Sources and temporal dynamics of arsenic in a New Jersey watershed, USA

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Abstract

We examined potential sources and the temporal dynamics of arsenic (As) in the slightly alkaline waters of the Wallkill River, northwestern New Jersey, where violations of water-quality standards have occurred. The study design included synoptic sampling of stream water and bed sediments in tributaries and the mainstem, hyporheic-zone/ground water on the mainstem, and seasonal and diurnal sampling of water at selected mainstem sites. The river valley is bordered by gneiss and granite highlands and shale lowlands and underlain by glacial deposits over faulted dolomites and the Franklin Marble. Ore bodies in the Marble, which have been mined for rare Zn ore minerals, also contain As minerals. Tributaries, which drain predominantly forested and agricultural land, contributed relatively little As to the river. The highest concentrations of As (up to 34 µg/L) emanated from the outlet of man-made Lake Mohawk at the river's headwaters; these inputs varied substantially with season—high during warm months, low during cold months, apparently because of biological activity in the lake. Dissolved As concentrations were lower (3.3 µg/L) in river water than those in ground water discharging into the riverbed (22 µg/L) near the now-closed Franklin Mine. High total As concentrations (100–190 mg/kg) on the <0.63 µm fraction of bed sediments near the mine apparently result from sorption of the As in the ground-water discharge as well as from the As minerals in the streambed. As concentrations in river water were diluted during high stream flow in fall, winter and spring, and concentrated during low flow in summer. In unfiltered samples from a wetlands site, diurnal cycles in trace-element concentrations occurred; As concentrations appeared to peak during late afternoon as pH increased, but Fe, Mn, and Zn concentrations peaked shortly after midnight. The temporal variability of As and its presence at elevated concentrations in ground water and sediments as well as streamwater demonstrate the importance of (1) sampling a variety of media and (2) determining the time scales of As variability to fully characterize its passage through a river system.
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1. Introduction

Arsenic is toxic and a human carcinogen (National Research Council, 1999; USEPA, 2001) and has been measured in amounts that range from <0.5 µg/L to >5000 µg/L in natural waters (Smedley and Kinniburgh, 2002). The As that enters ground water and surface-water bodies can be derived from geologic materials, typically metalliferous deposits, through natural weathering processes. Anthropogenic sources of As to the atmosphere, soils, sediment, and water include mining

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and smelting operations; industrial releases; sewage-effluent discharges; applications of arsenical pesticides to crops, orchards, rights-of-way, and lakes; fertilizer use (including chicken manure); and leaching from arsenic-treated wood products (Woolson et al., 1971; Cullen and Reimer, 1989; Tamaki and Frankenberger, 1992; Bowell et al., 1994; Stillwell and Gorny, 1997; Arai et al., 2003; Dubey and Townsend, 2004; Durant et al., 2004).

In northwestern New Jersey, samples of the slightly alkaline waters of the Wallkill River (Fig. 1) have been collected for up to 45 years at various locations, but samples seldom have been analyzed for As. When analyzed, As concentrations in the river water have ranged from <1 to 29 µg/L, in some cases exceeding current World Health Organization (WHO), USEPA, and New Jersey maximum contaminant levels (10, 10 and 5 µg/L, respectively) (WHO, 1996; USEPA, 2001; N.J.A.C7–10 et seq), also the health-based New Jersey Surface Water Quality Standard, which is calculated as a 1:1,000,000 risk level for a carcinogen at 0.017 mg/L (N.J.A.C. 7:9B-1.5(c)2). Additionally, concentrations of As on bed sediments in several locations have exceeded the New Jersey Cleanup Criterion of 20 mg/kg for soils and sediments (N.J.A.C.7:26D). In accordance with the Federal Clean Water Act, the New Jersey Department of Environmental Protection (NJDEP) developed Total Maximum Daily Loads (TMDLs) for As for river reaches in the lower part of the Wallkill basin. Little was known about As concentrations at the river's headwaters prior to this study, however. The river is used for recreation and an impoundment at the river's midsection, Franklin Pond, has been used in the past as a drinking-water source.

This paper presents the findings of a study by the US Geological Survey (USGS) and NJDEP during 2004–05. Study objectives included determining where elevated levels of As enter the river system and by what medium (surface water, ground water, sediments), and identifying temporal fluctuations in As concentrations and the processes controlling As variability.

2. Study area

2.1. Hydrology and geology

Average annual precipitation (1895–1999) to the Wallkill River watershed is about 117 cm. The river flows north into New York State, and since 1927, has originated at the outflow of shallow (<7 m deep) Lake Mohawk, which was created on former wetlands and pastureland (Kummel and Vermeule, 1916). The river

channel lies on valley fill of glacial sands and gravels (Stone et al., 2002) underlain by faulted Cambrian and Ordovician dolomites and the Middle Proterozoic Franklin Marble; the channel is bordered by Middle Proterozoic gneiss and granitoid rock highlands at the headwaters and to the east, and shale lowlands to the west (Drake et al., 1996) (Fig. 1). Wetland areas are present south of Franklin Pond and also near the New York State border where the river channel lies within the Wallkill River National Wildlife Preserve.

Two ore bodies within the Franklin Marble were mined for the rare zinc minerals franklinite, zincite, and willemite; the ore assemblages included As-bearing minerals—primarily arsenopyrite and loellingite—but also Mn-, Zn-, and other metal-bearing arsenates and arsenate-hydrates (Dunn, 1995). The river channel is immediately adjacent to the sites of the Sterling Hill and Franklin mines.

Minor tributaries enter the river from the gneiss and granite highlands to the east and from Paleozoic sedimentary rocks that form lowlands to the west. Papakating Creek, the major tributary to the river in New Jersey, flows through glacial deposits underlain by shale bedrock (Drake and Monteverde, 1992) and enters the river from the west downstream from (north of) Franklin Pond (Fig. 1).

For the purposes of this study, we have divided the Wallkill Basin into an upper basin (upstream from (south of) Franklin Pond), and a lower basin (downstream from (north of) Franklin Pond to the New York border). Upper-basin sampling sites on the river are designated WAL-A through WAL-D; lower-basin sites are designated WAL-1 through WAL-5.

2.2. Land use

The watershed (540 km² in Sussex County) is one of the more rural areas in New Jersey. Urban/suburban development has been more intense in the upper (southern) part of the river basin than in the lower (northern) part near the border with New York State. Mining took place throughout the watershed from the early 18th century into the late 20th century—iron ores were extracted from mines in the Proterozoic gneisses and the Marble. Ores were processed from the late 18th through the late 19th centuries at the Franklin Furnace, adjacent to Franklin Pond. The Zn minerals (shipped to Pennsylvania for processing (NJDEP, 2004)) were extracted throughout the 19th and much of the 20th century from mines in the Franklin Marble at Sterling Hill and Franklin. These mines closed in 1986 and 1954, respectively (Dunn, 1995). There are

now museums and waste-rock dumps at both mine sites.

Agriculture, which currently comprises dairy farms and row crops, has long been present in the watershed. There are no poultry farms, to the authors' knowledge. Orchards have not been extensive, and few remain. A golf course borders the western shore of Lake Mohawk; the lake is also surrounded by unsewered residential
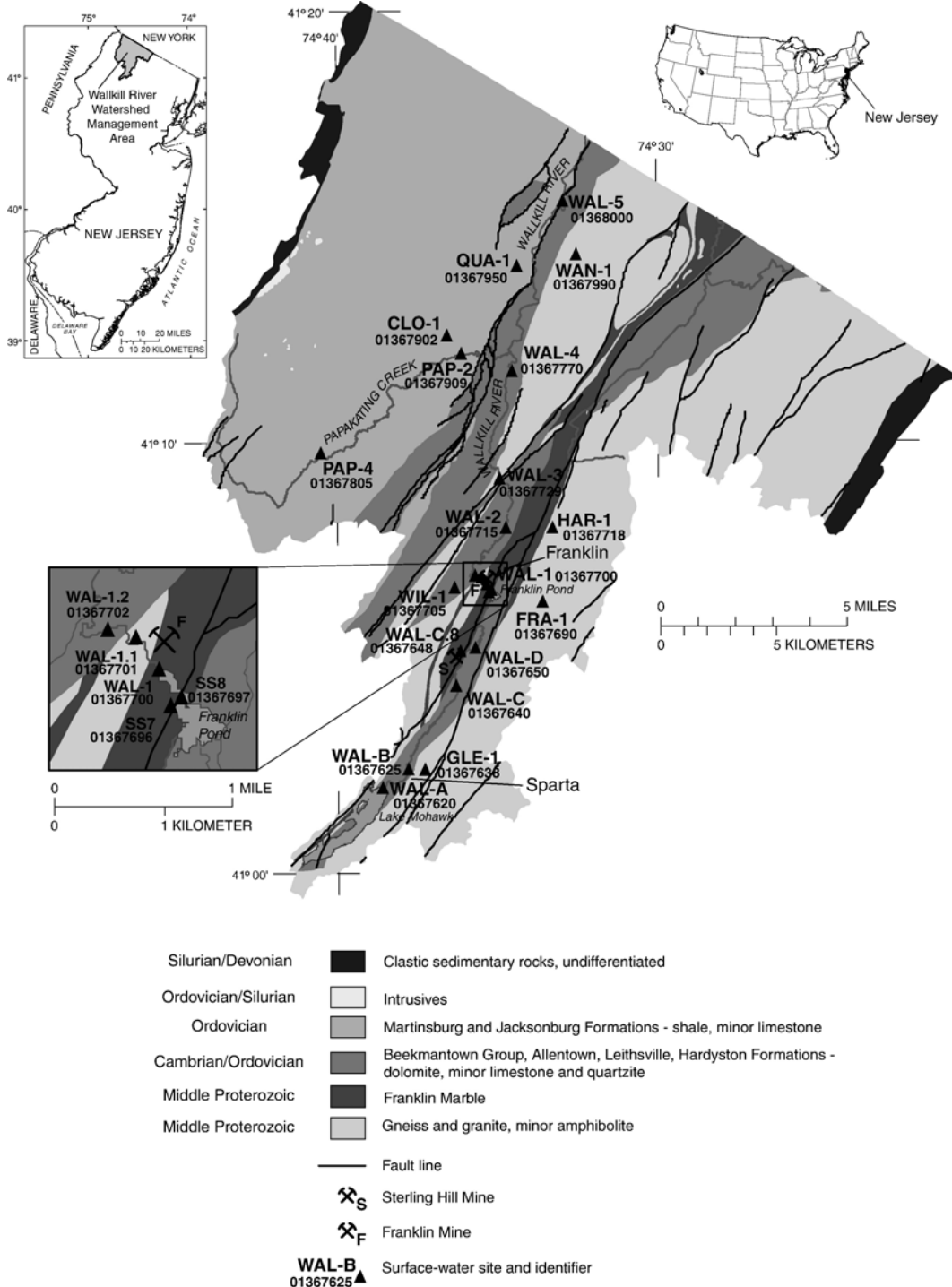

Fig. 1. Bedrock geology of the Wallkill River watershed, locations of Sterling Hill and Franklin Mines, and sampling sites. Low-order streams not shown.

development (commercial properties, below the lake in Sparta, are served by a small sewage-treatment plant). Algal blooms in the lake have resulted from an influx of nutrients, and are now controlled with copper sulfate. Alum currently is added to lake water to control PO_4, and aerators in the lake operate during the summer (E. Hofer, Sussex Co. MUA, 2005, pers. commun.). A golf course borders the river in the Borough of Franklin. Boroughs (including Franklin) in the lower (northern) part of the watershed are served by a municipal sewage-treatment plant that discharges to the river; rural areas are unsewered. Other permitted, relatively small discharges to the river include several local schools and two industrial facilities. Of the few scattered hazardous-waste sites in the watershed, at which volatile organic compounds are the principal contaminants, none are known to be arsenic sources.

3. Methods

3.1. Sample collection and analysis

Samples for this study were collected from July 2004 to September 2005, and included synoptic sampling of the river in the lower basin (August/September 2004) before Franklin Borough's scheduled dredging of Franklin Pond sediments in fall 2004. (These sediments had been found to contain high concentrations of As and Zn (up to 99 and 4870 mg/kg, respectively; Killam Associates (2001)).) Synoptic sampling of tributaries and the river in the upper basin took place in October 2004, and a one-day synoptic of the river's mainstem was carried out in April 2005. Both river water and ground water/hyporheic-zone water discharging to the river were sampled in gaining reaches during July and August 2005. River water also was sampled at selected sites during 2004–05 to determine seasonal variability in As concentrations. Additionally, bi-hourly sampling over a 24-h period in September 2004, was done using automated samplers to assess diurnal variations in As and metal concentrations at two sites (WAL-2 and WAL-4).

Unfiltered grab samples were collected at the centroid of flow for trace-element analysis in acid-washed, field-rinsed bottles at WAL-1 in July 2004. Because the river at the lower-basin sampling sites was well mixed, samples collected just prior to dredging in August were collected as grab samples from the centroid of flow. Subsequent grab samples were collected using an equal-width-interval method and composited in acid-washed churns. Samples for determination of arsenic species were collected as grab samples from the centroid of flow to avoid aeration that might affect As speciation.

Samples were processed, filtered, and preserved in glove bags in "clean" vans by personnel wearing powder-free disposable gloves that were changed between samples; tubing was acid washed, disposable 0.45-μm pore-size polysulfone capsule filters were rinsed with de-ionized water and then field rinsed with >250 mL of sample, and both tubing and filters were disposed of between samples. Samples for analysis of As species were preserved with EDTA (Garbarino et al., 2002). Samples for metals, total nutrients, and DOC analysis were preserved with ultrapure HNO_3 (metals) and H_2SO_4.

Field measurements of water temperature (T), pH, specific conductance (SC), and DO were made using YSI 6-series multiparameter sondes. Bed-sediment samples were collected at all sites using acid-washed plastic scoops and 2-mm opening-size sieves, or, in one case of unwadeable conditions, a clean BMH60 mechanical scoop from a bridge. Two sediment cores were collected from dredged areas on the east and west sides of Franklin Pond in January 2005, using a 1-m-long stainless-steel corer with butyl acetate liners. The method, including quality assurance measures and sample preparation, is described in Barringer et al. (1998).

About 10% of the environmental samples were collected as split replicates (from the same water in the churn) or as time-sequential replicates (samples collected and processed within about 5 min of one another). A sample spiked with arsenite/arsenate/methyl-As was analyzed for As species. Analyte-free water was passed through tubing and filters, and samplers and churns were rinsed with analyte-free water to provide equipment blanks for the various sampling rounds.

Sampling to determine diurnal fluctuations took place over about 26 h at WAL-2 and WAL-4 in September 2004 at base-flow conditions. During daylight hours, grab samples were collected from the centroid of flow in acid-washed, field rinsed bottles at approximately 2-h intervals and were processed immediately for analysis for selected unfiltered and filtered metals and As. An ISCO automatic sampler at each site collected unfiltered samples in acid-washed bottles every 2 h over a 24-h period. The ISCO sample bottles for metals analysis were preacidified with HNO_3. Field measurements of T, pH, SC, and DO were made using a YSI sonde. Replicates and blanks were collected during diurnal sampling as they were in the watershed sampling rounds. An open bottle containing analyte-free water was positioned at the center of each ISCO sampler to determine any sample contamination during the hours in which the samplers were operating.

Table 1
Analytical methods, precision, and reporting limits for selected characteristics and constituents in water and sediment samples

Characteristic/constituent—water	Method	Precision[a], RPD[b] or RSD[c]	LRL[d]
Temperature (°C)	Data sonde	0.15 °C[a]	na[e]
DO (mg/L)		2%[a]	
pH (units)		0.2 units[a]	
SC (μS/cm)		5%+1 μS/cm[a]	
Alkalinity (mg/L as CaCO$_3$)	Titration	0.007–0.02%[b]	5
Ca (mg/L)	ICP/AES[f]	1.0–4.3%[b]	0.02
Cl (mg/L)	Ion chromatography	0.09–1.0%[b]	0.20
Mg (mg/L)	ICP/AES[f]	0.9–2.0%[b]	0.008
Na (mg/L)		0.9–3.8%[b]	0.20
NH$_3$ (mg/L as N)	Colorimetry	10%[c]	0.04
NO$_2$+NO$_3$ (mg/L as N)		1.2–2.0%[b]	0.016
PO$_4$ (mg/L as P)		10%[c]	0.006
SO$_4$ (mg/L)	Ion chromatography	0.025–0.16%[b]	0.18
SiO$_2$ (mg/L)	ICP/AES[f]	0.32–1.5%[b]	0.018
DOC (mg/L)	Infra-red spectrometry	1.4–17%[b]	0.4
As (u, f) (μg/L)	AAS[g]; ICP/MS[h]	14.8–38%[b], 0.4–6.8%[b]	0.12, 0.12
As (V) (f)(μg/L)	ICP/MS[h]	7.9%[b]	0.8
As (III) (f) (μg/L)		3.3%[b]	0.6
B (f) (μg/L)	ICP/AES[f]	1.1–3.2%[b]	7.0
Fe (u, f) (μg/L)		0.8–2.3%[b], 0.18–11%[b]	6, 6
Mn (u, f) (μg/L)		0.39–1.8%[b], 1.2–1.5%[b]	0.6, 0.6
Zn (u,f) (μg/L)		0.34–9.9%[b], 0.7–27%[b]	2, 0.6
Constituent (total)—sediment			
As (mg/kg)	ICP/MS[h]	1.6–11.2%[c]	0.1
Cu (mg/kg)		2.3–15%[c]	1
Fe (wt.% element)		1.4–2.9%[c]	0.005
Mn (mg/kg)		0.7–2.0%[c]	4
Pb (mg/kg)		1.4–5.8%[c]	1
Zn (mg/kg)		0.9–3.7%[c]	2
Constituent (recoverable)—sediment			
As (mg/kg)	AAS[g]	11%[c]	1
Cu (mg/kg)	ICP/MS[h]	6–8%[c]	2
Fe (mg/kg)		8%[c]	2.1
Mn (mg/kg)		4–8%[c]	0.3
Pb (mg/kg)		9%[c]	0.001
Zn (mg/kg)		6–7%[c]	3.1

u = unfiltered; f = filtered.
[a]From YSI 6-Series Multiparameter Water Quality Sondes User Manual, 2005.
[b]RPD from replicate samples, this study.
[c]RSD = Relative standard deviation (unpublished 2005–06 NWQL data, G. Cottrell, USGS, written commun.; Briggs and Meier, 2002).
[d]LRL = Lower reporting limit, which is 2× the minimum detection limit.
[e]na = not applicable.
[f]ICP/AES = inductively coupled plasma/atomic emission spectrometry.
[g]AAS = Atomic absorption spectroscopy.
[h]ICP/MS = inductively coupled plasma/mass spectrometry.

Ground-water- and hyporheic-zone-discharge samples were collected under base-flow conditions from clean stainless-steel piezometers (either 1.27- or 0.64-cm ID with slotted screens) that were emplaced with a hammer drill in water-bearing strata in gaining reaches of the river, most at depths ranging from 30 to 60 cm below the streambed, at eight sites. Prior to sample collection, hydraulic heads of water in the piezometers and the river were measured using a manometer to determine gaining and losing reaches. After placing the piezometers, they were purged with a peristaltic pump until field parameters stabilized; T, pH, SC, and DO were measured with a YSI sonde in water flowing into a clean polyethylene cup. The ground-water/hyporheic-zone water samples were collected through acid-washed tubing with the peristaltic pump; the pump rate was about 530 ml/min. Surface-water samples were collected from the same location as grab samples from the centroid of flow, and field parameters were measured with the sonde. Samples were filtered, bottled, and preserved using ultraclean techniques and acid-washed supplies.

The water samples collected on the mainstem and tributaries were analyzed for major ions (filtered samples), alkalinity, and suspended sediment following standard methods (Table 1; see http://water.usgs.gov/pubs/twri/ for method references). Hereafter in this paper, all trace-element concentrations in filtered samples (the "dissolved" concentration, which may include colloids) are designated with the subscript f (as in Zn_f) and those in unfiltered samples (acid-leachable or recoverable) with a subscript u (as in Zn_u).

Forty-two major, minor, and trace elements were determined on the <63 mm fraction of bed sediments by ICP-MS using a Perkin Elmer Elan 6000 at the USGS Geologic Division (GD) Laboratory, Denver, CO. Samples were powdered and digested using a mixture of HCl, HNO_3, $HClO_4$, and HF (Arbogast, 1996; Briggs and Meier, 2002). (Not all elements are reported herein.) Additionally, the <2 mm fraction was analyzed for selected recoverable elements extracted with dilute HCl at the USGS NWQL.

Mineral separation, using a Frantz hydrodynamic separator and heavy liquids, were performed on selected samples at the USGS GD Laboratory, Mineral separates (C-1, magnetic; C-2, semi-magnetic; C-3; non-magnetic) and bedrock samples of the Franklin Marble and Allentown Dolomite were powdered, digested with an acid mixture, and analyzed for As using hydride generation and atomic absorption spectroscopy (AAS).

Bulk sediments (<2 mm fraction) were analyzed for mineralogical content by X-ray powder diffraction (XRD) using Cu Kα radiation on a PANalytical Xpert PRO MPD diffractometer at the University of Pennsyl-vania and at the USGS GD Laboratory, using Cu Kα radiation on a Scintag 1-X X-ray diffractometer. The mineral separates and samples of Franklin Marble and Allentown Dolomite also were analyzed by XRD at the GD laboratory. Additionally, the C-3 mineral separate from WAL-1 was examined optically; semiquantitative chemical analysis of As-bearing minerals was done using a JEOL JSM-5800LV scanning electron microscope (SEM/EDX) at the USGS GD laboratory.

3.2. Flow measurements

Low-flow measurements were made by wading according to standard USGS techniques, using a Price AA or a pygmy current meter mounted on a depth-setting wading rod. High-flow measurements from bridges were made using a Price AA current meter, depth-setting reel with suspension cable, and portable crane. In each case, the products of depth, width, and velocity from 20 or more partial stream sections were summed to obtain the total instantaneous discharge. During the diurnal sampling, river stage at the downstream wetlands site (WAL-4) was determined on a staff gage, and converted to discharge using a rating curve established for that site.

3.3. Geochemical modeling and statistical analysis

Equilibrium speciation calculations were done for water samples using PHREEQC (Version 2; Parkhurst and Appelo, 1999). The data set for this study is small, but non-parametric Spearmans rho (ρ) was used to determine correlations between constituents and characteristics of the river water where the number of observations was sufficiently large for analysis.

4. Results

Concentrations of As in tributary waters were lower than those in the mainstem, and those in mainstem waters were low in comparison with those reported recently in several rivers affected by geothermal inputs or mining activities (e.g., Nimick et al., 1998; Frau and Ardau, 2003; Olías et al, 2004). Consequently, minimal opportunity for sample contamination as well as maximal precision of analysis were important in identifying variations, either spatial or temporal, in concentrations of As and of associated trace elements in water in the Wallkill watershed. Results of quality-assurance measures indicated that observed concentration variations represented the results of differing inputs and effects of geochemical and (or) biochemical processes. Determining how and why As partitions

Table 2a
Discharge (Q), field pH, and concentrations of DO and As in unfiltered ($_u$) and filtered ($_f$) water samples from tributaries to the Wallkill River

Site name	Date	Q (m^3/s)	pH (units)	DO (mg/L)	As_u ($\mu g/L$)	As_f ($\mu g/L$)
GLE-1	10/13/04	0.125	8.06	10.1	nd[a]	0.24
FRA-1	10/13/04	0.170	7.45	10.5		0.30
WIL-1	10/13/04	0.077	7.34	7.09		0.21
HAR-1	10/28/04	0.028	7.41	10.1		0.16
PAP-4	10/28/04	0.456	7.38	12.2	0.25[b]	0.32
CLO-1	10/28/04	0.402	7.96	12.2	0.60[b]	0.32
PAP-2	10/28/04	1.303	7.47	10.7	nd[a]	0.35
QUA-1	10/28/04	0.091	7.51	12.1	0.29[b]	0.25
WAN-1	10/28/04	0.002	7.85	10.7	0.38[b]	0.49

[a] nd; not detected (raw data indicate concentrations ~zero).
[b] Raw data, below the lower reporting limit, so value is uncertain.

into different media and assessing the spatial and temporal variability in As concentrations is key to understanding how such a constituent of concern moves through a watershed.

4.1. Quality assurance

Analytical results indicate that concentrations of constituents consistently were undetected in equipment blanks (tubing, filters, churns) or (for a few major ions) barely detected at concentrations several orders of magnitude below levels measured in the environmental samples. As was never detected. Mn and Zn were detected at lower reporting limits (LRLs) in one or two blanks, respectively. Fe, Mn, and Zn were detected at concentrations less than LRLs but at minimum detection limits (MDLs) in one or both blanks from the open bottles at the ISCO samplers (Table 1).

Cation/anion balances for all water samples were within 3%. Relative percent differences (RPDs) for three replicate sets were <5% for most trace elements but the RPD for Zn_f at low concentration in one replicate set was higher and was also higher for Fe_f in another replicate set (Table 1). RPDs for As_f were 0.4%, 0.8% and 6.8% (the 2005–06 NWQL relative standard deviation for As_f analyses is 6%). The RPDs for As_u were substantially higher than those for As_f (Table 1), reflecting a lesser degree of analytical precision for the available method (AAS) at As concentrations <5 $\mu g/L$; precision is improved at higher concentrations, however. The RPD for arsenite was 3.3%; for arsenate, it was 7.9%. The sum of As species concentrations was about the same as, or slightly less than, the corresponding As_f concentration; concentrations of species commonly do not sum to the filtered total As concentration because As-bearing colloids are removed in the column used for

species separation before analysis. For As and metals in sediments, the relative standard deviations (RSDs) are generally less than 5% (Table 1), except for samples with concentrations near the MDL.

4.2. Streamwater

As_f concentrations in tributary waters ranged from 0.16 to 0.49 $\mu g/L$ in fall 2004. As_u concentrations in some tributary samples were below the LRL, but, where detected, were about the same as the As_f concentrations (Table 2a). Concentrations of As from the largest tributary (Papakating Creek) were similar to those of other tributaries, but although the concentrations were low, the As load from the Papakating Creek is relatively large because of the large volume of water from the creek.

In the October 2004 base-flow sampling of the upper basin, As_u and As_f concentrations were highest (20.6 and 16.5 $\mu g/L$) in the headwaters at WAL-A and decreased downstream to about 2 $\mu g/L$ at WAL-D, about 1 km downstream from the Sterling Hill mine site. At WAL-A, As concentrations decreased substantially during the following winter and spring but increased throughout the summer of 2005 to levels measured the previous fall. Concentrations of As_f at the downstream sites WAL-B through WAL-D were lowest during the spring of 2005 and highest during the following summer (Tables 2b, 3).

In the lower basin, under moderate flow conditions after an abnormally wet month, As_u concentrations in late August/early September 2004, were about 3.0 $\mu g/L$ at WAL-1 and WAL-2 (adjacent to and downstream from the Franklin mine site), and even lower in April 2005, under similar flow conditions. During the dry summer of 2005, As_f concentrations were higher than spring concentrations at sites WAL-1 through WAL-4 (WAL-5 was not sampled). In general, As_f concentrations in river water were less than As_u concentrations (Table 2b), indicating roughly about 10–30% of As was present on particles in the majority of samples. In the seasons sampled, concentrations of As_f decreased downstream from the Franklin area.

Seasonal variations in As_f concentrations in water from WAL-A and WAL-4 were apparent; higher concentrations occurred in warm months, lower concentrations in cold months; the seasonal variations were substantially larger than any variations due to analytical error (Fig. 2a, b). The As_f concentrations were strongly and negatively related to discharge ($\rho = -0.90$) at WAL-A, but were not at WAL-4 ($\rho = -0.20$). Concentrations varied seasonally at WAL-1 as well, but, because As-rich sediments were removed during fall

Table 2b
Discharge (Q), field pH, and concentrations of selected constituents in unfiltered ($_u$) and filtered ($_f$) water samples from the Wallkill River

Site name/sampling date	Q (m^3/s)	pH (units)	DO (mg/L)	As$_u$ (µg/L)	As$_f$ (µg/L)	AsV (µg/L)	AsIII (µg/L)	B$_f$ (µg/L)	Cl (mg/L)	Fe$_u$ (µg/L)	Fe$_f$ (µg/L)
WAL-A											
10/13/04	0.18	8.26	8.58	20.6	16.5	–	–	25.2	98.6	89.2	16.7
03/02/05	0.29	7.68	8.21	3.18	3.71	1.76	0.41	26.6	96.2	6.85	5.54
04/19/05	0.36	8.39	10.8	3.22	3.14	1.21	1.45	22.5	94.7	27.3	<6
06/07/05	0.15	8.30	8.69	7.53	6.62	5.16	0.35	21.0	96.9	31.2	<6
07/27/05	0.03	7.27	8.91	34.2	27.7	24.5	3.02	24.6	103	58.4	<6
WAL-B											
12/08/04	0.31	7.38	12.1	3.85	3.33	–	–	19.1	101	138	29.1
02/14/05	0.40	7.88	13.5	<2	2.53	–	–	16.5	119	684	22.3
04/19/05	0.49	8.22	10.6	3.15	2.92	1.69	0.98	20.4	109	127	25.1
WAL-C											
10/13/04	0.45	7.75	9.99	3.99	3.10	–	–	16.2	84.2	400	113
04/19/05	0.96	7.94	–^{a}	1.51	1.46	0.37	0.47	15.5	84.4	382	109
WAL-D											
10/13/04	0.57	7.49	9.97	1.86	2.16	–	–	18.1	84.5	298	92.0
04/19/05	1.28	7.69	10.6	1.96	1.29	0.54	0.49	17.1	85.0	289	108

Site name/ sampling date	Mn$_u$ (µg/L)	Mn$_f$ (µg/L)	Na (mg/L)	NH$_3$+N (mg/L as N)	NO$_3$+NO$_2$ (mg/L as N)	P$_u$ (mg/L)	SiO$_2$ (mg/L)	Zn$_u$ (µg/L)	Zn$_f$ (µg/L)	DOC (mg/L)
WAL-A										
10/13/04	85.0	7.27	50.1	0.80	0.05	0.04	1.46	1.61	1.84	3.32
03/02/05	1.36	1.34	–	–	–	–	–	12.4	3.97	–
04/19/05	17.2	2.26	48.9	0.29	0.06	ND	0.07	1.03	2.04	2.72
06/07/05	29.5	2.27	48.8	–	–	–	0.34	1.03	11.6	–
07/27/05	91.8	3.37	53.7	0.83	0.01	0.04	1.01	1.19	1.95	–
WAL-B										
12/08/04	32.5	14.6	53.1	0.24	0.27	0.03	5.34	3.32	1.48	3.08
02/14/05	132	17.3	61.5	0.17	0.48	0.03	4.13	13.0	4.68	2.21
04/19/05	32.5	16.2	57.3	0.35	0.31	0.03	2.21	2.52	1.97	2.34
WAL-C										
10/13/04	82.4	75.2	44.9	0.22	0.39	ND	8.36	2.61	2.28	3.18
04/19/05	116	98.9	45.7	0.22	0.30	0.02	3.85	3.64	2.21	2.55
WAL-D										
10/13/04	90.8	83.8	47.1	0.26	0.38	0.02	8.72	18.9	11.9	3.24
04/19/05	112	107	44.5	0.23	0.32	0.02	4.37	14.1	19.4	2.55

Site name/ sampling date	Q (m^3/s)	pH (units)	DO (mg/L)	As$_u$ (µg/L)	As$_f$ (µg/L)	AsV (µg/L)	AsIII (µg/L)	B$_f$ (µg/L)	Cl (mg/L)	Fe$_u$ (µg/L)	Fe$_f$ (µg/L)
WAL-1											
08/26/04	1.99	7.80	9.97	2.99	2.25	1.41	0.68	16.3	54.8	423	138
04/19/05	1.85	8.27	10.0	1.78	1.19	0.49	0.43	15.8	80.6	259	70
WAL-1.1											
06/07/05	1.02	8.36	7.84	4.20	3.23	1.31	1.02	17.7	87.8	387	182
WAL-1.2											
06/07/05	0.87	8.29	7.37	4.06	3.30	1.52	0.88	21.3	92.4	357	171
WAL-2											
09/01/04	1.14	7.99	13.9	3.06	2.49	1.35	0.11	22.9	71.0	297	86.9

Table 2b (continued)

Site name/ sampling date	Q (m³/s)	pH (units)	DO (mg/L)	As$_u$ (µg/L)	As$_f$ (µg/L)	AsV (µg/L)	AsIII (µg/L)	B$_f$ (µg/L)	Cl (mg/L)	Fe$_u$ (µg/L)	Fe$_f$ (µg/L)
WAL-2											
04/19/05	2.55	7.98	10.8	1.04	1.07	0.45	0.43	17.1	68.1	213	68.0
WAL-3											
08/26/04	–[a]	8.14	8.97	2.80	1.98	1.28	0.37	20.1	53.1	379	66.5
04/19/05	2.69	8.25	11.0	4.14	1.10	0.40	0.38	22.5	72.7	210	72.0
WAL-4											
08/26/04	3.23	7.71	8.32	2.63	1.87	1.27	0.44	22.7	54.8	480	106
02/14/05	2.18	7.63	13.0	2.74	0.62	–	–	16.7	62.9	131	29.1
04/19/05	2.80	8.08	9.54	1.18	0.90	0.3[b]	0.38	20.0	57.5	257	87
06/08/05	1.50	7.7	8.0	2.24	2.02	–	–	24.2	79.1	331	92.7
WAL-5											
08/26/04	6.08	7.09	7.42	2.11	1.46	0.69	0.51	20.0	45.9	837	346
02/14/05	5.97	7.4	12.7	0.22	0.46	–	–	12.9		–	159
04/19/05	7.17	8.06	9.75	1.13	0.83	0.1[b]	0.32	17.2	57.5	499	137

Site name/sampling date	Mn$_u$ (µg/L)	Mn$_f$ (µg/L)	Na (mg/L)	NH$_3$+N (mg/L as N)	NO$_3$+NO$_2$ (mg/L as N)	P$_u$ (mg/L)	SiO$_2$ (mg/L)	Zn$_u$ (µg/L)	Zn$_f$ (µg/L)	DOC (mg/L)
WAL-1										
08/26/04	140	102	29.1	0.41	0.16	0.03	7.55	21.6	5.54	4.84
04/19/05	108	89.2	43.4	0.25	0.23	0.01	3.58	17.7	9.49	2.78
WAL-1.1										
06/07/05	324	213	48.4	0.35	0.25	0.03	7.63	14.0	6.74	5.03
WAL-1.2										
06/07/05	270	179	48.4	0.35	0.27	0.03	7.83	13.2	7.45	6.42
WAL-2										
09/01/04	107	82.5	38.0	0.34	0.42	0.02	10.6	15.4	6.90	4.06
04/19/05	71.3	50.7	37.4	0.26	0.28	0.02	3.61	20.5	7.26	2.78
WAL-3										
08/26/04	91.8	41.3	30.0	0.39	0.48	0.04	9.05	20.6	3.11	4.29
04/19/05	53.2	37.1	37.4	0.28	0.99	0.02	3.83	15.3	8.52	2.74
WAL-4										
08/26/04	148	101	29.8	0.41	0.79	0.04	9.59	21.9	2.37	4.56
02/14/05	–	145	35.4	0.30	1.16	0.03	7.65	12.7	12.9	2.19
04/19/05	101	86.6	37.4	0.29	0.70	0.03	3.61	15.1	13.7	2.75
06/08/05	136	111	42.9	0.38	0.99	0.06	8.02	39.5	17.2	3.52
WAL-5										
08/26/04	191	168	25.8	0.63	0.62	0.06	11.0	12.3	7.84	7.20
02/14/05	143	111	30.5	0.27	0.90	0.04	7.48	10.3	15.2	3.10
04/19/05	106	89.3	30.6	0.36	0.61	0.03	3.31	9.64	5.16	3.53

[a]–, No data.
[b]Raw data less than lower reporting limit; subject to uncertainty.

and winter 2004 from Franklin Pond immediately upstream, some of the variation in As concentration at WAL-1 could be attributable to a change in the supply of sediments to the streambed.

In the spring, arsenite (As (III)), constituted a substantial portion of the As$_f$ present in the river water at the nine sites sampled in both the upper and lower basins, whereas arsenate (As (V)) had been dominant in

Table 3

Chemical characteristics of, and selected constituents in, ground water/hyporheic-zone water (GHW) and surface water (SW) in filtered samples from eight sampling sites on the Wallkill River, July–August 2005, collected at base flow

Characteristic/ constituent	Sampling site and date (downstream direction to the right)							
	GHW	SW	GHW	SW	GHW	SW	GHW	SW
	WAL-B 07/12/05		WAL-C.8 08/03/05		WAL-D 07/11/05		WAL-1 07/12/05	
T (°C)	24.54	23.72	17.33	26.15	23.82	24.26	25.36	30.08
Field pH	7.50	7.90	6.57	7.39	7.40	7.37	7.75	8.26
DO (mg/L)	5.99	11.67	6.92	6.48	1.34	2.84	2.90	7.70
SC (µS/cm)	729	709	1031	772	680	647	635	499
Alk. (mg/L as $CaCO_3$)	180.9	157.5	308.4	192.9	167.1	156.8	176.1	118.2
Al_f (µg/L)	3.76	31.7	0.87	3.91	3.61	5.28	20.3	3.39
As_f (µg/L)	2.58	13.6	2.02	4.50	2.17	3.36	6.90	3.57
Ca (mg/L)	51.7	53.4	103	56.0	55.6	51.2	54.0	40.7
Cl (mg/L)	111	120	126	122	97.4	99.3	89.6	75.6
Fe_f (µg/L)	5	59.1	<6	22	27	82	<6	74
Mg (mg/L)	20.6	22.1	29.7	23.7	18.7	20.2	18.4	14.3
Mn_f (µg/L)	555	18.1	0.69	289	1963	115	360	25.8
Na (mg/L)	54.8	56.8	54.5	57.3	48.4	48.7	41.5	40.3
NH_3 (mg/L as N)	0.16	0.02	<0.04	0.030	0.345	0.02	0.207	0.043
NO_2+NO_3 (mg/L as N)	0.069	0.842	3.29	0.404	0.183	0.506	<0.060	0.128
NO_2 (mg/L as N)	<0.008	0.02	<0.008	0.005	0.004	0.005	<0.008	0.004
PO_4 (mg/L as P)	0.006	0.076	<0.006	0.006	0.005	0.005	0.06	0.007
SiO_2 (mg/L)	9.02	6.6	16.3	8.06	9.72	9.03	15.6	10.5
SO_4 (mg/L)	10.5	14.9	16.8	12.3	16.4	15.2	3.5	12.6
Zn_f (µg/L)	5.52	5.35	1287	5.61	57.1	7.68	5.50	5.40
	WAL-1.2 07/13/05		WAL-2 07/13/05		WAL-3 08/04/05		WAL-4 08/04/05	
T (°C)	26.30	28.06	25.25	25.40	25.93	26.82	27.63	27.11
Field pH	7.32	8.08	7.79	8.01	7.63	8.29	7.75	7.76
DO (mg/L)	2.55	7.28	7.30	9.85	5.56	10.4	10.38	11.15
SC (µS/cm)	804	537	593	549	708	622	815	806
Alk. (mg/L as $CaCO_3$)	286.1	127.2	183	164.8	217.1	254.2	204.4	205.7
Al_f (µg/L)	5.24	2.73	3.9	4.29	4.01	2.09	4.56	4.40
As_f (µg/L)	22.0	4.27	4.25	2.61	3.04	2.27	2.57	2.49
Ca (mg/L)	75.1	41.3	55.3	46.1	59.9	69.7	58.6	58.9
Cl (mg/L)	64.6	80.9	69.1	66.6	83.9	101	109	109
Fe_f (µg/L)	3520	43	288	53	12.3	20.9	12.9	44.0
Mg (mg/L)	33.7	15.2	24.8	21.3	29.0	31.8	28.3	28.1
Mn_f (µg/L)	579	35.6	1126	65	8.15	24.6	129	106
Na (mg/L)	31.2	40.9	33.2	33.9	40.4	46.9	56.7	56.5
NH_3 (mg/L as N)	0.15	0.04	0.136	0.02	<0.04	<0.04	0.043	0.050
NO_2+NO_3 (mg/L as N)	<0.060	0.146	0.198	0.259	2.004	1.184	5.222	5.085
NO_2 (mg/L as N)	<0.008	0.005	0.005	0.006	0.015	0.005	0.038	0.039
PO_4 (mg/L as P)	0.019	0.005	0.023	0.006	0.024	0.070	0.042	0.046
SiO_2 (mg/L)	17.9	10.9	11.7	10.1	11.4	12.0	8.96	8.89
SO_4 (mg/L)	12.0	12.9	18.6	13.6	20.5	19.9	20.9	20.8
Zn_f (µg/L)	0.7	3.95	16.7	2.77	10.3	2.29	7.07	8.0

the August/September sampling in the lower basin (Fig. 3). Accounting for analytical uncertainty, arsenate at the lower basin sites WAL-1 through WAL-4 ranged from 65 to 93% of dissolved species in August/ September 2004, but only from 42 to 55% of dissolved species in April 2005. Arsenite was the dominant As species at the outlet of Lake Mohawk (WAL-A) in spring 2005, but by summer 2005, much of the arsenite in the lake water apparently was oxidized, making arsenate the dominant As species (Fig. 4). Again, the

seasonal differences in concentration of the inorganic species were larger than the analytical errors. Mono-methylarsonate (MMA) and dimethylarsinate (DMA) concentrations were highest in water at WAL-A in July 2005, but were low (generally less than LRLs) at other times of the year. Methylated species also were detected in water samples from downstream sites in April 2005, but concentrations were less than LRLs.

During the bi-hourly diurnal sampling at WAL-2, concentrations of Fe_u, Mn_u, and Zn_u increased through
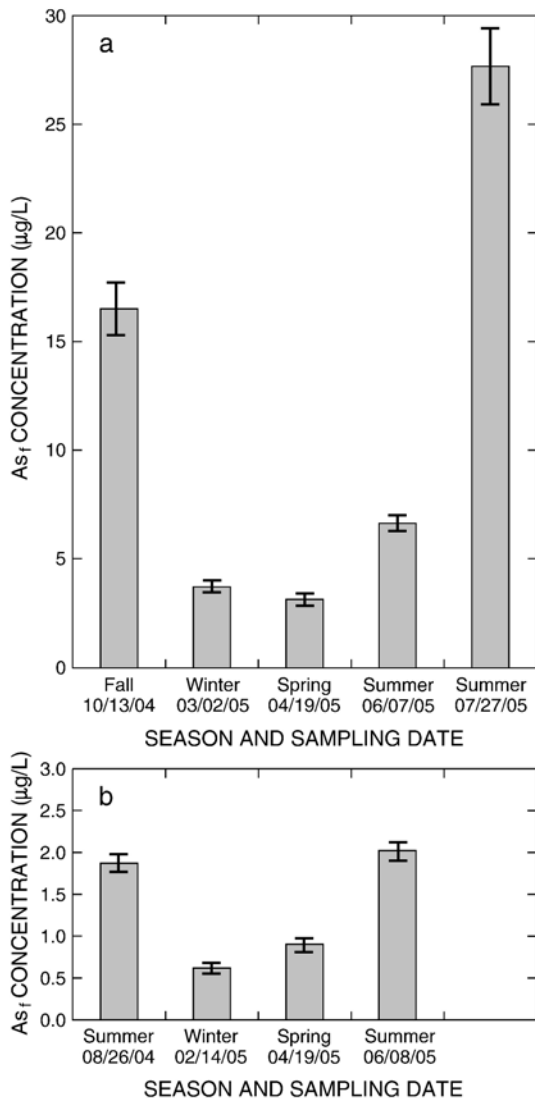
Fig. 2. As concentrations in single water samples from the Wallkill River by season at (a) WAL-A; and (b) WAL-4. (Error bars are based on a relative standard deviation of 6% for As_f).

the night to a peak shortly after midnight and the suspended-sediment concentration rose to a detectable level (15 mg/L). (Suspended sediment was detected in only one other sample during the diurnal sampling.) As_u concentrations also peaked and alkalinity and pH decreased. Concentrations of the metals decreased during the morning of the second day (Fig. 5a).

Diurnal sampling at WAL-4 indicated that As_u concentrations decreased and Fe_u, Mn_u, and Zn_u concentrations increased during nighttime hours (Fig. 5b). An undulating pattern in As_u concentrations—low at night, higher during daytime—was apparent in samples from WAL-4 but not in those

from WAL-2. The RPD for As_u was 20%; therefore, analytical error may account for the lack of pattern at WAL-2. The pattern at WAL-4, however, resembles those in other studies (e.g. Fuller and Davis, 1989; Nimick, 1998). Results from several unfiltered/filtered sample pairs collected during daytime hours indicated that most As and Mn was dissolved (or on colloids), but most Fe was particulate (data in Deluca et al., 2005.) The metals cycle did not appear to coincide with a nighttime rise in stream stage, where flow was calculated to have increased from about 1.4 m³/s to about 1.6 m³/s.

4.3. Ground-water/hyporheic-zone discharge and associated river water

We did not attempt to quantify the fraction (if any) of surface water in the water collected from streambed piezometers, and therefore refer to these as ground-water/ hyporheic-zone samples. No samples were collected at WAL-A because the stream is losing immediately downstream from WAL-A. Ground-water discharge to the river begins about 0.5 km downstream from WAL-A.

T and pH values and concentrations of DO in most ground-water/hyporheic-zone water samples typically were lower, and SC values were higher, than those in surface-water samples at the same location, indicating little or no exchange between ground water entering the stream bed and surface water at the level of the piezometer
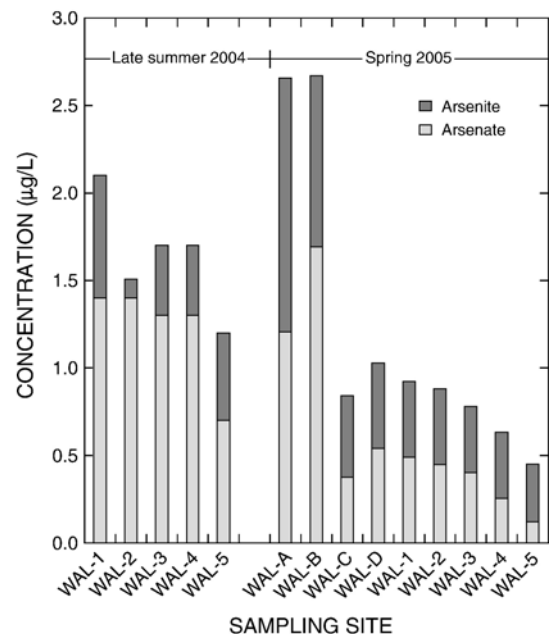

Fig. 3. Arsenate and arsenite concentrations in single water samples from the Wallkill River, August/September 2004 and April 2005.
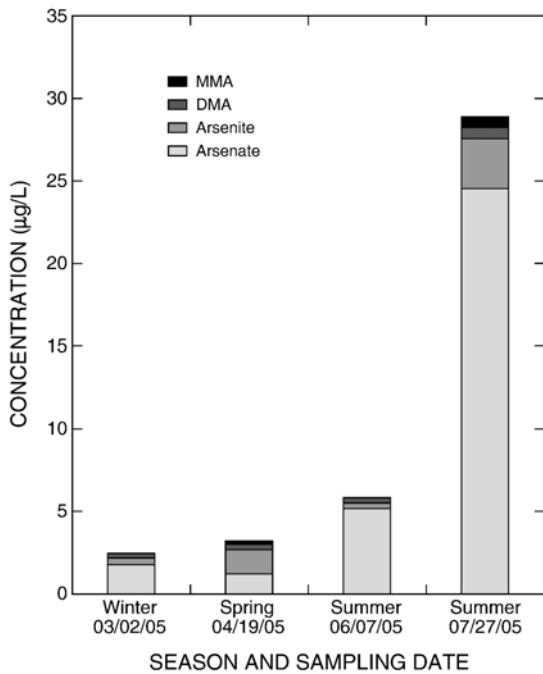
Fig. 4. As species in single water samples from the Lake Mohawk outlet (WAL-A), 2005.

screen (generally about 30 to 60 cm below the streambed surface). Exceptions were samples from WAL-C.8, where DO concentrations were slightly higher in ground water at about 30-cm depth than in surface water, and from WAL-4, where all field parameters were similar in ground water and surface water, indicating nearly complete ground-water/surface-water exchange at about 15-cm depth (Table 3). At sites immediately downstream from Franklin Pond (WAL-1, WAL-1.2), the DO concentration in what appeared to be mostly or entirely ground-water discharge was <3 mg/L, and the odor of H_2S was detected in the vicinity of the river at WAL 1.2. At many of the sites along the river, the low DO concentrations in shallow ground water entering the streambed were reflected in the concentrations of redox-sensitive constituents; NH_3, Fe, and Mn concentrations were higher and NO_3 concentrations were lower in ground-water/hyporheic-zone water than in surface water (Table 3).

Concentrations of As in water discharging to the river at base flow in July and August 2005 varied widely, from 2.02 µg/L at WAL-C.8 to 22 µg/L at WAL-1.2. Concentrations of As were highest immediately downstream from Franklin Pond, adjacent to the Franklin mine site (Fig. 6), but concentrations in the surface water were comparatively low. In contrast, Zn concentrations were highest in ground-water discharge at

WAL-C.8, immediately downstream from the Sterling Hill Mine, but Zn concentrations in surface water there also were substantially lower (Table 3).

4.4. Bed sediment: chemistry and mineralogy

Concentrations of As on bed sediments from the tributaries generally were lower than those on sediments from the river's mainstem, ranging from 1.5 to 9 mg/kg
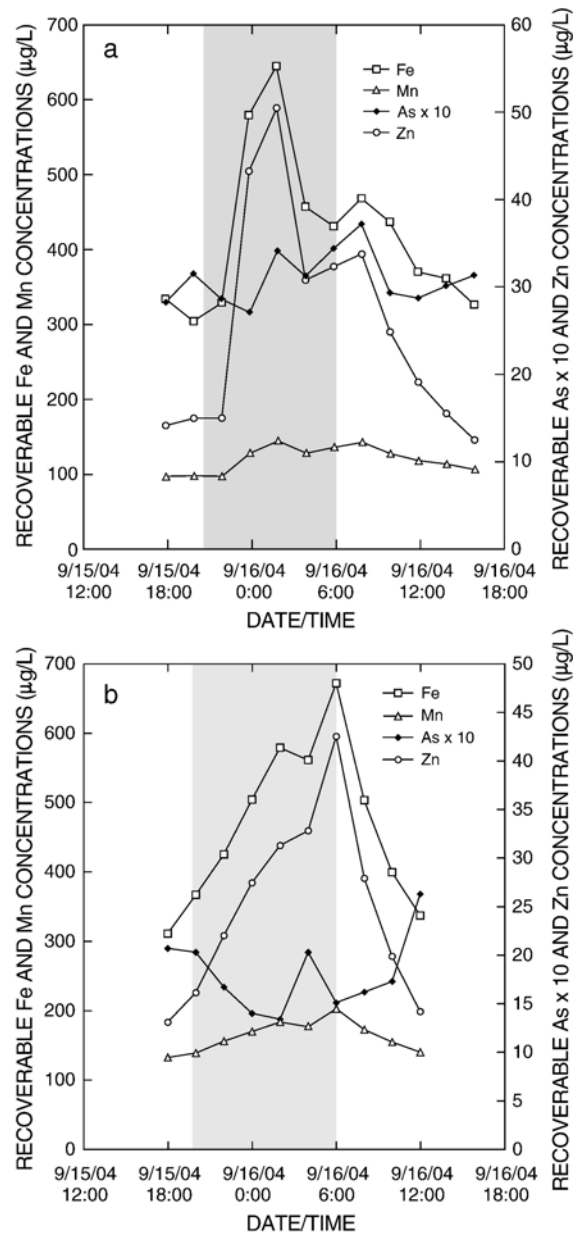

Fig. 5. Trace-element concentrations in unfiltered samples collected with ISCO samplers over a 24-h period at (a) WAL-2, and (b) WAL-4. Shaded area indicates nighttime hours.
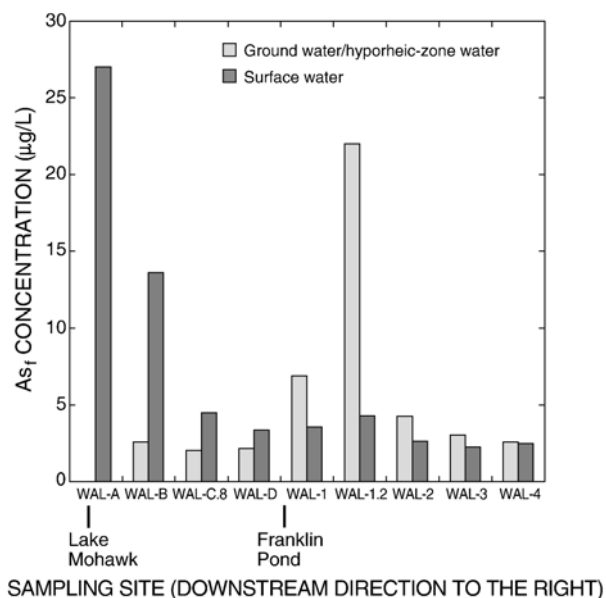
Fig. 6. Concentrations of As_f in ground water/hyporheic-zone and surface water with distance downstream from Lake Mohawk. (Concentrations in surface water at WAL-A are included; there is no ground-water discharge at WAL-A).

for total concentrations on the <63-μm fraction and from <1 to 1.6 mg/kg for recoverable (acid-leachable) concentrations on the <2-mm fraction (data not shown). Additionally, Zn concentrations on tributary sediments generally were substantially lower than those from the mainstem in the vicinity of the mines.

Concentrations of As on bed sediments from the river's mainstem were particularly high at WAL-A, where total and recoverable concentrations were 24 and 23 mg/kg, respectively, and at three sites (WAL-D, WAL-1, WAL-2) adjacent to, underlain by, or immediately downstream from the Franklin Marble outcrop, where total concentrations ranged from 17 to 190 mg/kg and recoverable concentrations ranged from 7 to 24 mg/kg (Fig. 7). Zn and Mn concentrations also were substantially higher on bed sediments at WAL-D (1 km downstream from the Sterling Hill Mine), and at WAL-1 and WAL-2 (adjacent to and downstream, respectively, from the Franklin Mine) than on sediments from elsewhere in the river (Tables 4a and 4b). Additionally, sediments near the Franklin Mine contained relatively higher Cu and Pb concentrations than elsewhere on the river; these metals also were associated with the Zn ores. The increases in As and metal concentrations on sediments adjacent to and downstream from the two mine sites were substantially greater than any variation due to analytical error,

increasing by an order of magnitude or more for total As, Mn, and Zn on the <63 μm fraction.

Sediment samples from WAL-1.1 and WAL-1.2 (adjacent to the Franklin Mine location) were collected after sediments were dredged from Franklin Pond, and contained lower As and Zn concentrations than the sediments sampled before and during dredging at WAL-1 and WAL-2. Cores SS-7 and SS-8 of Franklin Pond sediments, collected after dredging, also contained low (<20 mg/kg) concentrations of As.

Because sediments were moved southward during the Wisconsin glaciation in what is now northwestern New Jersey, minerals from the northern, downstream part of the watershed can appear in upstream locations. Bulk sediments from tributaries and the mainstem all contained quartz as a major phase and feldspars as major or minor phases. Dolomite, identified as a trace mineral in bulk sediments from several tributaries, was a minor phase, as was calcite, in mainstem bulk sediments (Table 5; tributary minerals not shown). Trace minerals in both tributaries and mainstem sediments included amphiboles and micas, and birnessite was tentatively identified at two sites. Willemite (a Zn ore) was a trace mineral in bulk sediments from WAL-D and WAL-2 and in the C-3 (non-magnetic) fraction of separates from WAL-1.1, WAL-1.2 and WAL-4. Trace amounts of minrecordite were identified in several sediment samples. This dolomite-structure mineral with substituted Zn (S. Sutley, USGS, written commun.) is not reported as part of the Franklin Marble ore assemblages and could be a secondary mineral.
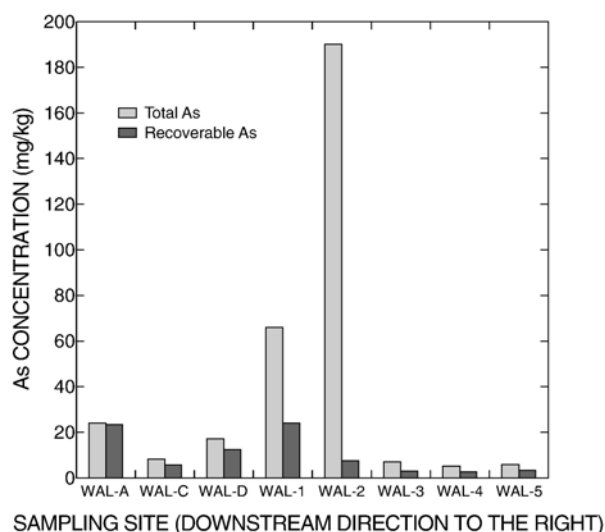

Fig. 7. Concentrations of total As (<63 μm) and recoverable As (<2 mm) on Wallkill River bed sediments with distance downstream from Lake Mohawk.

Table 4a

Concentrations of selected total major (in wt.% element) and trace elements in bed sediments from the Wallkill River and Franklin Pond sediment cores, and As concentrations in mineral separates from selected Wallkill River sites

Site and sampling date

	Upper basin				Franklin Pond				
Constituent	WAL-A 10/13/04	WAL-B 12/08/04	WAL-C 10/13/04	WAL-D 10/13/04	SS-7T 01/13/05	SS-7B 01/13/05	SS-8T 01/13/05	SS-8M 01/13/05	SS-8B 01/13/05
Fe (wt.%)	2.2	1.6	1.4	1.7	3.1	2.3	3.1	2	2
As (mg/kg)	24	17	8.1	17	15	9.9	12	10	13
Cu (mg/kg)	51	10	4.5	9.6	23	15	15	9.7	14
Mn (mg/kg)	710	470	500	2800	2400	1500	710	770	850
Pb (mg/kg)	7.2	24	8.9	44	50	30	38	20	39
Zn (mg/kg)	150	86	100	3800	590	310	190	210	420

Lower basin

Constituent	WAL-1 08/26/04	WAL-1 12/08/04	WAL-1.1 06/07/05	WAL-1.2 06/07/05	WAL-2 09/01/04	WAL-3 08/26/04	WAL-4 08/26/04	WAL-5 08/26/04
Fe (wt.%)	3	1.8	2.6	2.6	2.2	2.6	1.3	2.5
As (mg/kg)	66	100	39.8	13.4	190	7	5.2	5.7
Cu (mg/kg)	26	21	20.4	20.6	11	17	6.1	18
Mn (mg/kg)	4900	7300	3910	1300	11,000	1000	620	640
Pb (mg/kg)	130	310	105	29	73	34	14	15
Zn (mg/kg)	6900	4900	1450	430	66,000	420	400	260
Mineral separates								
As (Fraction C-1, mg/kg)		160	120	43	35			
As (Fraction C-2, mg/kg)		330	150	25	150			
As (Fraction C-3, mg/kg)		4800	380	270	1500			

The C-3 fractions of sediments from WAL-1, WAL-1.1, WAL-1.2, and WAL-2 contained the highest concentrations of As. In the WAL-1 C-3 fraction, which contained the highest As concentration, small amounts of arsenopyrite (FeAsS) and loellingite (FeAs$_2$) were identified (Barringer et al., 2006) (Table 5). These

Table 4b

Concentrations of selected recoverable (acid-leachable) trace elements in bed sediments from the Wallkill River and Franklin Pond sediment cores

Site and sampling date

	Upper basin				Franklin Pond				
Constituent	WAL-A 10/13/04	WAL-B 12/08/04	WAL-C 10/13/04	WAL-D 10/13/04	SS-7T 01/13/05	SS-7B 01/13/05	SS-8 01/13/05	SS-8M 01/13/05	SS-8B 01/13/05
As (mg/kg)	23	9	6	12	5.70	3.18	1.65	2.54	3.25
Cu (mg/kg)	78	7	4	10	3.86	4.65	8.16	4.52	7.86
Fe (mg/kg)	6300	6100	6000	7700	4194	5989	13,756	8696	9530
Mn (mg/kg)	480	270	270	1700	637	911	367	316	554
Pb (mg/kg)	5.2	19	4.5	42	97.7	17.1	36.8	13.5	32.4
Zn (mg/kg)	56	40	56	2900	199	111	81.7	108	234

Lower basin

Constituent	WAL-1 12/08/04	WAL-1.1 06/07/05	WAL-1.2 06/07/05	WAL-2 09/01/04	WAL-3 08/26/04	WAL-4 08/26/04	WAL-5 08/26/04
As (mg/kg)	24	28.2	9.1	7	3	3	3
Cu (mg/kg)	10	19.9	23.5	8	9	4	11
Fe (mg/kg)	5000	17,740	15,400	7300	10,000	6000	15,000
Mn (mg/kg)	2900	3750	1510	8500	750	300	450
Pb (mg/kg)	310	94	314	68	53	8.4	9.8
Zn (mg/kg)	2300	1040	529	54,000	140	220	120

Table 5
Minerals identified (X) or tentatively identified (?) in bulk samples and non-magnetic (C-3) separates of bed sediments from the Wallkill River and Franklin Pond

Site	WAL-A	WAL-B	WAL-C	WAL-D	SS-8	WAL-1	WAL-1.1	WAL-1.2	WAL-2	WAL-3	WAL-4	WAL-5
Mineral (bulk)												
Quartz	X	X	X	X	X	X			X	X	X	X
Feldspar (K, Na)	X	X	X	X	X	X			X	X	X	X
Calcite	X	X		X	X	X				X	X	
Dolomite	X	X	X	X	X	X				X		X
Amphibole	X	X		X	?	X			X	X	X	
Illite and (or) kaolinite				?							X	
Muscovite	X	X		X	X	X				X		X
Annite and (or) phlogopite		X							X	X		
Clinochlore	X	X		X	X	X				X		
Mn hydroxide						?						?
Willemite				?					X			
Minrecordite		X		X	?	?			X	X		
Fraipontite						?						
Mineral (C-3)												
Quartz							X	X			X	
Feldspar (K, Na)							X	X			X	
Calcite							X				X	
Dolomite							X	X			X	
Amphibole and (or) pyroxene							X	X			X	
Annite							X	X				
Clinochlore							X	X				
Willemite							X	X			X	
Minrecordite							?	?				
Fraipontite							?	?				
Apatite											X	
Monazite											X	
Zircon											X	
Mineral (C-3 As-bearing)												
Arsenopyrite						X						
Loellingite						X						
Native As						?						

were the most abundant As minerals at the Franklin Mine; loellingite was the predominant As mineral at the Sterling Hill Mine (Dunn, 1995).

5. Discussion

Our overall goal in this study was to track As in the watershed, determining its partitioning into different media, and identifying both the range of concentrations present and the processes that caused the concentration variations. Several general points can be made regarding our findings. First, despite a large analytical error for As_u, most of the As present in tributary and river water is As_f— either dissolved or on colloids <0.45 μm; much less is on particles >0.45 μm. At the slightly alkaline pHs of the streamwater, less As would be expected to be adsorbed to sediment particles than in an acidic environment. Second, concentrations of As were low in water and on sediments from the tributaries. Because several of the tributaries drain agricultural areas, it appears that inputs of As from agricultural chemicals have been small to negligible, and geologic inputs to the tributaries also appear to be minor. Third, the spatial distribution of As concentrations in river water, in ground-water discharge to the river, and in bed sediments indicates that substantial amounts of As enter the river from two main areas—one at the Lake Mohawk outlet in the upper basin, and the other in the vicinity of Franklin Pond and the Franklin Mine in the lower basin. Fourth, the flow regime and biological activity affect As concentration and speciation.

5.1. As dynamics in the upper basin

There is no ground-water discharge at and immediately downstream from WAL-A; therefore, when As concentrations in river water at the lake outlet are high, it

is because concentrations in the lake water are high. High concentrations of As at WAL-A occurred during summer and early fall and were associated with decreased flow from the lake ($\rho = -0.9$) in these seasons. In the past (late 1970 s), As concentrations have been high (29 µg/L) in water from the outlet in warm months, thus concentrations in the lake have been high (probably seasonally) for at least 30 years. (A planned study of the lake will investigate the magnitude and distribution of As concentrations in lake sediments and lake water.)

Anthropogenic inputs, including wastewater discharges, appear to have affected lake water and surface water in the southern, most developed part of the upper basin, as indicated by higher concentrations of Na, Cl, B, and N species in water from WAL-A and WAL-B than farther downstream. At WAL-A, arsenite concentrations were high in spring, when algae are growing in the lake, and concentrations of methylated As species increased during the summer. Algae can reduce and methylate As (Aurilio et al., 1994), consequently, it is likely that algae are processing As in the Lake Mohawk water. Additionally, $NH_3 +$ organic N are the more important N species in water at WAL-A, probably because algae in the lake also take up available NO_3.

Arsenate from the lake water adsorbs to bed sediments below the spillway at WAL-A, resulting in the high concentrations of recoverable (sorbed) As on sediments there relative to concentrations farther downstream (Barringer et al., 2006). The remaining As in solution is diluted downstream from WAL-A by groundwater discharge, in which As_f concentrations were about 2.0 to 2.5 µg/L in summer 2005, and by tributary water.

Given the low concentrations of As in hyporheic-zone/ground-water discharge at WAL-C.8 and WAL-D (2.02 and 2.17 µg/L, respectively), it appears that ground water in contact with the ore body at Sterling Hill contributes relatively little As to the river, although Mn and (or) Zn contributions appear to have been large at one or the other site (Table 3). Overall, processes—apparently biological—in Lake Mohawk control the major inputs of As to river water of the upper basin; instream processes then modify those inputs.

5.2. As dynamics in the lower basin

In the vicinity of Franklin Pond, at WAL-1 and WAL-1.2, ground water/hyporheic-zone water was more acidic than surface water, was poorly oxygenated, and, in addition to high concentrations of As, contained NH_3, no detectable NO_3, and, at WAL-1.2, a substantial concentration of Fe_f. These characteristics are similar to those reported for hyporheic-zone water discharging to an As-

contaminated stream in Montana (Nagorski and Moore, 1999). At Franklin, percolating precipitation and shallow ground water apparently leach As and metals remaining in the mined area. Speciation calculations indicate the ground-water discharge would contain predominantly ferrous Fe. We hypothesize that dissolved Fe (II) discharging to the river oxidizes and forms amorphous Fe hydroxide coatings on bed-sediment particles.

Ground water discharging to streambed sampling sites adjacent to the currently rock-filled mine shafts at Franklin contains more As than does the river water. Some of the arsenite in river water at and downstream from WAL-1 probably is released from the poorly oxygenated zone beneath the streambed, as in the study by Nagorski and Moore (1999). We hypothesize that, as the arsenite oxidizes to arsenate, it adsorbs to iron-hydroxide coatings on the bed sediments. This process would account for concentrations of As in river water being substantially lower than those in ground water/hyporheic-zone water at WAL-1, WAL-1.2, and WAL-2, and would also account for the high concentrations of As on bed sediments in the river reach below Franklin Pond. Some arsenite in the river water at Franklin also may derive from oxidation of arsenopyrite, as shown by Frau and Ardau (2003), and some may derive from processing of As by aquatic plants.

The most As-rich sediments were found at WAL-2, 2 km downstream from the Franklin mine site. Currently, there is insufficient information to determine whether these As-rich sediments were transported downstream from the Franklin area, or whether there is an unidentified area of mine tailings close to WAL-2 that could contribute As to the river.

Samples collected at WAL-1, WAL-1.1, and WAL-1.2 in summer 2005 indicate that, during hot, dry weather (when the water table is low and solutes in shallow ground water, hyporheic-zone water, and streamwater can become more concentrated), concentrations of As (and other trace elements) tended to increase. This finding is supported by elevated concentrations of As in samples collected at low flow in July 1999 by NJDEP (Fig. 8). The behavior of As in alkaline rivers such as the Wallkill, where it is mostly a solute, differs from As behavior under acidic conditions, such as those in the Odiel River in Spain. There, As from mining activities is sorbed or co-precipitated with Fe hydroxides during the warm months, and concentrations in the water column decrease (Olías et al., 2004).

Many solutes, including As, are diluted during periods of higher streamflow, as shown for the Thames River near Oxford, England (Neal et al., 2000); this occurs in the Wallkill River as well. At Franklin, the As-
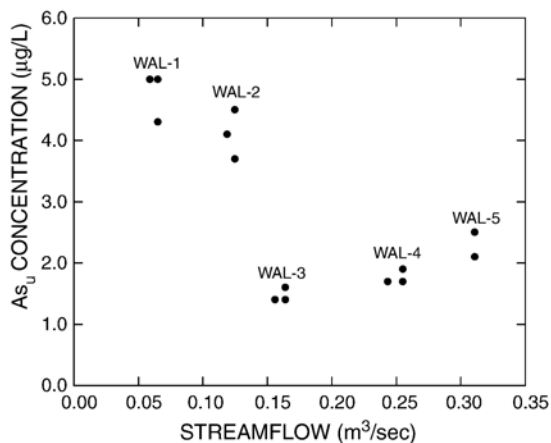
Fig. 8. Relation of As_u concentration to streamflow at five Wallkill River site, lower basin, sampled by NJDEP, July 13, 1999. (Downstream order from left to right).

rich shallow ground water probably is diluted also during wet periods, as the filled mine shafts likely facilitate the infiltration of precipitation to the shallow ground-water system.

Not all the seasonal variation in As concentration in water of the lower basin arises from dilution or concentration of solutes, however. At WAL-4, in the wetlands, concentrations of As were lower in the colder months (February and April) and higher in warm months (June and late August). (Seasonal variations in As concentrations were about an order of magnitude larger than the diurnal fluctuations at WAL-4.) There was no significant relation between concentration, either for As_u or As_f, and discharge, and it appears that, in addition to wet or dry conditions, other factors can affect As concentrations.

Concentrations of Fe also were low in river water during winter and spring and high during summer and fall; the seasonal variations were substantially larger than the largest analytical error for Fe. There was a higher proportion of Fe_f and less particulate Fe present during spring and summer. Because Fe hydroxides can supply binding sites for arsenate, bacterial reduction of Fe in hydroxides, subsequent solubilization, and release of sorbed As could account, in part, for increases in concentrations of Fe and As during warm months. Such a mechanism has been proposed to explain seasonal increases in As and Fe concentrations in a eutrophic lake basin in Japan (Sohrin et al., 1997).

There may be other influences on As dynamics at WAL-4. Macroalgae and macrophyte populations have increased over time at WAL-4 (R. Schopp, USGS, 2004, oral commun.), likely in response to relatively high

nutrient inputs to the river there. Arsenite in water at WAL-4 (and at WAL-5, downstream) constituted a larger proportion of the As_f concentrations in April 2005 than in late August 2004 (Fig. 3), and traces of both MMA and DMA (below the LRL) were detected, probably indicating that biological transformations had occurred with uptake of arsenate during spring algae and macrophyte growth. The effect of aquatic vegetation in spring was seen throughout the river, where arsenite concentrations increased relative to arsenate (Fig. 3), accompanied by a substantial decrease in SiO_2 concentrations (Table 2b), the likely result of biological uptake, as shown by Neal et al. (2005).

At WAL-4, As is contributed by upstream sources and probably by local ground-water discharge as well. Some of the As in streamwater continues on downstream, in dissolved form or sorbed to fine suspended sediments, but some apparently is taken up and released by algae (and probably other aquatic plants), and some may be stored during cold months in sediment coatings, biofilms, and in plaques on aquatic plant roots (Blute et al., 2004). The same processes likely occur at other wetlands sites on the river.

5.3. Mechanisms for diurnal cycles in As and metals

Particulate forms made up substantially different proportions of each of the metals (Fe, Mn, Zn) at all of the sampling sites in the lower basin, and did so in the daytime filtered/unfiltered sample pairs collected during the diurnal sampling at WAL-2 and WAL-4. Although proportions varied, Mn was mostly dissolved, proportions of Zn_f to Zn_u were more nearly equal, and most of the Fe was in particulate form. Because no nighttime filtered samples were collected during diurnal sampling, changes in proportions of filtered to unfiltered metals and As during the night are unknown.

The post-midnight peak in Fe_u, Mn_u, and Zn_u concentrations at WAL-2 is attributable to an increase in the suspended-sediment concentration to a detectable level (15 mg/L) during the same period. A smaller concentration peak occurred at about 8 AM the second day (Fig. 5a) when suspended sediment was again detected, at 11 mg/L. As_u concentrations, which showed no clear pattern, also increased after midnight at WAL-2.

Measurements made during daylight hours indicate that DO concentrations and pH tended to increase during the day, which would be expected if photosynthesis and respiration were the primary cause of DO and pH cycles. As_u concentrations also tended to increase at WAL-4 during the day as pH increased. Fe_u, Mn_u, and Zn_u concentrations tended to decrease

as pH (and DO) increased at both WAL-2 and WAL-4. Trends for the metals in the limited number of filtered samples with pH were not obvious. At WAL-2, the variations in As_u concentrations during nighttime hours did not illustrate cyclic behavior. At WAL-4, the apparently opposing diurnal behaviors of metals and As in unfiltered water at WAL-4 may be attributed to more than a single process controlling the variations in metals and As concentrations, as the As cycle resulted mostly from the behavior of dissolved As, but the Fe and Zn cycles were dependent primarily on the behavior of particulate Fe and Zn. Mn behavior appears more complex; despite being predominantly "dissolved," the data for Mn_u indicates a particulate cycle like those of Fe and Zn.

At WAL-4, the time/concentration pattern for As_u is similar to dissolved As patterns shown by Nimick et al. (2003), with As concentrations decreasing during the night and increasing during daylight hours and Mn concentrations showing the reverse behavior. The As (and possibly Mn) cycles at WAL-4 may be attributable to pH-driven adsorption and desorption reactions, similar to processes in western USA alkaline rivers (Fuller and Davis; 1989; Nimick et al., 2003). The behavior of Fe_u and Zn_u (and perhaps some portion of the Mn) at both WAL-2 and WAL-4, however, appears to derive more from releases of particles than of increases in solutes. Brick and Moore (1996) observed nighttime increases in particulate Cu, Fe, Mn, and Zn and attributed the phenomenon to particle suspension arising from movement of benthic macroinvertebrates within the stream sediments.

The results of diurnal sampling partially answered our primary question, which was whether metals concentrations peaked at night and As concentrations peaked during the day. Measurements of total Fe, Mn, and Zn concentrations in daytime samples clearly do not adequately represent the maximum concentrations of these metals in the streamwater, whereas maximum As concentrations may be better represented by daytime samples, particularly those collected during the late afternoon. Nevertheless, additional work is needed to identify the processes responsible for diurnal fluctuations in these constituents in the Wallkill River.

6. Conclusions

Inputs of As to the river are greatest at the headwaters—from Lake Mohawk waters—and immediately downstream from Franklin Pond—from ground water in contact with mined materials, and sediments, whereas tributaries to the Wallkill contribute relatively less As to the river. The river's As concentrations vary

as a result of dilution of solutes during wet periods, and concentration of solutes during dry periods, and, in the case of Lake Mohawk water and streamwater in the wetlands, apparently as a result of biological activity as well. The ground-water/hyporheic zone samples provided crucial information for identifying the second of the two major sources of As to the Wallkill and for understanding As dynamics. Thus, sampling a variety of media can prove useful in characterizing the passage of a constituent such as As through a river system. Because the temporal dynamics of As in the Wallkill River indicate both seasonal and diurnal variability, different pictures of As magnitude and distribution could emerge depending upon when river-water samples are collected.

Acknowledgments

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