnal variations in concentrations of **a** B, Cl, SO_4 and $NO_2 + NO_3$ and **b** dissolved Zn and As in water at WAL-4, September 2005. (*Shaded area* shows nighttime hours.)

bidity cycle, as turbidity also increased during the night to a maximum at 0600 hours of the second day (Figs. 2a, 4a). The recoverable metals cycles were significantly related to turbidity ($R^2 = 0.51$–0.62; $t = 3.24$–4.04). The turbidity, recoverable, and particulate metals cycles peaked and declined while discharge continued to increase. Statistical relations of changes in turbidity and recoverable and particulate constituents with changes in discharge were not significant.

Statistical relations among concentrations of recoverable metals as well as those of particulate metals were significant ($R^2 = 0.83$–0.99; $t = 7.22$–28.8). Recoverable As concentrations showed a slight peak at night, but it was much smaller than the peaks of the recoverable metals (Fig. 4a). The magnitude of variations in recoverable As concentrations was small, and, based on As data for the filtered samples, most of the As at any given time was dissolved or colloidal, not particulate. Consequently, the evidence for a particulate As cycle is not strong.

A perturbation in concentrations of recoverable metals occurred at 0400 hours as it had the previous year, resulting in a sharp decrease in concentrations. This perturbation coincided with the sharp increase in dissolved As and Zn concentrations. A rerun of analyses of the recoverable metals indicated that the sharp decrease in concentration was unlikely to be analytical error.

Changes in dissolved Ca and Mg concentrations were significantly related to each other ($R^2 = 0.57$; $t = 3.82$). A decrease in concentrations occurred at 0400 hours at the same time as decreases in recoverable and particulate metal concentrations (Fig. 4a, b, Ca shown). Alkalinity concentrations also decreased at about the same time, but changes were not significantly related to those of Ca and Mg. The Ca and Mg concentration minima (at about 2200 h) nearly

Table 3 A Field parameters and concentrations of major ions and nutrients (filtered water samples), and (B) dissolved (d) and recoverable (acid-leachable (r)) trace elements in filtered and unfiltered water samples, respectively, from the Wallkill River at WAL-4, 13–14 September 2005

A	Date/ time	T (°C)	pH	DO (mg/L)	Turbidity (NTU)	SC (µS/cm)	Alkalinity (mg/L)[a]	Ca (mg/L)	Mg (mg/L)	NH_3 (mg/L)[b]	Cl (mg/L)	$NO_2 + NO_3$ (mg/L)[b]	PO_4 (mg/L)[b]	SO_4 (mg/L)
	9/13/05 1215	18.80	ND	9.05	3.40	871	233	66.0	33.1	0.036	111	5.53	0.065	24.4
	9/13/05 1400	19.60	7.88	9.45	2.90	872	230	66.0	33.1	0.036	113	5.77	0.073	24.8
	9/13/05 1600	20.58	7.97	10.28	2.53	877	227	65.4	32.7	0.038	114	6.00	0.076	25.1
	9/13/05 1800	21.33	8.03	10.52	2.01	874	226	64.5	32.3	0.036	114	5.75	0.078	25.0
	9/13/05 2005	21.67	8.10	10.58	2.70	853	228	64.9	32.5	0.037	111	5.19	0.072	24.8
	9/13/05 2215	21.79	8.09	9.93	4.36	847	229	64.2	32.5	0.036	110	4.98	0.071	24.6
	9/14/05 0010	21.49	8.05	9.18	4.63	851	229	65.4	32.9	0.034	111	4.95	0.069	24.6
	9/14/05 0210	21.05	7.96	8.15	7.28	858	224	67.0	33.1	0.039	115	5.33	0.069	24.9
	9/14/05 0400	20.44	7.86	7.05	7.46	898	224	64.8	32.8	0.044	123	6.30	0.070	25.5
	9/14/05 0600	19.80	7.80	6.75	7.67	914	225	67.7	33.0	0.048	127	6.73	0.070	26.0
	9/14/05 0800	19.20	7.77	6.54	6.87	920	229	66.9	33.1	0.048	125	6.45	0.076	26.0
	9/14/05 1000	19.16	7.78	6.65	4.64	899	227	67.5	33.3	0.048	120	5.89	0.076	25.6
	9/14/05 1200	19.60	7.86	7.72	4.92	880	233	68.2	33.5	0.045	115	5.39	0.067	25.2
	9/14/05 1205	ND	ND	ND	ND	ND	229	67.7	33.2	0.040	114	5.29	0.073	25.1

B	Date/ time	Al (d) (µg/L)	Al (r) (µg/L)	As (d) (µg/L)	As (r) (µg/L)	As(V) (µg/L)	As (III). (µg/L)[c]	B (d) (µg/L)	Fe (d) (µg/L)	Fe (r) (µg/L)	Mn (d) (µg/L)	Mn (r) (µg/L)	Zn (d) (µg/L)	Zn (r) (µg/L)
	9/13/05 1215	2.15	53.2	1.54	1.79	1.10	0.17	72.1	21.5	199	96.9	104	9.26	14.9
	9/13/05 1400	2.00	40.9	1.61	1.73	1.13	0.10	75.7	16.3	173	90.3	95.8	10.1	14.8
	9/13/05 1600	2.43	31.6	1.62	1.84	1.17	0.14	77.5	34.0	154	84.3	90.6	9.87	14.1
	9/13/05 1800	2.53	26.5	1.75	1.76	1.23	0.16	77.3	13.9	141	79.5	84.7	9.52	12.5
	9/13/05 2005	2.58	34.8	1.86	1.81	1.25	0.15	73.7	18.5	154	76.5	84.9	8.86	13.4
	9/13/05 2215	2.65	73.5	1.77	1.93	1.26	0.10	72.6	17.4	234	77.9	98.0	8.55	19.1
	9/14/05 0010	2.60	108	1.75	1.97	1.28	0.20	73.9	13.6	311	80.9	114	8.63	23.2
	9/14/05 0210	2.79	131	1.67	2.01	1.19	0.26	76.8	5.70	370	87.0	129	10.2	28.0
	9/14/05 0400	2.92	119	1.95	1.93	1.18	0.23	86.2	19.2	329	89.4	121	12.8	24.7
	9/14/05 0600	2.32	127	1.64	1.86	1.08	0.23	90.8	19.9	343	92.9	126	11.8	27.5
	9/14/05 0800	2.18	106	1.56	1.82	1.13	0.23	88.1	17.2	306	96.2	122	11.6	23.5
	9/14/05 1000	2.53	76.1	1.52	1.73	1.22	0.32	82.1	13.7	233	96.4	112	12.0	19.6
	9/14/05 1200	2.59	98.5	1.77	1.83	1.08	0.22	76.5	22.3	293	89.6	127	11.5	23.0
	9/14/05 1205	2.25	50.2	1.62	1.72	1.16	0.23	76.3	18.3	184	92.9	103	10.9	15.1

ND no data

[a] Alkalinity as $CaCO_3$

[b] N species as N; PO_4 (orthophosphate) as P

[c] Raw data; values below reporting limit and subject to uncertainty

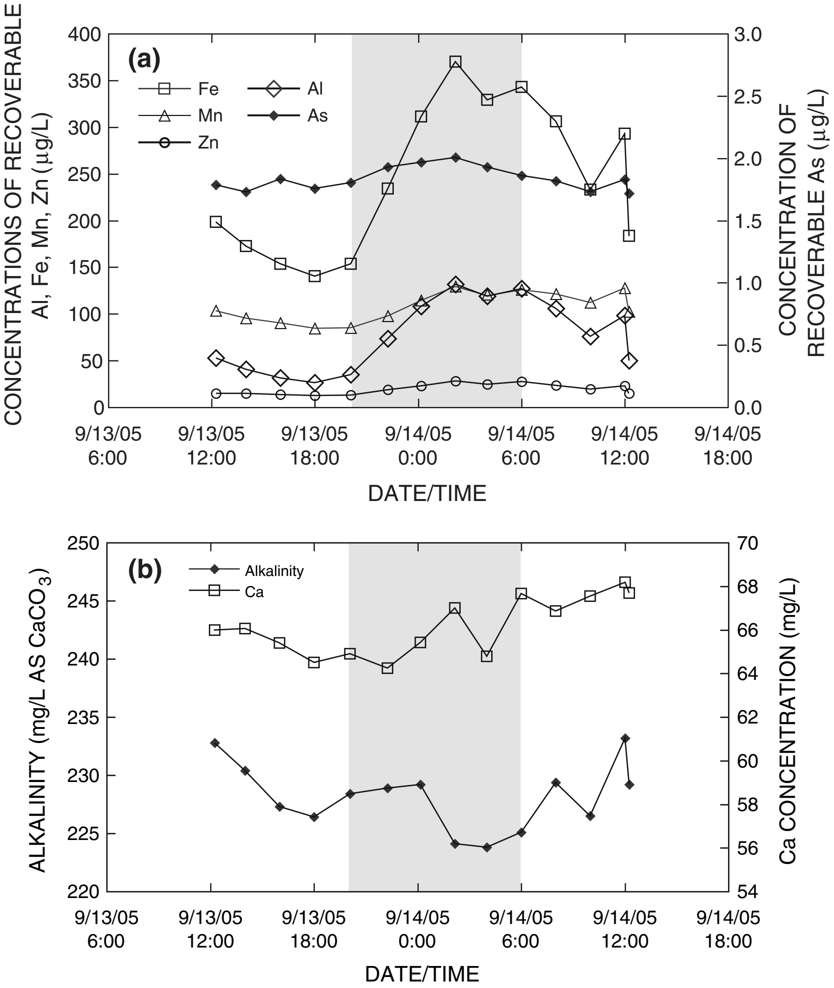


Fig. 4 Diurnal variations in concentrations of **a** recoverable metals and As, and **b** Ca and alkalinity in water at WAL-4, September 2005. (*Shaded area* shows nighttime hours.)

coincided with the pH maximum and the alkalinity minimum (Figs. 2b, 4b), but, probably because of scatter in the Ca, Mg, and alkalinity values, none of these cycles was significantly related to pH.

Equilibrium speciation calculations indicated that stream water at WAL-4 was oversaturated with respect to hydroxyapatite ($Ca_5(OH)(PO_4)_3$, ferrihydrite ($Fe(OH)_3$) and other Fe hydroxides and oxides, calcite ($CaCO_3$), and dolomite ($CaMg(CO_3)_2$), but slightly undersaturated with respect to Al, Mn, and Zn hydroxides and oxides. Calculations indicated that Mn was predominantly present as Mn^{2+}. Dissolved Zn, as an uncharged carbonate complex ($ZnCO_3$), accounted for about 40% of the Zn present (on a molal basis); Zn^{2+} and $Zn(CO_3)_2{}^{2-}$ were the other important forms. The water at WAL-4 was undersaturated with respect to willemite (Zn_2SiO_4), which is present in the bed sediments.

Repeatability of cycles, 2004 and 2005

Overall, the recoverable metals cycles in Wallkill River water at WAL-4 in 2005 (Fig. 4a) were similar to those in

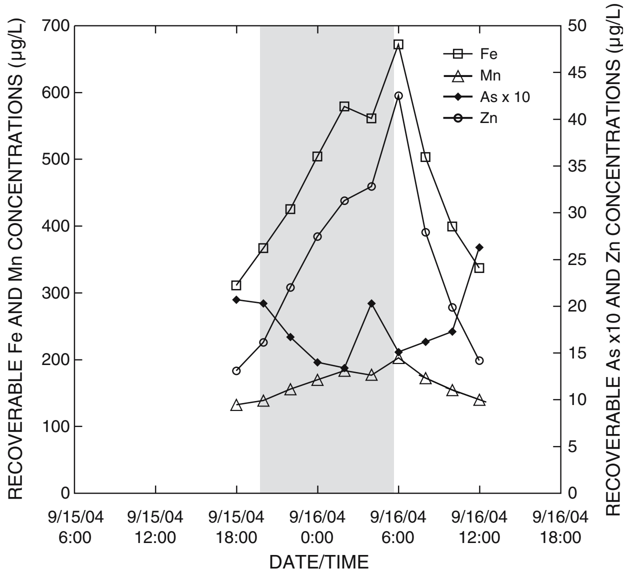


Fig. 5 Diurnal variations in recoverable metals and As concentrations in water at WAL-4, September 2004. (Data from Deluca et al. (2005); *Shaded area* shows nighttime hours.)

2004 (Fig. 5) including the perturbations in the cycles that occurred at 0400 hours. Therefore, these cycles appear to be repeatable over time. Moreover, data for the daytime filtered samples from 2004 (Deluca et al. 2005) indicated that the dissolved/particulate proportions for Fe, Mn and Zn were similar to the proportions determined in 2005. The recoverable As cycle in 2004, assumed on the basis of daytime filtered samples to represent mostly dissolved As, had a pattern more similar to the dissolved As cycle in 2005 than to the recoverable cycle in 2005. Additionally, the double-peaked cycle for B, with maxima at about 1800 and 0600 hours, occurred in both 2004 and 2005. Consequently, the cycle for B is repeatable over 2 years. SC exhibited a double-peaked cycle in 2004 similar to that in 2005. It is reasonable to assume that double-peaked cycles in concentrations of Cl, SO_4, and nutrients, not measured in 2004, occurred then also.

Discussion

Most of the diurnal cycles observed at WAL-4 have been observed in alkaline rivers in the western USA and in France where concentrations of As and metals are substantially higher than those in the Wallkill River. Parts of the area through which this eastern USA river flows are gradually yielding to urbanization, and so it is appropriate to question whether effects of development on the observed As and metals cycles at WAL-4 can be identified.

The double-peaked cycles for B, Cl, SO_4, and nutrients have not been reported in the studies cited herein. Cycles involving nutrients could be expected in rivers where rates of primary production are high; indeed, NO_3 concentrations in water from a Montana river varied diurnally, being low during the day and increasing during the night to a maximum at dawn. This fluctuation was attributed to uptake by biota during the day and release at night (Brick and Moore 1996). Similar daytime uptake of injected NO_3 was observed in a California stream (Triska et al. 1989). But no natural processes, such as biological uptake or sorption/desorption reactions, appear as plausible explanations for the double-peaked fluctuations in B, Cl, SO_4, and nutrients at WAL-4. The substantial increase in $NO_2 + NO_3$ concentrations during the summer of 2005, compared to that of an upstream site where nutrient inputs might be expected (Table 1, WAL-3), indicates a local source of nutrients to the river near WAL-4. The double-peaked fluctuations, particularly in concentrations of conservative constituents such as Cl, indicate pulsed inputs.

High concentrations of Na, B, Cl, SO_4, and nutrients are found in water affected by sewage/septic-system effluent (LeBlanc 1984; Ptacek 1998; Barringer et al. 2006b). Treated water discharges from the STP 4 km upstream from WAL-4 are continuous and unlikely to cause pulsed increases in concentrations of anions and nutrients at WAL-4. The nearby industrial facility discharges local groundwater from which VOCs have been air-stripped. Recently discovered unpermitted sewage discharges to a tributary about 1.5 km upstream from WAL-4 (L. Moore, NJDEP, 2006, personal communication) may have increased concentrations of B, Cl, SO_4, and nutrients in the river water, but nearby septic systems along the river upstream from WAL-4 could be a more likely source. The processes driving the other diurnal cycles in T, DO, pH, As, and metals, and the possible effects of septic-system effluent inputs and (or) other discharges on those processes are evaluated and discussed below, beginning with those processes known to drive various cycles and progressing to those the influences of which are less well understood.

Photosynthesis and respiration

It is well established that solar irradiance is a driver of diurnal cycles in T in stream water, and that photosynthesis and respiration by vegetation (in response to irradiance cycles) are drivers for diurnal cycles in DO and pH. These master variables, in turn, affect cycles of various constituents. The T and pH cycles at WAL-4 were small in amplitude (only 3°C for T and 0.33 units for pH). Both cycles at WAL-4 differed in timing, as did the DO cycle, from summer and fall cycles reported for some western USA streams. Differences in air temperature, elevation, latitude, and a shorter photoperiod in September than in summer months may account for larger amplitude T cycles in the western USA streams, but there could have been other influences on the T cycle at WAL-4. A small range in T at WAL-4 might, in turn, have affected photosynthesis and respiration rates, the range of oxygen solubilities, and the amplitude of the DO cycle.

The small amplitude of the pH cycle at WAL-4 could be ascribed to less biologically active macrophytes and algae in mid-September than during the height of summer. Amplitudes of pH cycles in other rivers have been shown to be larger in midsummer than in late summer (e.g., Nimick et al. 1998), and a decrease in amplitude of T, DO, and pH cycles in September relative to August at a site at a Montana river with substantial algal growth also was noted (Parker et al. 2005). The amplitude of the pH cycle at WAL-4 in September was, nonetheless, smaller than the September amplitude reported by Parker et al. (2005).

Maxima in T, DO, and pH cycles in western USA rivers and streams sampled during September typically, although not always, occurred in the afternoon, between about 1300 and 1800 hours (Nagorski et al. 2003; Nimick et al. 2003; Parker et al. 2005)—several hours before maxima in these cycles at WAL-4. Only in two Montana rivers (Nimick et al. 1998) were the pH cycles shifted as late as the cycle at WAL-4. The DO and pH cycles at WAL-4 were partly in phase with the Cl and related cycles ($R^2 = 0.61$ and 0.66, respectively, for DO and pH on Cl). There are several inputs, both natural and anthropogenic that could have affected amplitude and timing of T, DO, and pH cycles at WAL-4.

The causes of the cycle in streamflow observed in 2004 and 2005 (increase at night, decrease during the day) are likely to be mostly if not entirely natural. Evapotranspiration during the day by streamside vegetation can cause decreased shallow groundwater discharge leading to lower streamflow; the streamflow then increases as evapotranspiration declines at nightfall (Lundquist and Cayan 2002). Because T, DO, and pH of groundwater discharging to the Wallkill River in summer 2005 were lower than the surface water (Deluca et al. 2006), increased groundwater inputs during late afternoon and evening may have damped the rise in surface water T, DO concentration and pH, and affected both amplitude and timing of peaks. Additionally, it is possible that the treated groundwater discharge from the industrial facility to the wetlands could have a similar damping effect on amplitudes, and shift of peak timing. Permitted T and pH ranges for discharge from the facility are large, however [*T* to 30°C and pH from 6 to 9, respectively (L. Moore, 2007, personal communication)], so these effects could vary over time. Similarly, if T, DO, and pH of local effluent discharges differed from stream water T, DO, and pH, this also could affect amplitude and timing, although it seems this effect would be small. The relative effects of groundwater discharge, both natural and treated, and effluent inputs on T, DO, and pH would be difficult to test. Although the direct effects of any anthropogenic inputs to the river on T, DO, and pH cycles are not easily determined, local nutrient inputs to the river at WAL-4 have apparently encouraged the growth of macrophytes and algae and thus probably indirectly affect DO and pH cycles through enhanced photosynthesis and respiration.

Sorption/desorption reactions

The dissolved As cycle in western USA streams has been ascribed to As (V) sorption to and desorption from sediments (bed and suspended); these processes occur as stream water pH decreases and increases, respectively, over a 24-h period (e.g., Fuller and Davis 1989; Nimick et al. 2003). As (V) concentrations in stream water at WAL-4 generally increased as pH increased, indicating desorption is a likely explanation for increases in dissolved As (V) concentrations.

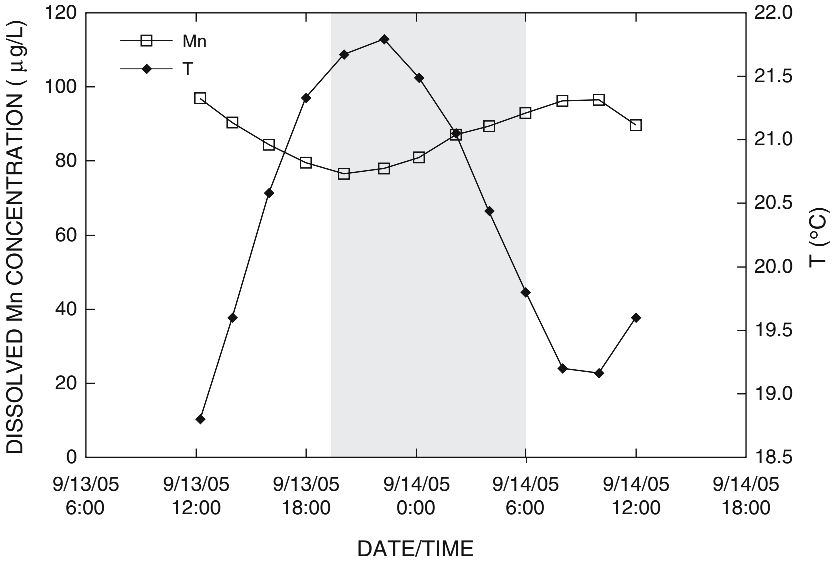
Overall, the dissolved As cycle mostly coincided with the pH cycle; both showed maxima at about 2000 hours and minima at 1000 and 0800 hours, respectively. At WAL-4, As probably is preferentially sorbed to amorphous Fe and Al hydroxides because, at slightly alkaline pH, As (V) shows the greater affinity for Fe and Al hydroxides than for organic matter or clays (Thanabalasingam and Pickering 1986; Goldberg 2002).

The coincidence of the dissolved As cycle with the pH cycle also occurs at sites on the Madison River, Montana (Nimick et al. 1998). In other western USA streams and rivers, the dissolved As cycle has been shown to lag the pH cycle, typically by several hours (e.g., Fuller and Davis 2003). Such a lag at Whitewood Creek, South Dakota, was ascribed to a kinetically slow approach to equilibrium (Fuller and Davis 1989). It has been shown that there is initially rapid sorption of As, within minutes (Raven et al. 1998; Jia and Demopoulos 2005); slow, diffusion-controlled sorption occurs later (Fuller et al. 1993). [Desorption has been shown to be hysteretic (Zhang and Selim 2005) and diffusion-limited (Fuller et al. 1993).] At WAL-4, As concentrations are several orders of magnitude lower than those in many of the western USA streams that are downstream from areas strongly affected by mining activities. Consequently, where there are relatively low As concentrations and relatively high concentrations of a (presumed) hydroxide substrate, pH-driven As sorption likely would be rapid (there is little to sorb) and As cycles would tend to coincide with pH cycles.

The dissolved Mn and Zn cycles at WAL-4 were anti-coincident to the dissolved As cycle, similar to the cycles shown for these metals and As in western USA rivers (e.g., Brick and Moore 1996; Nimick et al. 2003, 2005). The dissolved Mn cycle was anti-coincidental with the pH cycle and also the T cycle (Fig. 6). Although the dissolved Zn cycle at WAL-4 showed some similarities to that of the Mn cycle (Figs. 3b, 6), the anti-coincidence of the Zn cycle with the pH and T cycles was less clear because of the perturbation in Zn concentration at 0400 hours. Because cationic metals could be expected to sorb increasingly as sediments (suspended and bed) become less protonated as pH increases, and to desorb increasingly with increased protonation as pH decreases, sorption/desorption reactions are a reasonable explanation for the dissolved Mn and Zn cycles in the Wallkill River water. Competition for sorption sites from B contributed by the presumed effluent releases appears unlikely for these divalent cations, although B, mainly present as $B(OH)_3^0$ at the pHs of the river, does sorb to clays and Fe oxides and hydroxides (Kim and Kirkpatrick 2006, and sources cited therein).

Experiments by Shope et al. (2006) simulated Mn and Zn exchanges with biota and streambed materials, primarily algae and biofilms on boulders. Their results indicate that Mn and Zn concentrations in stream water responded not only to changes in pH but to changes in T as

Fig. 6 Diurnal variations in dissolved Mn concentrations and water temperature (*T*) in water at WAL-4, September 2005



well. Experiments by Jones et al. (2004) did not find a relation between Zn mobility and T, however. Because the T and pH cycles at WAL-4 were nearly coincident, the effect of changes in T alone on the Mn sorption/desorption cycle was not clear, although the relation appears strong (Fig. 6).

Competition with PO_4 for inorganic and organic (algal) sorption sites can inhibit As (V) sorption (Manning and Goldberg 1996; Kuwabara et al. 2003). At WAL-4, the dissolved As cycle lags the PO_4 cycle by about 2 h, which could demonstrate replacement of sorbed As by PO_4.

Precipitation and dissolution

Precipitation of Fe hydroxides on bed sediments likely is ongoing upstream at WAL-2, where groundwater discharge, at lower pH and DO than surface water, also contains higher Fe concentrations than surface water (Deluca et al. 2006, p. 539); this may occur at WAL-4 as well. Precipitation of Fe hydroxides seems unlikely to account for the cycles in metal-bearing particles, however, although the particles clearly contain Fe, as well as Al, Mn and Zn. Should any episodic precipitation of Fe hydroxides (on the order of minutes) occur at WAL-4, the bi-hourly sampling at WAL-4 would be unlikely to capture such events.

At the low concentrations of As in the river water, precipitation of an As-bearing mineral is unlikely, although As might be incorporated into a mineral such as apatite. Speciation calculations indicate that apatite could precipitate from the river water. Both apatite and monazite, a phosphate mineral associated with granites and gneisses (Hurlbut 1971), are present in the bed sediments at WAL-4. Because apatite occurs in the same rock types, materials weathered from the gneiss highlands are a likely source of the apatite in the bed sediments. Minima in Ca and PO_4 concentrations do not coincide; consequently, there is no evidence for apatite precipitation.

At WAL-4, concentrations of Ca (filtered sample) and alkalinity (Fig. 4b) varied over the 24-h sampling period in 2005, with decreases in the afternoon and increases during the early night. The cycle for alkalinity was roughly similar to the cycle from the year before (Deluca et al. 2005), and was similar to that reported by Fuller and Davis (2003) for Whitewood Creek, South Dakota, where the variation is ascribed to algal productivity. Fluctuations in Ca and Mg concentrations are cited as evidence for a diurnal cycle of carbonate precipitation and dissolution for a highly productive Indiana river (Tobias and Bohlke 2004). Whether the 0400-hours decrease in dissolved Ca and alkalinity concentrations at WAL-4 represented precipitation of a carbonate phase is not clear, however.

The equilibrium speciation calculations also indicated that, although dissolved Zn concentrations included Zn-carbonate species, the water at WAL-4 was oversaturated with respect to a Zn-silicate ($ZnSiO_3$) and, further, that willemite, one of the primary Zn ores from the Franklin mine upstream, would be dissolving. Presumably, some Zn is supplied to the water by dissolution of willemite, but whether Zn is also removed from solution by precipitation of another mineral phase, either a carbonate or silicate, currently is not clear.

Redox reactions

In acidic streams, photochemical reduction of Fe can cause daytime variations in dissolved Fe concentrations (McKnight and Bencala 1989; Gammons et al. 2005) and

Mn oxidation and removal by precipitation can be facilitated by light (Scott et al. (2002). Oxidation of As (III) also can be photochemically induced (Kocar and Inskeep 2003; Buschmann et al. 2005) and can occur in waters of circumneutral pH (Hug et al. 2001).

At WAL-4, where stream water is alkaline, no trend in the low concentrations of Fe in filtered samples could be detected; this Fe may have been colloidal. At the pH of the river water, rapid oxidation of any Fe (II) would be likely. Redox reactions involving microbial activity and Fe probably take place in the adjacent wetlands, but our data did not capture clear evidence for any diurnal redox reaction involving Fe in the river water. Although dissolved Mn concentrations decreased during the daytime, the anti-coincidence of the dissolved Mn cycle with the T, pH, and dissolved As cycles indicates sorption/desorption reactions are more likely than photo-oxidation and precipitation of Mn hydroxides to explain the dissolved Mn cycle.

Oxidation of As (III) by DO is a relatively slow process (days), although photo-induced oxidation of As (III) can occur within hours (Hug and Leupin 2003; Kocar and Inskeep 2003). Typically, both As (V) and As (III) are present in the oxic waters of the Wallkill River, indicating photo-induced oxidation probably is not a major process affecting As in the river water.

Reactions resulting in reduction of As (V) to As (III) can occur when algae take in As (V) along with PO_4; the algal metabolism reduces As (V) and produces methylated species. As (III) and the methylated species are subsequently released (Andreae 1979; Aurilio et al. 1994). These reactions also may have occurred at WAL-4; monomethylarsonate and dimethylarsinate have been detected in water samples collected at WAL-4 previously and during the diurnal sampling, but the detections were less than the LRL.

Physical processes

One of the questions that has arisen with regard to diurnal cycles is whether they are driven by physical or biogeochemical processes (e.g., Nimick et al. 2003; Shope et al. 2006). In both 2004 and 2005, streamflow at WAL-4 increased at dusk (2000 hours) to a high in the morning of the second day. This streamflow cycle did not coincide with the particulate metals cycles, where concentrations of particulate Fe, Mn, and Zn were declining as flow continued to increase (Fig. 7; Fe cycle shown). The particulate cycles do not appear to depend upon cycles in streamflow.

Biological activity

Where particulate metals cycles are reported, concentrations begin to increase at dusk and to decrease at or shortly after dawn (Brick and Moore 1996; Nagorski et al. 2003; Gammons et al. 2005). Such an increase in a Montana river was attributed to stirring and suspension of fine sediment particles by benthic invertebrates (Brick and Moore 1996). Some benthic organisms and zooplankton do migrate vertically for nocturnal feeding (Pearre 1979; Leibold 1990). Nevertheless, other types of biological activity may be involved in the particulate cycles and in the 0400-hours perturbation in the cycles seen at WAL-4.

Spring and autumn releases of DOC during algal blooms have been shown to decrease at night to a predawn minimum (Kaplan and Bott 1982). With increasing concentrations of DOC, colloidal Fe tends to be stabilized, and coagulation of colloidal material and scavenging rates of Fe by particles are inhibited (Curtis 1993). Therefore, although nocturnal behavior of aquatic invertebrates may stir and suspend sediments, variations in DOC releases from algae (and macrophytes) may play an important role in

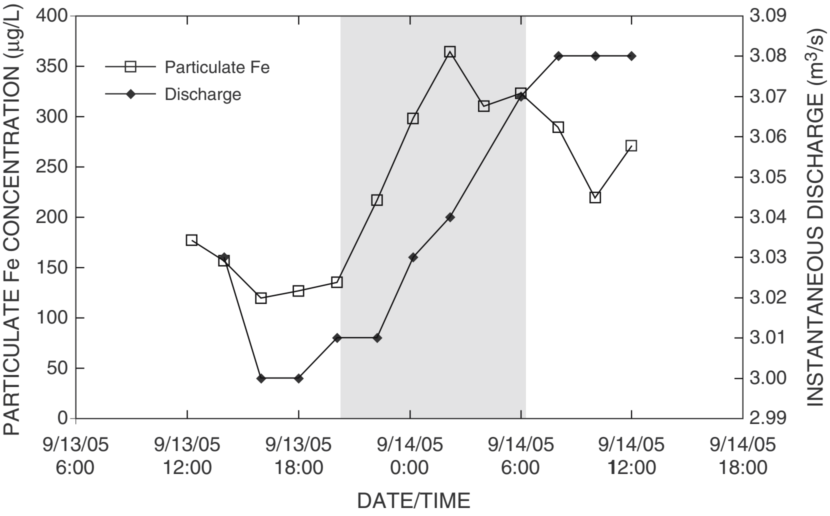


Fig. 7 Diurnal variations in streamflow (instantaneous discharge) and particulate Fe concentration at WAL-4, September 2005. (*Shaded area* shows nighttime hours.)

inhibiting metal scavenging by particles, in keeping particles in suspension, or in promoting coagulation and particle removal. The 0400-hours decrease in particulate metal concentrations appears to reflect removal of particles, which could be promoted by a decline in releases of DOC at about 0400 hours, as indicated by the Kaplan and Bott (1982) study. DOC was not measured in this study because the only available study of diurnal As and metals variations in which DOC was measured (Bourg and Bertin 1996) reported no DOC cycle. Clearly, at WAL-4, DOC data would have improved interpretation of the particulate cycles. Determining the nature of the metal-bearing particles—whether composed of inorganic or organic materials—also would shed light on the processes influencing the cycles.

The apparent release of As at 0400 hours (both in 2004 and 2005) when suspended metal-bearing particles were removed may indicate a change in particle surface charge. Because As (V) concentrations did not show a similar peak at 0400 hours, the ‘‘dissolved'' As peak could have represented release of As-bearing colloids. Microbially mediated reduction of ferrihydrite caused an increase in negative surface charge and release of As-bearing colloids (Tadanier et al. 2005), but ferrihydrite was also deflocculated in these experiments. The particulate Fe data for WAL-4 do not seem to support a deflocculation event at 0400 hours, but, rather, a brief incidence of particle removal. The processes involved in the 0400 perturbation may be yet more complex. The decrease in Ca and alkalinity concentrations at 0400 hours could perhaps indicate carbonate precipitation on suspended particles, insofar as rapid precipitation of Ca-carbonate can occur as bacteria degrade urea in solution (Warren et al. 2001). The processes causing the particulate cycles and the 0400 perturbations remain elusive.

Conclusions

Although concentrations were lower than in streams strongly affected by mining, diurnal variations in As and trace metal concentrations occurred in a wetlands reach of the Wallkill River. The dissolved As, Mn, and Zn cycles appear to be driven by sorption and desorption reactions related to changes in pH and, possibly, T. A particulate metals cycle, distinct from dissolved-metals cycles, appears to be caused by biological activities. Discharges of septic-system effluent probably caused double-peaked variations in major anions and nutrients; the nutrient inputs likely have encouraged macrophyte, algal, and microbial growth that can directly or indirectly affect As and particulate metal cycling. Discharges of groundwater, natural and treated, and the effluent discharges all may have affected amplitude and timing of T, DO, and pH cycles, which in turn would affect timing of dissolved metals cycles.

As noted by other researchers, diurnal variations in water characteristics and constituents indicate that a single water sample collected at a particular time during the day may not be fully representative of constituent concentrations in, or characteristics of, the river water. In particular, in instances where the constituents of concern are assessed as recoverable concentrations, nighttime sampling might be needed in order to capture peak concentrations in some river systems.

Anthropogenic inputs of nutrients to rivers elsewhere may complicate interpretation of diurnal cycles; this possibility indicates a need to determine more fully how biological activity in a river system affects inorganic geochemical processes. Characterization of suspended particles, of DOC, and the identification of any organic-carbon diurnal cycles (also SiO_2 cycles) would be useful in future work of this nature.

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