

Prepared in cooperation with the New Jersey Department of Environmental Protection

Arsenic in New Jersey Coastal Plain Streams, Sediments, and Shallow Groundwater: Effects from Different Geologic Sources and Anthropogenic Inputs on Biogeochemical and Physical Mobilization Processes

Scientific Investigations Report 2013–5107

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U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2014

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Suggested citation:

Barringer, J.L., Reilly, P.A., Eberl, D.D., Mumford, A.C., Benzel, W.M., Szabo, Zoltan, Shourds, J.L., and Young, L.Y., 2014, Arsenic in New Jersey Coastal Plain streams, sediments, and shallow groundwater: Effects from different geologic sources and anthropogenic inputs on biogeochemical and physical mobilization processes: U.S. Geological Survey Scientific Investigations Report 2013–5107, 38 p., <http://dx.doi.org/10.3133/sir20135107>.

ISSN 2328-0328 (online)

Acknowledgments

The geochemical work was supported through a cooperative agreement between the New Jersey Department of Environmental Protection and U.S. Geological Survey (USGS). The microbiological portion of this study was funded in part by a New Jersey Water Resources Research Institute grant to A. Mumford. We are particularly grateful to our many colleagues at the USGS New Jersey Water Science Center and Rutgers University who assisted with field work, data analysis, and report editing. We would also like to thank USGS colleagues Joseph Ayotte and Lisa Senior for their helpful reviews.

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Conversion Factors and Abbreviations

SI to Inch/Pound

Multiply	By	To obtain
Length		
micrometer (μm)	0.000039	inch (in)
millimeter (mm)	0.03937	inch (in)
centimeter (cm)	0.3937	inch (in)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
square kilometer (km^2)	0.3861	square mile (mi^2)
Volume		
liter (L)	0.2642	gallon (gal)
Flow rate		
cubic meter per second (m^3/s)	35.31	cubic foot per second (ft^3/s)
Mass		
microgram (μg)	0.0000003527	ounce, avoirdupois (oz)
milligram (mg)	0.00003527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)

Temperature in degrees Celsius ($^{\circ}\text{C}$) may be converted to degrees Fahrenheit ($^{\circ}\text{F}$) as follows:
 $^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

Chemical unit abbreviations

$\mu\text{g}/\text{L}$	micrograms per liter (equivalent to parts per billion)
mg/L	milligrams per liter (equivalent to parts per million)
mg/kg	milligrams per kilogram (equivalent to parts per million)

Abbreviations

Al	aluminum
As	arsenic
Cl ⁻	chloride
Cu	copper
CKKD	Kirkwood-Cohansey aquifer system
CRO	Crosswicks Creek
DOC	dissolved organic carbon

EDTA	ethylenediaminetetraacetic acid
Fe	iron
FeCO ₃	siderite
GEHR	Great Egg Harbor River
HAMM	Hammonton Creek
HCl	hydrochloric acid
HClO ₄	perchloric acid
Hg	mercury
HF	hydrofluoric acid
ICP/MS	inductively coupled plasma-mass spectrometry
ICP/AES	inductively coupled plasma-atomic emission spectrometry
Mn	manganese
MCL	maximum contaminant level
N	nitrogen
NH ₄ ⁺	ammonium
NJDEP	New Jersey Department of Environmental Protection
NO ₃ ⁻	nitrate
NO ₂ ⁻	nitrite
OC	organic carbon
OLD	Oldmans Creek
OM	organic matter
P	phosphorus
Pb	lead
PbHAsO ₄	lead arsenate
Ra	radium
RAC	Raccoon Creek
Sb	antimony
SiO ₂	silicon dioxide
SO ₄ ²⁻	sulfate
STP	Sewage Treatment Plant
SWQS	surface water quality standard
TOC	total organic carbon
TMDL	total maximum daily load
Zn	zinc
<	less than

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By Julia L. Barringer¹, Pamela A. Reilly¹, Dennis D. Eberl¹, Adam C. Mumford², William M. Benzel¹, Zoltan Szabo¹, Jennifer L. Shourds¹, and Lily Y. Young²

Abstract

Arsenic (As) concentrations in New Jersey Coastal Plain streams generally exceed the State Surface Water Quality Standard (0.017 micrograms per liter ($\mu\text{g/L}$)), but concentrations seldom exceed 1 $\mu\text{g/L}$ in filtered stream-water samples, regardless of geologic contributions or anthropogenic inputs. Nevertheless, As concentrations in unfiltered stream water indicate substantial variation because of particle inputs from soils and sediments with differing As contents, and because of discharges from groundwater of widely varying chemistry.

In the Inner Coastal Plain, streams draining to lower reaches of the Delaware River traverse As-rich glauconitic sediments of marine origin in which As contents typically are about 20 milligrams per kilogram (mg/kg) or greater. In some of these sedimentary units, As concentrations exceed the New Jersey drinking-water maximum contaminant level (5 $\mu\text{g/L}$) in shallow groundwater that discharges to streams. Microbes, fueled by organic carbon beneath the streambed, reduce iron (Fe) and As, releasing As and Fe into solution in the shallow groundwater from geologic materials that likely include (in addition to glauconite) other phyllosilicates, apatite, and siderite. When the groundwater discharges to the stream, the dissolved Fe and As are oxidized, the Fe precipitates as a hydroxide, and the As sorbs or co-precipitates with the Fe. Because of the oxidation/precipitation process, dissolved As concentrations measured in filtered stream waters of the Inner Coastal Plain are about 1 $\mu\text{g/L}$, but the total As concentrations (and loads) are greater, substantially amplified by As-bearing suspended sediment in stormflows.

In the Outer Coastal Plain, streams draining to the Atlantic Ocean traverse quartz-rich sediments of mainly deltaic origin where the As content generally is low (<8 mg/kg). In unfiltered and filtered water samples, As concentrations typically are less than 1 $\mu\text{g/L}$ in the acidic stream water and

groundwater of the Outer Coastal Plain, but are greater in waters from urban areas. Despite the generally small geologic contributions to Outer Coastal Plain groundwater, where wastewater inputs were indicated, concentrations of As in unfiltered shallow groundwater discharging to small urban streams exceeded the maximum contaminant level.

With a history of agriculture in the New Jersey Coastal Plain, anthropogenic inputs of As, such as residues from former pesticide applications in soils, can amplify any geogenic As in runoff. Such inputs contribute to an increased total As load to a stream at high stages of flow. As a result of yet another anthropogenic influence, microbes that reduce and mobilize As beneath the streambeds are stimulated by inputs of dissolved organic carbon (DOC). Although DOC is naturally occurring, anthropogenic contributions from wastewater inputs may deliver increased levels of DOC to subsurface soils and ultimately groundwater. Arsenic concentrations may increase with the increases in pH of groundwater and stream water in developed areas receiving wastewater inputs, as As mobilization caused by pH-controlled sorption and desorption reactions are likely to occur in waters of neutral or alkaline pH (for example, Nimick and others, 1998; Barringer and others, 2007b). Because of the difference in As content of the geologic materials in the two sub-provinces of the Coastal Plain, the amount of As that is mobile in groundwater and stream water is, potentially, substantially greater in the Inner Coastal Plain than in the Outer Coastal Plain. In turn, streams within the Inner and Outer Coastal Plain can receive substantially more As in groundwater discharge from developed areas than from environments where DOC appears to be of natural origin.

Introduction

Arsenic (As), long recognized as a toxic element, is also a carcinogen (National Research Council, 1999; U.S. Environmental Protection Agency, 2001). Recent investigations of As contamination in groundwater worldwide have reported

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that geologic contributions of As to groundwater can be large, and that the biogeochemical reactions affecting the release of As from geologic materials commonly involve elevated levels of organic matter (OM) (for example, Welch and Lico, 1998; Nickson and others, 2000; Akai and others, 2004; Zheng and others, 2004; Bhattacharya and others, 2006; Lipfert and others, 2006). Arsenic also may enter soils and waters in areas where arsenical pesticides are used (for example, Renshaw and others, 2006) and through industrial discharges (Smedley and Kinniburgh, 2002)

Because of the carcinogenic status of As, in 2006, the State of New Jersey adopted a drinking water maximum contaminant level (MCL) for public water supplies of 5 micrograms per liter ($\mu\text{g/L}$; New Jersey Department of Environmental Protection, 2009), which is the lowest As MCL in the United States. The State also adopted a stringent Surface Water Quality Standard (SWQS) for human exposure to As of $0.017 \mu\text{g/L}$, which represents a one-in-one million risk of cancer for exposure to this carcinogen (New Jersey Department of Environmental Protection, 2011). As of 2010, the New Jersey Department of Environmental Protection (NJDEP) had listed segments of 14 streams and tributaries wholly within and traversing the New Jersey Coastal Plain Province as impaired for As because concentrations in the waters exceed the SWQS.

The exceedences of the SWQS require investigation into whether Total Maximum Daily Loads (TMDLs) will need to be developed and implemented, as mandated by the U.S. Environmental Protection Agency (USEPA). Where As impairment is due to naturally occurring inputs, TMDLs are not developed, but anthropogenic inputs may require TMDL development and implementation. Earlier, a national survey indicated that the As content of streambed sediments was elevated in the New Jersey Coastal Plain (Averett, 1984), but the sources and implications of the elevated As were not addressed until the current study.

To assist TMDL-related investigations, the U.S. Geological Survey (USGS), in cooperation with NJDEP, surveyed five representative Coastal Plain streams during 2006–09 to determine background levels of As in stream water, and partnered with Rutgers University to begin an assessment of microbial interactions with geogenic As. The geologic materials underlying two of the selected streams were substantially different (quartz-rich) from those underlying most reaches of the other three streams (glauconitic). Effects of land development (either agricultural or urban) in southern New Jersey on the mobility of contaminants such as nitrate (NO_3^-), radium (Ra), and mercury (Hg) have been previously documented (for example, Kozinski and others, 1994; Barringer and others, 2006; Barringer and Szabo, 2006; Barringer and others, 2010a); consequently, the current study examines potential effects of land use on As presence and mobility in various media. Because the current study provides fundamental baseline delineation and a better understanding of “natural background” (geogenic) inputs of As, as well as potential “legacy” inputs (such as pesticide residues) to the aqueous environment, it can be used to inform environmental-protection and

land-management activities. Insofar as groundwater discharge supplies most of the water to Coastal Plain streams, an important focus of the current investigation was on interactions between groundwater, sediments, and stream water.

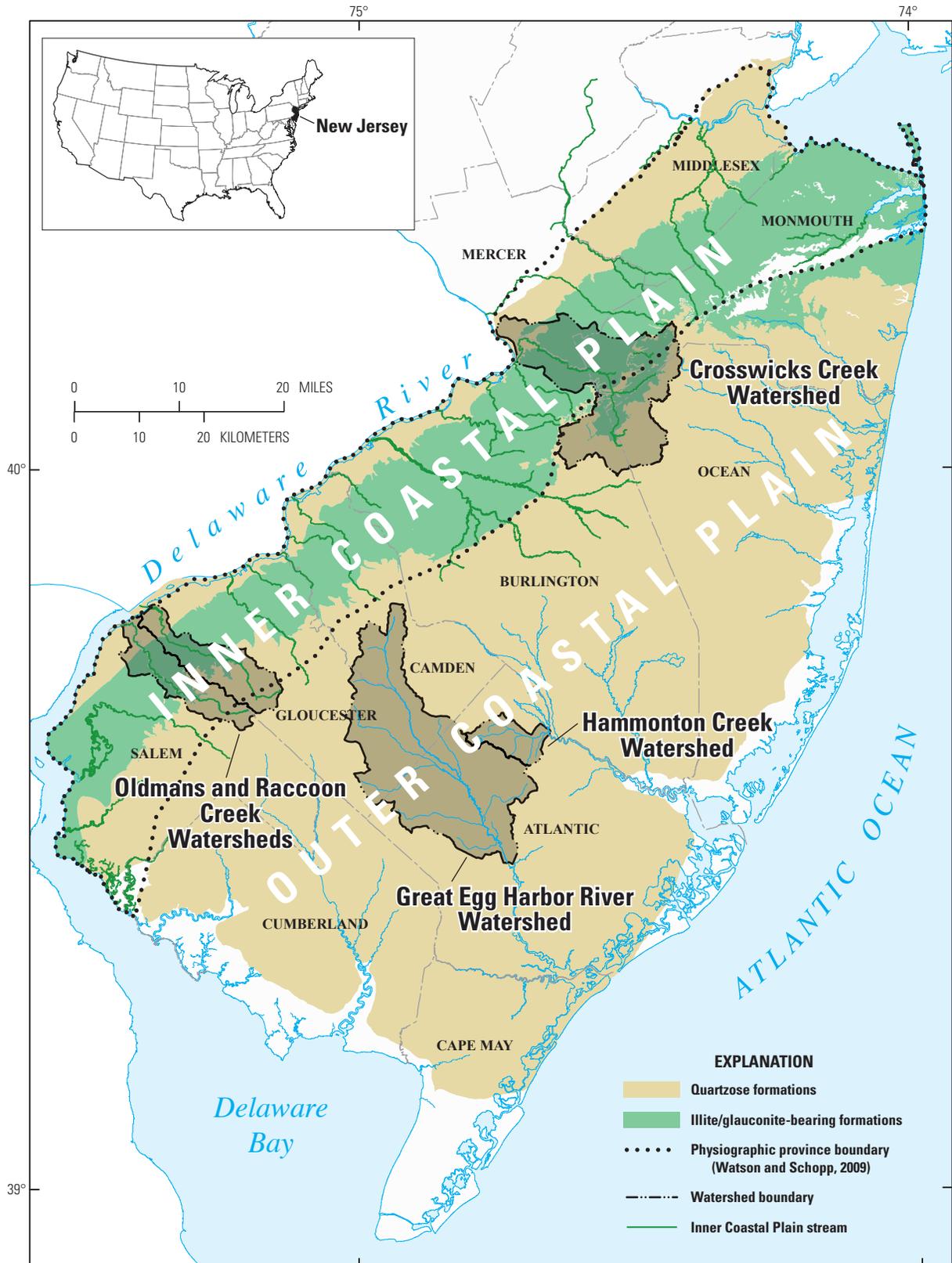
Purpose and Scope

This report presents results of studies of five individual watersheds in the Coastal Plain of New Jersey in which the geologic and anthropogenic contributions of As to New Jersey Coastal Plain streams were assessed. The biogeochemical processes that affect As mobility and levels in the groundwater discharging to streams, in the streams, and in the streambed sediments are discussed with regard to natural (geologic) contributions of As; additionally, the effects of anthropogenic alterations to groundwater and stream-water biogeochemistry and flow are explored.

Study Area

A seaward dipping wedge of unconsolidated sediments forms the Coastal Plain in New Jersey; these deposits range in age from the Cretaceous to the late Tertiary Periods. In the Inner Coastal Plain (as defined by Watson and Schopp, 2009), most streams drain to lower, mainly tidal, reaches of the Delaware River (fig. 1). These streams generally rise among fine-grained sands and the basal clays of the Miocene Kirkwood Formation and traverse bands of successively older sedimentary units of marine and marginal marine origin (fig. 2; appendix 1). Adjacent to the Delaware River, however, Cretaceous quartzose sediments of deltaic and marine origin (Potomac and Magothy Formations) crop out (Owens and Sohl, 1969) and are partially overlain by quartzose sands and gravels of the Miocene Pennsauken Formation (not shown in fig. 2) (Owens and Minard, 1979). Sediment units composed mostly of clays act as confining units; the sandier units form aquifers (Zapecza, 1989; appendix 1). The sediments of marine origin, reworked surficial deposits, and the soils developed upon them, contain quartz and phyllosilicate minerals (biotite, muscovite, illite), and, in particular, the mineral glauconite. Glauconite mineral separates from formation sediments, and from glauconitic soils developed on those sediments, have As contents that range from about 7 to 136 milligrams per kilogram (mg/kg) (Dooley, 1998; 2001). Apatite-rich phosphorite deposits, which contain marine-organism bone fragments and glauconite, occur at the Hornerstown/Navesink and Navesink/Mt. Laurel Formation contacts (Sugarman, 1999; fig. 2); samples of these deposits were determined to contain about 20 to 57 mg/kg of As (Barringer and others, 2011a).

In the Outer Coastal Plain, streams drain to the Atlantic Ocean (fig. 1). Their channels are underlain primarily by the Miocene Cohansey Formation, which is composed of sands, silts, gravels, and clay lenses (Owens and Sohl, 1969). The mineralogy of Outer Coastal Plain geologic formations (Cohansey and Kirkwood—hereafter referred to together

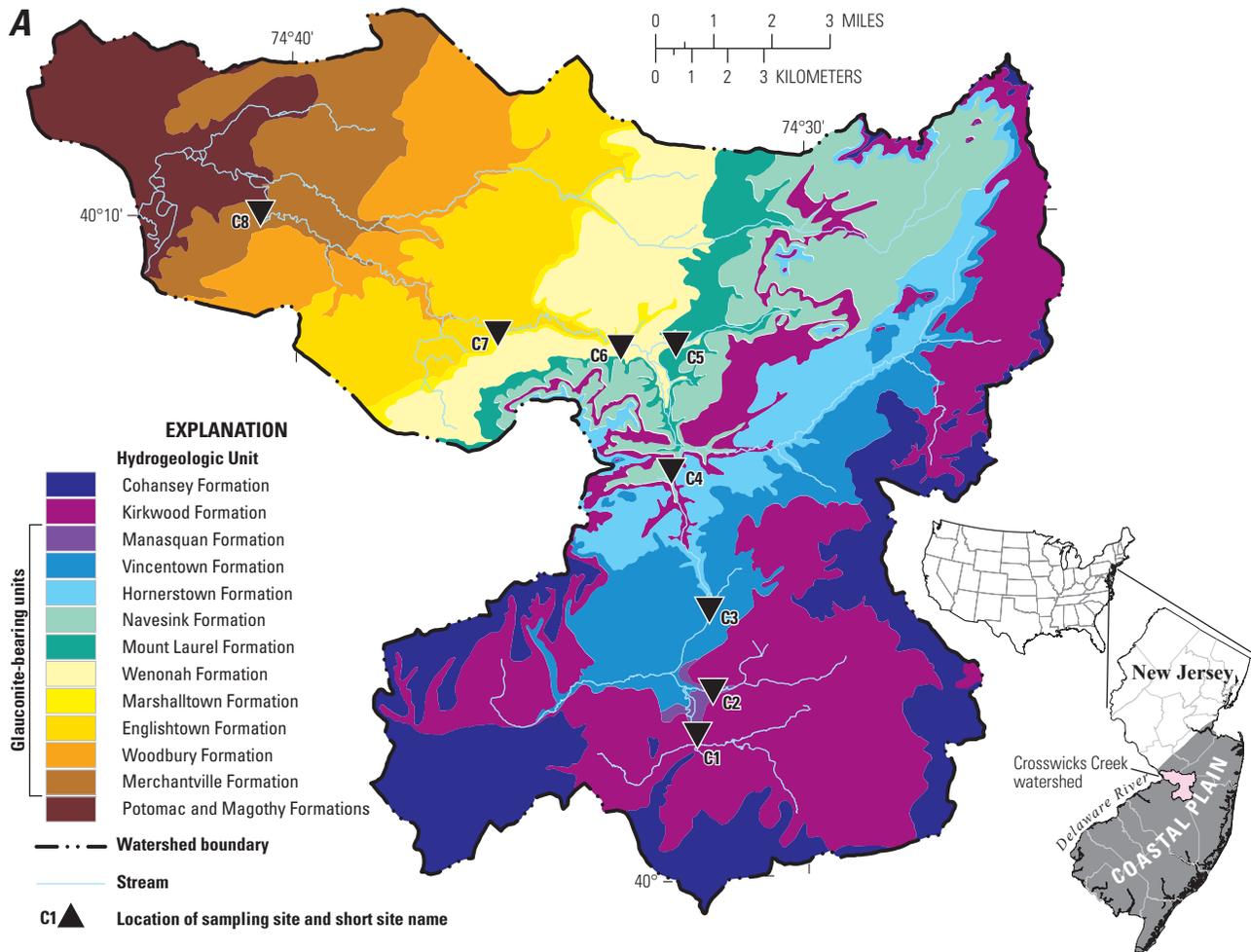


Base from U.S. Geological Survey 1:24,000-scale digital data
 Universal Transverse Mercator, Zone 18
 North American Datum of 1983

Geology from Zapecza, 1989 and New Jersey Department of Environmental Protection, 1999

Figure 1. Inner and Outer Coastal Plain sub-provinces of New Jersey, with generalized geology and locations of five watersheds.

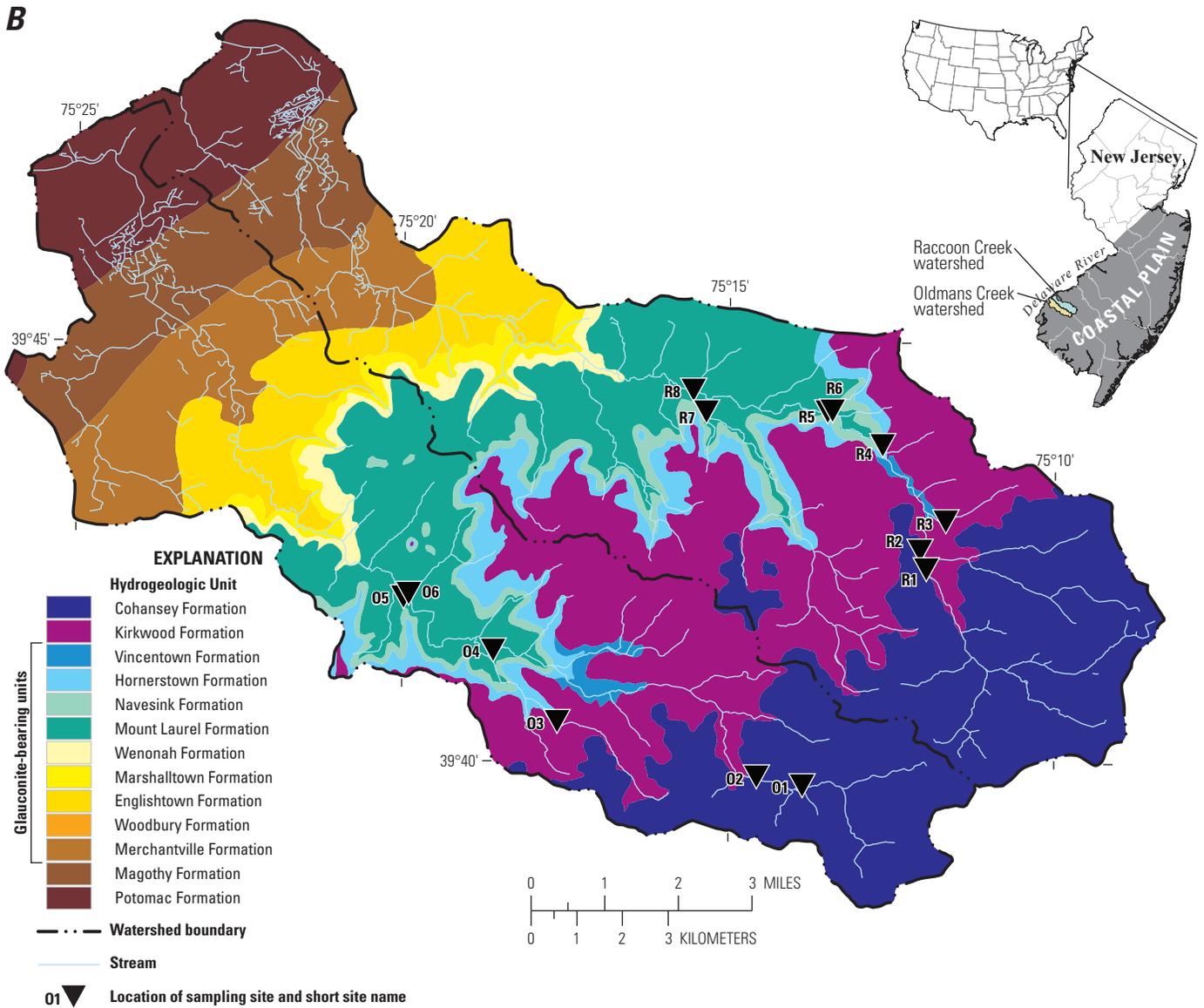
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Geology from Zapezca, 1989 and New Jersey Department of Environmental Protection, 1999

Figure 2. Detailed geology of three Inner Coastal Plain watersheds in New Jersey: *A*, Crosswicks, *B*, Raccoon and Oldmans Creeks.



Base from U.S. Geological Survey 1:24,000-scale digital data
Universal Transverse Mercator, Zone 18
North American Datum of 1983

Geology from Zapecza, 1989 and New Jersey Department of Environmental Protection, 1999

Figure 2. Detailed geology of three Inner Coastal Plain watersheds in New Jersey: *A*, Crosswicks, *B*, Raccoon and Oldmans Creeks.—Continued

as CKKD; fig. 1) is dominated by quartz that commonly is coated with amorphous or poorly crystalline Fe hydroxides. Ilmenite is an accessory mineral, although, in some areas, it is present as mineable accumulations (Markewicz, 1969). Clays are predominantly kaolinite, with minor illite and smectites, which are expandable clays (Owens and Sohl, 1969; this study). Arsenic in the CKKD sediments appears to be mainly contained in clays, but the data for aquifer sediment chemistry are limited because, to the authors' knowledge, no analyses of As in sediments of the CKKD had been performed until the current study.

Although the unconsolidated material that forms the CKKD is composed mainly of sediments of the Cohansey and Kirkwood Formations, remnants of the quartz-rich, gravelly Miocene Bridgeton Formation and the Beacon Hill Gravel (not shown in fig. 2) are found in some upland areas, and reworked materials from the underlying sands and gravels constitute surficial sediments (Owens and Minard, 1979; Rhodehamel, 1979). Well to excessively drained upland soils developed on the Cohansey and Bridgeton Formations are Quartzipsaments (some are spodosols) and Hapludults. Poorly drained lowland soils are Haplaquods, and muck soils are found bordering streams. Outer Coastal Plain soils typically are extremely to very strongly acidic (Markley, 1979).

In the Inner Coastal Plain, the drainage areas of three creeks—Crosswicks (CRO), Raccoon (RAC), and Oldmans (OLD)—are 254, 70, and 54 square kilometers (km²), respectively, from headwaters to the farthest downstream point sampled (table 1, figs. 1, 2, and 3). Streams in the other two of the five selected watersheds—the Great Egg Harbor River (GEHR) and its tributaries, and Hammonton Creek (HAMM)—traverse the Outer Coastal Plain (figs. 1 and 3). The GEHR watershed is about 400 km² to the farthest downstream sampling point above head-of-tide, whereas the HAMM watershed to the farthest downstream sampling point is only 39 km². Sites on the tidal segments of the GEHR, HAMM, OLD, and RAC watersheds were not sampled during the current study. Although some of the study sites within the CRO and OLD fall just outside of the Inner Coastal Plain boundary (fig. 1), they contribute water and sediments to Inner Coastal Plain streams and are, for the context of this report, discussed as Inner Coastal Plain sites.

Streams of the New Jersey Coastal Plain typically receive most of their water from groundwater discharge. In general, base flow constitutes a higher percentage of total flow in Outer Coastal Plain streams than it does in the Inner Coastal Plain streams. Base flow (principally groundwater discharge) is nearly 90 percent of annual streamflow in the GEHR, compared to about 72 percent of total flow in the RAC (V.T. DePaul, U.S. Geological Survey, written commun. 2008) and only about 66 percent of total flow in the CRO (Watt and others, 2003). Inner Coastal Plain streams traverse areas of moderate relief where segments of the streams are incised into the underlying geologic units, whereas Outer Coastal Plain streams flow mainly through areas of low relief. Extensive

Table 1. Short site name, U.S. Geological Survey site number, drainage area, and predominant land use for sampling locations on three Inner Coastal Plain streams, New Jersey.

[km², square kilometer; Sampling locations can be found on figure 3; the underlying geology for sites is listed in appendix 1; U.S. Geological Survey site numbers and drainage area from the National Water Information System database at <http://waterdata.usgs.gov/nj/nwis>]

Short site name	U.S. Geological Survey site number	Drainage area (km ²)	Land use ¹
Crosswicks Creek			
C1	01464290	60.9	Forest, wetlands
C2	01464330	11.8	Forest, wetlands
C3	01464400	107	Urban
C4	01464430	129	Agriculture
C5	01464480	8.16	Urban/agriculture
C6	01464485	203	Agriculture
C7	01464500	211	Agriculture
C8	01464504	254	Urban/forest
Raccoon Creek			
R1	01477081	16.7	Mixed
R2	01477100	26.2	Mixed
R3	01477102	1.89	Agriculture
R4	01477105	33.1	Mixed
R5	01477109	1.86	Urban
R6	01477110	40.4	Urban
R7	01477118	21.5	Agriculture
R8	01477120	69.7	Agriculture
Oldmans Creek			
O1	01477440	10.7	Agriculture
O2	01477445	12.3	Forest/agriculture
O3	01477480	35.7	Agriculture
O4	01477488	4.30	Agriculture
O5	01477509	3.63	Urban/agriculture
O6	01477510	54.4	Urban/agriculture

¹Predominant land use for each site was defined within the upstream arc of 1-kilometer radius.

wetland areas are relatively few in the Inner Coastal Plain compared to the Outer Coastal Plain, where they constitute major features of the landscape.

According to the NJDEP 2002 ArcGIS Land use/Land coverage polygon, land use in the studied watersheds is varied. The Inner Coastal Plain watersheds contain much agricultural land, particularly in their headwaters areas, and become more urbanized in downstream areas, near their confluences with the Delaware River (table 1). The Outer Coastal Plain watersheds typically contain extensive wetlands and forested areas as well as some agriculture in downstream areas, but there are urban



Base from U.S. Geological Survey 1:24,000-scale digital data
 Universal Transverse Mercator, Zone 18
 North American Datum of 1983

Figure 3. Locations of sampling sites in five Coastal Plain watersheds in New Jersey.

areas near their headwaters (table 2). Of the five watersheds, recent urbanization is most pronounced in the RAC watershed (New Jersey Department of Environmental Protection, 2008).

Land use of the Coastal Plain sampling sites is mainly designated as urban, agriculture, or forest/wetland, when the drainage area to the stream site is occupied by 50 percent or greater of one of these land uses. Where no land use is dominant, the land use is described as “mixed.” Most drainage areas of mixed land use contain a substantial percentage of urban land. Where two of the three major land uses are about equal in extent, they are designated as urban/forest or urban/agriculture, for example.

Table 2. Short site name, U.S. Geological Survey site number, drainage area, and predominant land use of sampling locations on two Outer Coastal Plain streams, New Jersey.

[Sampling locations can be found on figure 3; the geologic formation underlying all sites is the Cohansey Formation of Miocene age; km², square kilometer; na, not applicable; U.S. Geological Survey site number and drainage area from the National Water Information System database at <http://waterdata.usgs.gov/nj/nwis>]

Short site name	U.S. Geological Survey site number	Drainage area (km ²)	Land use ¹
Great Egg Harbor River			
GA	01410789	1.35	Urban
GC	01410810	20	Mixed
GD	01410865	7.82	Urban
GE	01411035	11.7	Mixed
GF	01411071	161	Forest/wetlands
GG	01411140	51.8	Forest/wetlands
G1	01410770	5.18	Urban
G2	01410770	4.87	Urban
G3	01410784	39.1	Mixed
G4	01410788	59.0	Mixed
G5	01410820	96.6	Forest/wetlands
G7	01411000	148	Forest/wetlands
G8	01411105	399	Forest/wetlands
G9	01411107	na	Forest/wetlands
G10	01411110	399	Forest/wetlands
Hammonton Creek			
H1	0140941198	6.58	Urban
H2 ²	393759074460301	na	Mixed
H3	01409414	7.02	Mixed
H4	01409416	24.8	Agriculture
H5	01409418	38.9	Agriculture

¹Predominant land use for each site was defined within the upstream arc of 1-kilometer radius.

²Site H2 is a sewage-treatment plant out-fall.

Methods

Sampling Site Names

Sampling sites have identifying site numbers and names in the USGS National Water Information System (NWIS) database. For simplicity, we have given sampling sites short names (figs. 2 and 3, tables 1 and 2), such as H1 for the farthest upstream site on Hammonton Creek. Sites on Crosswicks and Raccoon Creek are numbered (for example, C1 and R1) as they are in Barringer and others (2010b). Sites on the GEHR main stem are assigned numbers (for example, G1), and tributary sites are assigned letters (for example, GA) as they are in Barringer and others (2010a). Sites GB and G4 in the GEHR watershed were sampled in September 2006 with other GEHR sites for mercury (Barringer and others, 2010a) but not for arsenic, and the data from that sampling are not included here.

Streamflow Measurements

There are USGS streamgages on three of the five streams sampled—at sites G7 (01411000), R8 (01477120), and C7 (01464500) (fig. 3, tables 1 and 2). Before stream-water sampling, the hydrograph for previous and current streamflow was examined at the above streamgages, and at the Albertson Brook streamgage (01409410; not shown) adjacent to the HAMM watershed; the R8 streamgage in the adjacent RAC watershed was used to plan sampling on OLD. During stream-water sampling, streamflow was determined from stage-discharge relations at the streamgages and was measured at the ungaged sites by wading, using a pygmy current meter, or from a bridge, using a Price AA meter, using standard USGS techniques (Carter and Davidian, 1968).

Sample Collection

The streams in the five watersheds were sampled in a synoptic fashion during 2006–09—all sites in a given stream in one or two consecutive days under elevated- to high-flow conditions (at least 10 percent above to greatly above the streamgage period of record median flow for the date) and at low-flow conditions (at least 10 percent below the streamgage period of record median flow for the date) (table 3). Additional sampling efforts included low base-flow conditions (CRO), bi-hourly at low base-flow conditions for 22 hours (GEHR), sewage treatment plant (STP) discharge (HAMM site H2), and high-flow stream water and runoff at two detention basins (RAC). Stream-water samples were collected from midway in the water column using an equal-width interval method and composited in acid-washed churns (U.S. Geological Survey, variously dated).

Groundwater discharging to selected main stem and tributary sites in all five watersheds was sampled. Groundwater samples were collected using single acid-washed 0.5-inch

inner diameter polyvinyl chloride (PVC) piezometers driven into the streambed in gaining reaches, where water levels in the piezometers typically were about 4.6 centimeters (cm) or higher above water levels in the streams. The piezometers were developed until the water withdrawn was clear and turbidity less than 10 Nephelometric Turbidity Units (NTU), with purging lasting from 10 minutes to 2 hours, as needed. The groundwater sample was slowly withdrawn through acid-washed Teflon-lined tubing with a peristaltic pump, as described previously (Barringer and others, 2010a; Barringer and others, 2011a); the tubing extended down the piezometer to the slotted screen. Cross-sectional transects of piezometers at three sampling sites, one each on the GEHR and a tributary, and one on the CRO, also were installed and sampled.

Filtered aqueous samples were collected through an in-line 0.45-micrometer (μm) pore-size capsule filter. All sample processing and preservation was done inside chambers (polyethylene bags on a PVC frame) that were changed between samples. All equipment, including piezometers, was acid-washed (5 percent hydrochloric acid (HCl)) and rinsed with de-ionized water between uses, and USGS “clean hands/dirty hands” protocols were followed throughout (Wilde and others, 2004). Samples for analysis of As species were filtered and preserved with ethylenediaminetetraacetic acid (EDTA) in the field as prescribed by Garbarino and others (2002). Samples for sulfide analysis were collected and preserved with zinc (Zn) acetate, according to Clesceri and others (1998).

Streambed-sediment samples were collected from randomly selected areas of sediment deposition within the streams at all sampling sites under low-flow conditions and sieved to less than 2 millimeters (mm) using acid-washed, field-rinsed plastic scoops and sieves.

Two adjacent streambed-sediment cores from the streambed at C6 on the CRO were retrieved by driving 1-meter- (m) long stainless steel corers with clean butyl acetate liners into the sediments about 1 m from the right streambank. Cleaning and preparation of the corers is described in Barringer and others (1998). Streambed sediments retrieved from the first core were frozen for mineralogical and chemical analysis.

The second, adjacent streambed-sediment core was retrieved for microbiological analysis and frozen on dry ice. Stream water and groundwater samples were also collected from site C6 on CRO (fig. 3) for microbiological analysis, using sterile tubing, filters, and bottles and frozen until analysis. Microbial deoxyribonucleic acid (DNA) was extracted and amplified, and genes were cloned and sequenced, as described in detail in Barringer and others (2010b).

Soil samples were collected from orchard areas adjacent to the CRO, from the detention basin and nearby wetland adjacent to the RAC, and from the banks of a small tributary to the GEHR, using either a 1-m-long stainless steel corer with pre-washed butyl acetate liners or, where gravel prevented driving the corer, a clean stainless steel hand auger. The soil cores were subsampled by horizon, and soil subsamples were sieved to less than 2 mm and sent for analysis. Samples of aquifer sediments from the Kirkwood-Cohansey aquifer system were

collected, using a split spoon with butyl acetate liners, from observation wells drilled along rights-of-way in Williamstown near GEHR tributary site GD (fig. 3), Gloucester County, New Jersey.

Sample Preparation and Analysis

Aqueous Samples

Preparation for analysis of major cations and trace elements in unfiltered samples involved first digesting the sample by addition of HCl to the sample bottle. Cations and trace elements in unfiltered and filtered samples were analyzed by inductively coupled plasma-mass spectrometry or atomic emission spectrometry (ICP/MS; ICP/AES), or by collision-cell ICP/MS (As and As species; Garbarino and others, 2006) at the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colorado. Nutrients were analyzed by colorimetry or photometry, organic carbon by infrared spectrometry, and anions by ion chromatography at NWQL. See the publication USGS Techniques of Water Resources Investigations at <http://water.usgs.gov/pubs/twri/> for method references. Of the trace elements determined, only selected elements are presented in the appendixes in this report. The full dataset is available online from the USGS National Water Information System database (NWIS) at <http://waterdata.usgs.gov/nj/nwis>. It should be noted that, for unfiltered (whole water) samples, concentrations of some trace elements, such as Fe and As, may be less than those in filtered samples because the in-bottle HCl digestion apparently did not completely digest suspended particles, or re-precipitation occurred after digestion.

Sulfide analyses of water from piezometers and wells at C6 were analyzed at the USGS New Jersey Water Science Center (NJWSC) laboratory, using the colorimetric method of Cline (1969). Where results for As and metals in unfiltered and filtered samples are differentiated, they will be referred to with a subscript u or f, respectively, as in As_u or As_f . Particulate concentrations of As and metals are calculated as the difference between concentrations in unfiltered samples and those in filtered samples (for example: $\text{As}_u - \text{As}_f = \text{As}_p$).

Sediment and Soil Samples

Streambed-sediment samples were analyzed at the NWQL for recoverable (HCl-leachable) As and for metals by ICP/MS and ICP-AES and, at the USGS Geologic Discipline Laboratory (GDL) in Denver, Colorado, for total As, trace metals, major cations, and phosphorus (P) (digestion by nitric acid (HNO_3), HCl, hydrofluoric acid (HF), perchloric acid (HClO_4)) by ICP/MS (Arbogast, 1996; Briggs and Meier, 2002), and for total carbon and carbonate carbon by titration and LECO analyzer (Brown and Curry, 2002; Brown and others, 2002). Organic carbon (OC) was determined by calculating the difference between total and carbonate carbon. Aquifer-sediment samples also were analyzed for As, metals,

10 Arsenic in New Jersey Coastal Plain Streams, Sediments, and Shallow Groundwater

Table 3. Summary of sample collection in five Coastal Plain watersheds, New Jersey.

[SW, stream water, RNF, runoff; GW, groundwater; SED; streambed sediments; SLC, soil cores; SL, soil samples; MCR, microbiological; ~, about; %, percent; > greater than; ×, times; <, less than; NA, not applicable; ND, not determined]

Date	Flow regime relative to daily median discharge	Sampled medium	Number of sites	Comments
Crosswicks Creek				
04/10/07, 04/11/07	~25% below median	SW	8	Main stem and two tributaries.
		GW	4	Main stem; piezometers.
		SED	8	Main stem and two tributaries.
05/03/07, 05/04/07	tidal cycle	SW	1	C8, bi-hourly automatic sampling.
07/13/07	>50% below median	SW	3	Main stem.
		GW	2	Main stem; piezometers
10/12/07	~6× above median	SW	6	Main stem.
10/17/07	~50% below median	SW	1	C6.
		GW	1	C6, piezometer transect.
		GW	¹ 1	Artesian well, C6.
11/07/07	NA	SLC	1	Two soil cores collected at C6, orchard areas.
02/11/08	NA	GW	¹ 1	Deep well, C6.
08/18/09	~ 60% below median	SW	² 1	C6.
		GW	² 1	C6.
		MCR	² 1	C6.
11/05/09	NA	SED	6	Main stem.
12/03/09	~3× above median	SW	6	Main stem.
Raccoon Creek				
02/28/07, 03/01/07	~ 25% above median	SW	² 6	Main stem and two tributaries.
		GW	² 4	Main stem, one tributary; piezometers.
		SED	² 6	Main stem and two tributaries.
05/24/07, 05/25/07	~30% below median	SW	² 6	Main stem and two tributaries.
		GW	² 2	Main stem; piezometers.
05/16/08	ND	SW	³ 1	R4.
		RNF	³ 2	Detention basin, R4.
06/20/08, 07/10/08	ND	SLC, SL	³ 3	Detention basin, bankside, R4.
09/06/08	ND	SW	³ 1	R1.
		RNF	³ 4	2 detention basins, R1, R4.
10/01/08	NA	SL	1	Bankside, R1.
Oldmans Creek				
03/22/07	~40% above median (data from gage at 01477120— Raccoon Creek at Swedesboro)	SW	6	Main stem, two tributaries.
		GW	1	Main stem.
		SED	² 6	Main stem, two tributaries.
05/16/07	~20% below median	SW	6	Main stem, two tributaries.

Table 3. Summary of sample collection in five Coastal Plain watersheds, New Jersey.—Continued

[SW, stream water, RNF, runoff; GW, groundwater; SED; streambed sediments; SLC, soil cores; SL, soil samples; MCR, microbiological; ~, about; %, percent; > greater than; ×, times; <, less than; NA, not applicable; ND, not determined]

Date	Flow regime relative to daily median discharge	Sampled medium	Number of sites	Comments
Great Egg Harbor River				
08/22/06, 08/23/06	~45% below median	SW	1	G8, bi-hourly, manual samples.
		GW	2	G8, G9, piezometers, spring.
10/16/06, 10/26/06	>50% above median	SW	6	Great Egg Harbor River tributaries.
		SED	6	Great Egg Harbor River tributaries.
11/02/06, 11/03/06	>50% above median	SW	6	Main stem.
		GW		
12/06/06	NA	SED	6	Main stem.
06/07/07	~ 15% above median	SW	1	G5.
		GW	1	G5, four piezometer transect.
07/02/07	< 10% below median	SW	5	Main stem.
07/02/07, 07/07/07		GW	2	G1, G4, piezometers, summer.
07/25/08	~ 40% below median (data from gage at 01411000—Great Egg Harbor River at Folsom)	SW	4 ¹	4 sampling sites on Squankum Branch, upstream of primary sampling site GD.
11/17/08, 11/18/08	~ 30% above median	SW	4 ¹	2 sampling sites on Squankum Branch, upstream of primary sampling site GD.
		GW	4 ¹	3 piezometer transects on Squankum Branch, upstream of primary sampling site GD.
		SED	4 ¹	2 sampling sites on Squankum Branch, upstream of primary sampling site GD.
03/24/09–03/30/09	NA	SED, SLC	4 ¹	5 sampling sites on Squankum Branch, upstream of primary sampling site GD.
Hammonton River				
12/05/06	~ 15% above median (data from gage at 01409410—Albertson Brook)	SW	4	H1, H3–H5.
03/14/07	ND	SW	1	H2, sewage-treatment-plant outlet.
		SED	4	H1, H3–H5.
05/09/07	>50% above median	SW	5	H1–H5.
		GW	2	H3, H5.
		SED	1	H2.
09/20/07	~45% below median	SW	5	H1–H5.

¹Refer to Barringer and others, 2011a for Crosswicks Creek data and discussion.

²Refer to Barringer and others, 2010b for Inner Coastal Plain data and discussion.

³Refer to Barringer and others, 2011b for Raccoon Creek data and discussion.

⁴Refer to Barringer and others, 2010a, 2011b, 2013 for Squankum Branch data and discussions.

P, and OC at the GDL. Selected elements are presented in the tables and appendixes in this report. Additional streambed-sediment data are available at <http://waterdata.usgs.gov/nj/nwis>.

Splits of the Inner Coastal Plain streambed-sediment samples analyzed for total chemistry at the GDL were analyzed for mineralogy by X-ray diffraction (XRD) at the USGS Research Laboratory in Boulder, Colorado using a Siemens D500 instrument. Weighed samples containing an internal zincite standard were ground in a McCrone mill, prepared as randomly oriented powder packs, and scanned, using Copper K-alpha ($\text{Cu K}\alpha$) radiation, from 5° to 65° 2θ . Mineralogy of selected aquifer-sediment samples—bulk and mineral separates—was determined by XRD, using a Scintag 1-X diffractometer at the GDL.

Of the two streambed-sediment cores from sampling site C6, one was used for the microbiological study. The chemical composition and mineralogy of the adjacent streambed-sediment core was determined at the GDL. The frozen core was sectioned into 2- to 4-cm segments; these were retrieved from 33 to 36 cm; 43 to 46 cm; 56 to 58 cm; 63 to 66 cm, 71 to 74 cm, and 86 to 90 cm to assess changes in chemistry and mineralogy reflective of changes in redox conditions in the sediments at and below the interval in the first core selected for microbial analysis.

Subsamples of the adjacent C6 streambed-sediment core sent to the GDL for analysis were prepared by removing the outer rim (approximately 0.5 cm) of each sample plug; the remaining material was freeze dried, loosely consolidated, and disaggregated. Each bulk sample was riffle split into three 50-g aliquots. One aliquot was ground and chemically analyzed at the GDL. Analyses for carbon were done by titration and LECO analyzer at the GDL (Brown and Curry, 2002; Brown and others, 2002). Major- and trace-element analysis was done by ICP/MS, following total acid digestion (Arbogast, 1996; Briggs and Meier, 2002).

A fraction of the bulk sediment from the C6 streambed-sediment core was analyzed for mineralogy by XRD to determine mineral abundances. Samples were crushed by hand to $<250\ \mu\text{m}$, micronized in a McCrone mill with isopropanol, randomly packed into holders, and analyzed on a Scintag 1-X diffractometer. Heavy mineral concentrates of the five deepest samples were examined optically.

Polished grain mounts were made from aliquots of the five deepest samples from the C6 streambed-sediment core. Unconsolidated sediment was stirred into slow-set epoxy and centrifuged to create graded grain sizes. The epoxy plugs were cut on an angle, yielding a section through the graded grains, and polished. A JEOL 5800LV Scanning Electron Microscope (SEM) scanned several hundred particles in each mount for minerals with substantial As content. Select areas and individual grains also were studied by SEM to document texture and growth habits of the grains. Glauconite and siderite separates were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) to determine the As content.

Samples from soil cores collected in orchard areas at sampling site C6 were analyzed at the USGS Georgia Water

Science Center laboratory at Doraville, Georgia, and at the GDL. Samples analyzed at the Doraville laboratory were digested with hydrofluoric/perchloric acids and analyzed by ICP/AES for metals, P, and sulfur (S), and for As by ICP/AES with hydride generation. Total carbon and organic carbon (OC) were analyzed by combustion (Arthur Horowitz, U.S. Geological Survey, written commun. 2007).

Microbiological Samples

In the Rutgers microbiological laboratory, sediments at 15 to 30 cm from the inner part of the first streambed-sediment core were sectioned, composited, and well mixed under sterile conditions. DNA was extracted from groundwater, stream water, and sediment samples; these extractions, amplification of the 16S small subunit Ribosomal Ribonucleic acid (rRNA) gene in sediment and water extracts, and identification of the arsenic respiratory reductase gene (*arrA*) are described in detail by Barringer and others (2010b).

Microcosms of sediment and groundwater were used to test whether As(V) was reduced to As(III) by the indigenous microbes and released into the respective media. Sediment and groundwater microcosms were prepared by inoculating 10 grams of sediment or 10 milliliters (mL) of groundwater into 30 mL of defined anaerobic medium (see appendix 2 for composition). The medium was adjusted to pH 7.2 and filter sterilized with a Millipore Millex® GP 0.22 μm filter before use. Following the observation of activity, 5 mL was transferred to 45 mL of fresh medium.

Abiotic controls were prepared by autoclaving inoculated microcosms. The microcosms were incubated under anaerobic conditions at temperature (T) = 25 degrees Celsius ($^\circ\text{C}$) [about the same T as the groundwater during the summer months (ranging from 21–26.5 $^\circ\text{C}$)]. Each week, 600 microliters (μL) was anaerobically sampled and analyzed for As species until complete reduction of arsenate to arsenite was observed. The reduction of As(V) to As(III) was monitored using a Beckman System Gold® HPLC equipped with a Hamilton PRP X-100 anion exchange column as described by Perez-Jimenez and others (2005). Samples were analyzed for As released from site sediments by ICP-OES.

Quality Assurance Measures

One or more sets of replicate sample pairs of aqueous samples were collected in each of the watersheds during each sampling for a total of 13 replicate pairs. Seventeen equipment blanks were collected. Blanks for surface-water were collected in the field by passing inorganic analyte-free water through the sampling train; for the piezometers, blanks were collected in the NJWSC laboratory by passing inorganic analyte-free water through the piezometer, tubing, and filter. In most cases, constituents in blanks were less than the reporting limit. Quality-assurance results for aqueous samples are presented in appendix 3. Further, ion balances for aqueous

samples generally were less than 5 percent. For the microbiological microcosm studies, each set of microcosms contained duplicate autoclaved abiotic controls and background controls containing only medium and inoculum that were not amended with additional As(V) or organic carbon.

Data Analysis

Quantitative mineralogy of Inner Coastal Plain streambed sediments was calculated using the RockJock program (Eberl, 2003). The HandLens program was used to fit constituent concentrations (from total digestion analyses) to quantitative mineral analyses by solving simultaneous linear equations, using the Excel Solver (Eberl, 2008). Mineral content of the aquifer sediments was quantified using the program Jade 9.1 (MDI, Inc.©). The RockJock program (Eberl, 2003), used to quantify the mineralogy, yielded semi-quantitative mineral contents because the analysis did not consider amorphous and poorly crystalline material. Pearson and Spearman correlation analyses and linear regression were used to assess relations among chemical constituents in water and soil/sediment samples collected during this study. Data for water samples collected from observation wells installed near the GEHR watershed divide for an ongoing National Water Quality Assessment Program (NAWQA) study also were evaluated.

All microbiological gene sequence data were screened for sequencing vector contamination using the National Center for Biotechnology Information (NCBI) VecScreen tool (NCBI, 2009); 16s sequences were aligned using the SINA webaligner© (Pruesse and others, 2012), and results were imported into the ARB software package for phylogenetic analysis (Ludwig and others, 2004; Pruesse and others, 2007). Nearest neighbors were picked from the SILVA 102 Ref Non-redundant database. The arsenic respiratory reductase gene *arrA* was identified, a reference database of 93 *arrA* sequences retrieved from Genbank was constructed in ARB, and alignment of the *arrA* sequences was performed using the ClustalW algorithm within ARB (Ludwig and others, 2004; Larkin and others, 2007). Sequences were separated into Operational Taxonomic Units (OTUs), based on a cutoff of 85 percent similarity using the mothur software package (Schloss and others, 2009).

Sediment and Soil Chemistry, Mineralogy, Microbiology, and Arsenic Content

Inner Coastal Plain

Although rising in the quartz sands of the Cohansey and Kirkwood Formation sediments, most of the CRO basin is underlain by glauconite-bearing marine sediments. In contrast,

a larger part of the upper reaches of the RAC and OLD Basins is underlain by weathered quartz sands and finer-grained deposits that typify the Outer Coastal Plain. The total As content of the quartz-rich streambed sediments from CRO, RAC, and OLD near their headwaters were about 4 mg/kg or less and increased sharply—ranging from about 10 to 30 mg/kg—where the channels cut through the glauconite-rich sediments (fig. 4).

The total As contents determined for the soil and streambed-sediment cores at C6 and for the soil and bankside-sediment cores at R1 and R4 were similar or greater than the streambed sediments from other Inner Coastal Plain sites. The total As contents of six samples from the C6 streambed core at CRO ranged from 15 to 26.4 mg/kg (median 21.6 mg/kg); a glauconite mineral separate contained 33.7 mg/kg of As, and a siderite mineral separate contained 184 mg/kg (Mumford and others, 2012; appendix 4). The total As content of glauconite-bearing former orchard soils along the bank at site C6 and farther upslope from C6 ranged from 12 to 110 mg/kg; increased contents of Cu, Pb, and Sb in the two soil samples with the greatest As content were tentatively ascribed to inputs, along with As, from pesticide residues (Barringer and others, 2011a). The total As content of bankside soils and glauconite clays at site R4 on RAC ranged from 12 to 45 mg/kg (Barringer and others, 2011b), with the highest As contents associated with the glauconitic clays. Site R1 on RAC is underlain by quartzose sediments of the Kirkwood Formation; the As content of the surficial soil from a core at R1 was greater than that of the deeper soils, and thus inputs from past pesticide use may have led to the observed vertical distribution of As in the soil (Barringer and others, 2011b).

Quartz was a dominant mineral in the streambed sediments for CRO, RAC, and OLD, but a variety of phyllosilicates also were present; some, like glauconite, made up a substantial proportion of the total minerals present (table 4), and minor phases were important as likely hosts of As. In these sediments, the total As content was strongly associated with the weight percent of apatite ($R^2 = 0.77$). Arsenate can substitute for phosphate in the apatite crystal lattice (Stamatakis, 2004), and apatite-rich phosphorite deposits along the Hornerstown/Navesink, and Navesink/Mt Laurel contacts (fig. 2) are highly enriched in As (Barringer and others, 2011a.) The total As contents of the streambed sediments also were strongly associated with the weight percents of the phyllosilicate minerals biotite, illite/glauconite, chlorite, muscovite, and kaolinite, with an overall R^2 of 0.81 for the sum of all phyllosilicate weight percents (Barringer and others, 2010b). When the total As content of CRO, RAC, and OLD sediments was regressed against the sum of weight percents of apatite, all phyllosilicates, and goethite, the R^2 was 0.84 (fig. 5). The total As content of the sediments also was strongly related to total contents of aluminum (Al) and Fe ($R^2 = 0.88$), indicating association with phyllosilicate minerals (particularly Fe-rich biotite and glauconite), as well as likely sorption to Fe oxides and hydroxides with which As has a strong affinity (Goldberg and Johnston, 2001; Yang and others, 2002). No manganese

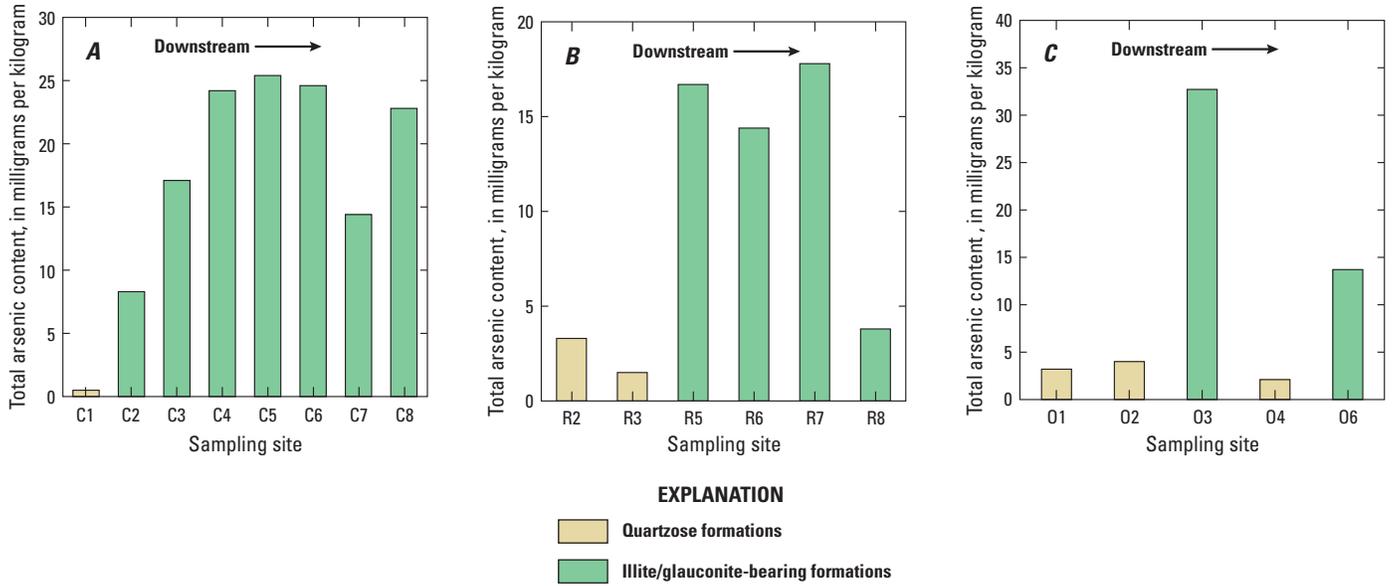


Figure 4. Contents of total arsenic in streambed sediments from *A*, Crosswicks Creek, *B*, Raccoon Creek, and *C*, Oldmans Creek, Inner Coastal Plain, New Jersey, 2007.

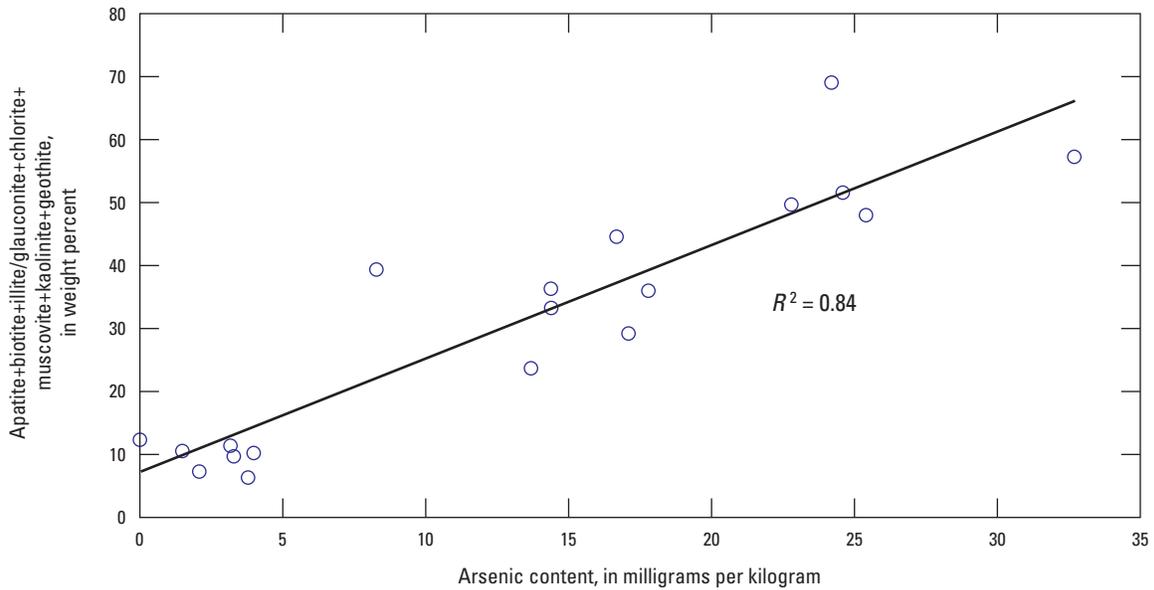


Figure 5. Linear regression results for total arsenic content of streambed sediments from Crosswicks, Raccoon, and Oldmans Creeks, New Jersey, as a function of sediment mineralogy.

(Mn) oxides, which can oxidize As(III) (Lafferty and others, 2010), were identified.

Although not present in surficial streambed sediments and, therefore, not considered in the above analyses, the mineral siderite (FeCO_3) was found in deeper sediments from the streambed core at C6. In that core, Fe hydroxide and oxide minerals (goethite and hematite) were detected in the upper parts of the core, but undetected or barely detected at depth, whereas siderite appeared as individual grains and as cements in the deeper segments of the core (fig. 6). This indicates that, along the length of the 90 cm of the core, a gradient towards more reducing conditions with depth existed such that Fe(III)-bearing minerals were increasingly unstable with depth, and Fe(II)-bearing minerals could precipitate. Arsenate has been documented to sorb to siderite (Jönsson and Sherman, 2008); in the sediments below the streambed at C6, siderite clearly is a sink for As, but also could be a source when the biogeochemical environment promotes either dissolution or microbial activity that releases the As.

Anthropogenic inputs of As were likely in the upper RAC watershed where quartz-rich bankside soils received runoff

from a residential areas built on old orchard land; surficial soils contained 16 mg/kg of total As, but at deeper levels, As concentrations decreased to 3 mg/kg (Barringer and others, 2011b). In the CRO watershed, the total As contents of glauconite-bearing soils at C6 in old orchard areas along the streambank and uphill from the creek ranged from about 20 to 110 mg/kg, as mentioned above. Insofar as the As content of glauconite mineral separates and glauconitic soils in New Jersey may range from 7 to 136 mg/kg (Dooley, 1998; 2001), it was difficult to determine how much As in soils at C6 resulted from pesticide residues amplifying geogenic As and how much derived from natural concentration processes during weathering and soil formation. In a previous USGS study done a few kilometers to the east, the As content of soils in both active and abandoned orchards did not exceed 40 mg/kg, but in that study, native soils with no detectable glauconite (developed on the Englishtown Formation) were reported to contain little As (typically <5 mg/kg) of geologic origin (Barringer and others, 1998). In light of results to date (2013), it appears plausible that, where the geologic substrate contains As-rich minerals such as glauconite, the natural As levels (generally about 20 to

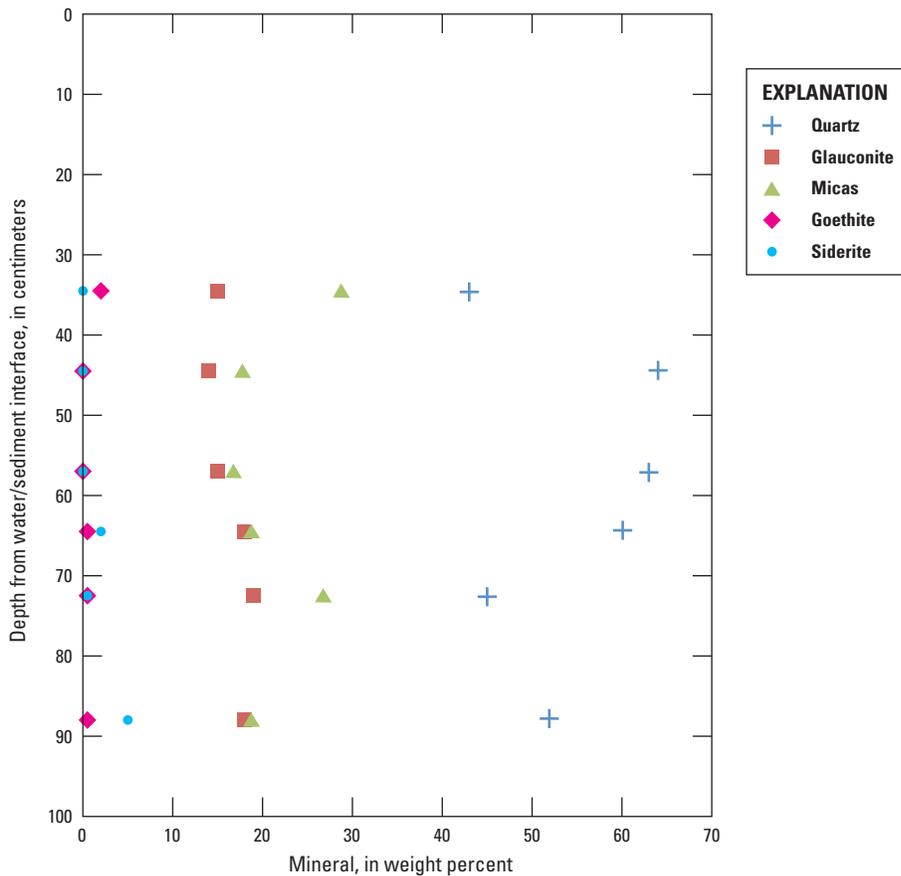


Figure 6. Weight percent of minerals with depth below water/sediment interface in core of streambed sediments at site C6 on Crosswicks Creek, Inner Coastal Plain, New Jersey.

30 mg/kg) in overlying soils can be increased substantially by legacy pesticide residues.

Recoverable (HCl-leachable) As contents are probably mainly representative of sorbed As, whereas total As contents represent sorbed As and As within the crystal lattice of minerals. Recoverable As was about 60 to 90 percent of the total As content of Inner Coastal Plain streambed sediments (Barringer and others, 2010b), indicating that a substantial amount of the As present in the surficial streambed sediments is sorbed, most likely to Fe hydroxides and to the phyllosilicates. Thus, the sediments are not only a source of As contained within minerals, such as glauconite and apatite, but are a sink for the As released from those minerals.

Outer Coastal Plain

Although CKKD aquifer sediment samples are dominated by quartz, deep (22–40 m) core samples of CKKD aquifer sediments collected in Williamstown, New Jersey, for the ongoing NAWQA study contained lignite (fig. 3, table 5). Organic-rich, black clay and silt layers in two cores contained pyrite—8 weight percent in one (table 6). The total As content of the CKKD quartz-rich aquifer-sediment samples ranged from <1.0 to 7.7 mg/kg (table 5). Samples of organic-rich black clay and red-brown to orange silt had the highest As content; in analyses performed for this study, As was significantly and positively related to Fe ($R^2 = 0.65$, $p = 0.002$).

Table 5. Contents of selected trace elements (total digestion) and organic carbon in core samples of Kirkwood-Cohansey aquifer system sediments from wells installed along rights-of-way in Williamstown, near the Great Egg Harbor River tributary site GD, Gloucester County, New Jersey.

[Location of Williamstown shown in figure 3; site names are those of streets along which the wells are installed; mg/kg; milligrams per kilogram; <, less than]

Site name	Depth interval (meters)	Hand-sample description	Arsenic (mg/kg)	Mercury (mg/kg)	Lead (mg/kg)	Organic carbon (percent)
Academy	15.5–15.7	Fine quartz sand, ilmenite	1.20	<0.01	2.06	0.07
	29.0–29.1	Quartz sand, clay, ilmenite	5.40	0.10	10.4	0.28
Denise	9.0–9.1	Fine sand, gray clay	3.80	0.01	2.27	0.09
	25.6–25.7	Brown/black clay	3.40	0.08	10.0	1.97
	33.0–33.1	Black clay	7.70	0.13	17.1	2.85
Oak	15.6–15.7	Medium sand, silt, mica	5.90	0.01	2.24	0.14
	22.4–25.6	Sand, clay, lignite	4.90	0.11	19.7	2.06
	39.8	Coarse quartz sand	<1.00	0.01	5.64	0.19
	39.9–40.1	Black sand, lignite	1.30	0.01	2.74	0.33
Church	26.9–27.0	Gray clay, mica	3.40	0.06	13.3	0.16
	27.1–27.2	Quartz sand, ilmenite	<1.00	0.01	9.83	0.08

Table 6. Bulk mineralogy of selected core samples of Kirkwood-Cohansey aquifer-system sediments from wells installed along rights-of-way in Williamstown, near the Great Egg Harbor River tributary site GD, Gloucester County, New Jersey.

[Location of Williamstown shown in figure 3; site names are those of streets along which the wells are installed; wt. %, weight percent; nd, not detected]

Site name	Depth interval (meters)	Hand-sample description	Quartz (wt. %)	Kaolinite (wt. %)	Muscovite (wt. %)	Goethite (wt. %)	Ilmenite (wt. %)	Pyrite (wt. %)	Rutile (wt. %)	Total (wt. %)
Denise	8.80–8.84	Light gray and red clay	81	13	5	nd	nd	nd	1	100
	30.3	Dark gray silt, sand	76	3	12	nd	nd	8	1	100
	30.4–30.5	Black silt and clay	61	14	19	nd	nd	3	2	99
Oak	40.2	Black silt, fine sand	93	Trace	5	nd	nd	1	1	100
Church	26.9	Gray clay	72	19	8	1	nd	nd	1	101
	27.1	Light brown sand	88	1	1	nd	3	nd	7	100

for all 11 samples, probably indicating associations with the Fe hydroxides present as coatings on sand and silt grains, and with pyrite in those reduced segments where the pyrite is present.

The total As contents of the quartz-rich GEHR and HAMM streambed sediments collected during this study generally were less than 2 mg/kg or not detected. Recoverable (HCl leachable) concentrations (determined with greater precision than total As) ranged from 0.01 to 1.28 mg/kg for most samples; these appear to represent naturally occurring, geogenic concentrations, but probably are also representative of sorbed As. Relations of recoverable As with total Al were strong and significant at better than the 95-percent confidence level ($R^2 = 0.70$), probably indicating As association with clays. Relations of recoverable As also were moderately strong (and significant) with recoverable (HCl leachable) Fe ($R^2 = 0.62$), likely indicative of As sorption to, or co-precipitation with, Fe hydroxides (the HCl tends to dissolve Fe hydroxides and carbonates with which the As is associated).

The As content (total digestion) of bankside soils/sediments about 600 and 1,200 m upstream from GEHR urban tributary site GD, Squankum Branch, formerly surrounded by orchards and farm fields, ranged from <1 to 13.3 mg/kg (table 7, Barringer and others, 2013). Several samples contained As contents greater than 10 mg/kg, which may indicate presence of arsenical pesticide residues amplifying the natural, geogenic inputs of As in the soils. A strong positive association ($R^2 = 0.86$, $p < 0.05$) of total As with total Pb in the bank-side soils upstream from site GD, and a positive (although not significant) trend with Hg may support the attribution of the elevated As to former pesticide use, as mercurial as well as arsenical pesticides (mainly acid lead arsenate) are known to have been used in agricultural areas of southern New Jersey (Murphy and Aucott, 1998, 1999; Barringer and others, 2013).

In the HAMM watershed, As content, both raw and normalized to Al and Fe, was high for sediments at site H1 (the outlet of Hammonton Lake) and H3 (figs. 3 and 7). Normalizing (dividing by) the Fe content can correct for As contents that are elevated because Fe contents are elevated—assuming a strong association between the two elements is present. The same technique, when using Al content to normalize As, can illustrate where As content may be anomalously high because of an abundance of clay minerals that contain As. An anomalously high As content not accounted for by normalization might then indicate an anthropogenic source, such as residues from pesticide applications, to the sediments. Given the proximity of Hammonton Creek to potential As sources such as the STP and agricultural land, normalizing As to Fe and Al was considered a useful technique in the assessment of As sources to that stream. The similarity of patterns in an upstream to downstream direction for the raw and normalized data illustrates that, even accounting for sediment composition (clays and Fe hydroxides), the As content of the streambed sediments is lowest at H2 and highest at H1 and H3.

Table 7. Concentrations of trace elements (total digestion) in bankside soil/sediment core samples collected about 600–1,200 meters upstream from site GD, Squankum Branch, Great Egg Harbor River watershed, New Jersey.

[Sample numbers and data from Barringer and others, 2013; m, meters; mg/kg, milligrams per kilogram; <, less than]

Location	Sample number	Depth interval (m)	Arsenic (mg/kg)	Copper (mg/kg)	Lead (mg/kg)
U.S. Geological Survey site number 01410862					
Left bank	MA1	0–3	4.4	29.8	115
Left bank	MA2	0.3–1.0	<1	2.3	3.83
Right bank	MC1	0–0.3	12.4	70.1	337
Right bank	MC2	0.3–1.0	6.2	58.2	229
U.S. Geological Survey site number 01410863					
Left bank	DA1	0.4–0.7	12.7	158	245
Left bank	DA2	0.7–1.0	3.3	36.2	65.6
Right bank	DC1	0–0.3	13.3	65.9	386
Right bank	DC2	0.3–0.8	9.5	101	404

There is not an obvious explanation for the increased As content of sediments at site H1 at the outlet of Hammonton Lake. The lake has a past history of eutrophic conditions, but there no known history of arsenical pesticide application (typically used mid-20th century to kill algae; for example, Durant and others, 2004). Concentrations of As in the lake water and the As content of sediments at the lake outlet were not at the high levels found in lakes elsewhere where arsenical pesticides are known or suspected to have been used, as shown by Durant and others (2004) and Barringer and others (2010c). Because the lake provides a sink for materials in runoff from urban Hammonton; it appears likely that small amounts of As, perhaps from commercial or industrial uses or from minor (undocumented) pesticide applications to the lake, have accumulated with time.

The distribution of As (and other trace elements) in HAMM streambed sediments downstream (low at H2, greater at H3) probably occurs because of continuous input of effluent to the stream at H2 even when streamflow is otherwise low. Consequently, fine materials bearing As (also P and metals) from upstream and, perhaps, from the STP are constantly swept away from H2. These materials then can be deposited and accumulate downstream, at H3. At sites H4 and H5, the HAMM passes through agricultural land that once included orchards. In the downstream sediments, raw and Al- and Fe-normalized contents of As also were moderately high (as were Cu and Pb contents) in streambed sediments at H5 (fig. 7), perhaps indicative of inputs of pesticide residues.

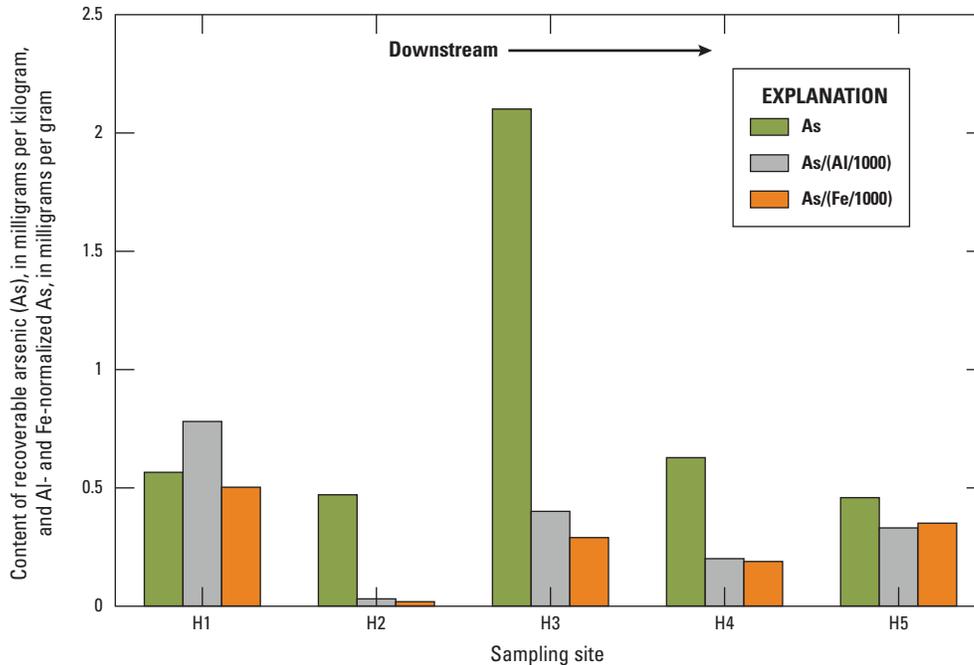


Figure 7. Streambed-sediment contents of recoverable arsenic (As) and As normalized to iron (Fe) and aluminum (Al) at five sampling sites on Hammonton Creek (HAMM), Outer Coastal Plain, New Jersey, 2007.

Overall, variations in the As content of streambed sediments in the two Outer Coastal Plain watersheds (GEHR and HAMM) may indicate more clearly that anthropogenic inputs of As are adding to the low geogenic As contents than do variations in As content in streambed sediments from CRO, RAC, and OLD in the Inner Coastal Plain. In the Inner Coastal Plain, the geogenic As contents of streambed sediments can be so high that anthropogenic additions are not easily recognized (Barringer and others 2011a).

Groundwater Chemistry, Microbiology, and Arsenic Concentrations

Inner Coastal Plain

The groundwater from Inner Coastal Plain aquifers typically is slightly acidic; the pH was about 6.4–6.9 in most samples of shallow groundwater discharging to streams, but above 7 at an urban and agricultural site (R6 and R8, respectively). In an acidic pH range of about 4.5 to 6.5, studies show that the tendency of arsenate (As(V)) to sorb to aquifer materials likely would be strong, although such sorption would be inhibited by competing anions such as phosphate (for example, Frau and others, 2010; Violante and others, 2009). In 2007, a relatively dry year (110 cm precipitation), As_f concentrations in shallow

groundwater discharging to the stream at the rural CRO site C6 were 18.89 $\mu\text{g/L}$ in the spring (April 11, 2007); 89.2 $\mu\text{g/L}$ in the hot, dry summer (July 13, 2007); and 60.4 $\mu\text{g/L}$ in the fall (October 17, 2007) (appendix 5). Virtually no As appeared to be present on particles. In the summer of 2009, a relatively wet year (140 cm precipitation), the As_u concentration of 16.6 $\mu\text{g/L}$ was less than in the summer of 2007, a likely indication of percolating precipitation diluting As in the shallow groundwater (Barringer and others, 2010b). Concentrations of As_f were only about 8 $\mu\text{g/L}$ in the sample collected at C6 in the summer of 2009 (August 18, 2009) because, in an experiment, the unfiltered sample was collected under N_2 , but the water to be filtered was exposed to air and As co-precipitated with Fe as hydroxide particles formed in the water (Barringer and others, 2010b). At C7 on CRO, Fe concentrations exceeded 100,000 $\mu\text{g/L}$ in the shallow groundwater, and Fe hydroxides were observed forming at a groundwater seep.

At other sites where glauconitic sediments underlie the CRO and RAC channels, As concentrations in shallow groundwater were lower than those at C6, but exceeded the State drinking-water MCL of 5 $\mu\text{g/L}$ at C7, R7, and R8 (appendix 5). In groundwater samples where As species were determined and detected, about 50 percent or more of the As was present in reduced form as arsenite (As(III)) (Barringer and others, 2010b, 2011a; fig. 8). The piezometers installed in the CRO and RAC watersheds apparently withdrew water from adjacent microenvironments with differing redox

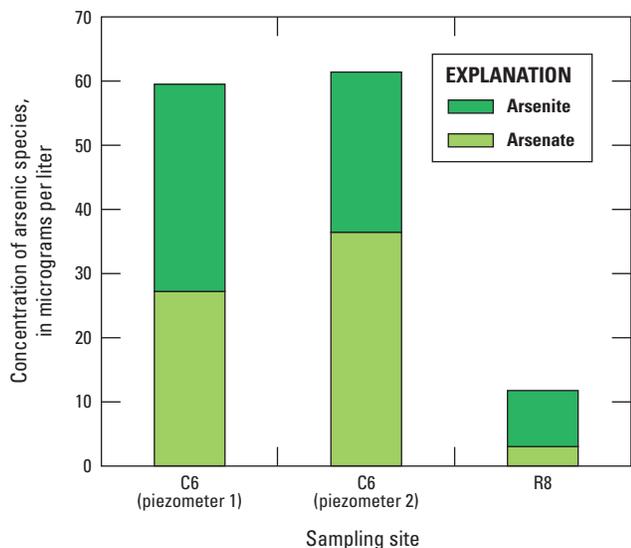


Figure 8. Proportions of arsenate and arsenite concentrations in groundwater samples from two sampling points at site C6 on Crosswicks Creek and site R8 on Raccoon Creek, Inner Coastal Plain, New Jersey.

characteristics, as both aqueous sulfide and sulfate (SO_4^{2-}), and arsenite (As(III)) and arsenate (As(V)), could be present (Barringer and others, 2010b). Nitrogen typically was present as NH_4^+ in the groundwater, and NO_3^- generally was not detected (appendix 5). Phosphorus (P) concentrations were rarely detected or below the reporting limit of <0.04 mg/L, perhaps indicating sorption to bed sediment.

At C6 on the CRO, the shallow groundwater contained concentrations of DOC of 13–14 mg/L, NH_4^+ concentrations from 3.2 to 7.0 mg/L as N, and chloride (Cl^-) concentrations of about 20 mg/L, likely indicating influxes of wastewater from a site with more than 200 years of human (and domesticated animal) occupation (Barringer and others, 2010b). Microbial DNA was extracted from groundwater beneath the stream at C6, and amplification revealed the arsenic respiratory reductase gene *arrA* (Barringer and others, 2010b; Mumford and others, 2010), signaling the likely presence of As-respiring microbes that derives energy from the reduction of arsenate (As(V)) to arsenite (As(III)) (Malasarn and others, 2004). The microcosm experiments at Rutgers University indicated that As is microbially reduced in the shallow aquifer pore waters at C6 (Barringer and others, 2010d). Results from the microcosm experiments also indicated that microbes did not reduce arsenate sorbed onto the sediments except in those microcosms where sediment volume was diluted to decrease the number of sorption sites (Barringer and others, 2010d). The early results from this study do indicate that arsenate (As(V)) present in the shallow groundwater beneath the streambeds of Inner Coastal Plain streams can be reduced by microbial action to

arsenite (As(III)), which, with a lesser propensity for sorption at slightly acidic pH, is more mobile than arsenate (Mumford and others, 2012).

Microbial activity capable of reducing and mobilizing Fe and As in geologic materials has been demonstrated in studies by Kostka and others (1999); Dong and others (2003); Rosso and others (2003); and McLean and others (2006). The identification of gene sequences similar to a *Geobacter* species (a Fe-reducing bacterium) in groundwater at CRO site C6 indicated that such activity is likely to be occurring there, resulting in high concentrations of Fe_r (43,400–55,400 $\mu\text{g/L}$) in the groundwater samples (appendix 5; Barringer and others, 2011a). Microbial reduction of Fe (III) in minerals such as Fe hydroxides also provides a mechanism for releasing As to water because, when the Fe-bearing mineral is reductively dissolved, sorbed As can be released into the groundwater, as indicated in studies of As in groundwater elsewhere (for example, Anawar and others, 2006; Sharif and others, 2008; Reza and others, 2010). This reductive dissolution and As release probably takes place within the shallow aquifer at C6 and within the accumulated streambed sediments, which contain Fe-hydroxides, tentatively identified Fe-phosphate cements, and siderite cements (Mumford and others, 2012).

Other Fe- and As-bearing minerals at C6 from which As could be released include biotite [as documented by Seddique and others (2008) and Hopf and others (2009) in studies of southeastern Asian aquifer sediments], as well as glauconite and siderite. Microbes also have been shown to solubilize apatite to access phosphate (Mailloux and others, 2009); apatite is a probable As source in the Inner Coastal Plain sediments (Barringer and others, 2011a). The activity carried on by a community of microbes at C6 likely is fueled by DOC inputs to the shallow groundwater there, a scenario that is indicated by studies in southeast Asia (for example, McArthur and others, 2004; Islam and others, 2004; Rowland and others, 2009) as well.

Despite strong evidence for microbial release of As to groundwater at C6, microbial activity probably waxes and wanes seasonally. Increased concentrations of As in shallow groundwater during the summer (particularly during 2007) at C6 probably are, in part, indicative of greater microbial activity during warm weather. Fluctuations in hydrologic conditions also exert a control on the As-release process. At Inner Coastal Plain stream sites C7 (on CRO) and R7 (on RAC), inputs of As-rich groundwater apparently occur only when groundwater levels are relatively high. During dry spells in 2007, some gaining reaches became losing reaches as lenses of water above areally discontinuous clay layers no longer discharged to the streams (Barringer and others, 2010b).

In addition to shallow groundwater near streams, deeper groundwater from the glauconitic aquifers also may contain As at elevated levels. Water from an observation well completed in sediments of the Englishtown Formation contained 112 $\mu\text{g/L}$ of As_r (dePaul and Szabo, 2007), and there are isolated instances of As_v at concentrations that exceed the MCL in domestic well waters sampled in the Inner Coastal

Plain pursuant to the Private Well Testing Act (New Jersey Department of Environmental Protection, 2009) in New Jersey (Dr. Judith Louis, New Jersey Department of Environmental Protection, 2010, oral commun.).

Outer Coastal Plain

In the Outer Coastal Plain watersheds underlain by the CKKD, the pH ranged from about 4.6 to 6.0 in groundwater discharging to the GEHR, its tributaries, and HAMM. This range is typical of deeper groundwater in the CKKD as well.

Data in the USGS NWIS database indicate concentrations of As exceeding 1 $\mu\text{g/L}$ rarely have been detected in well water from the CKKD, although concentrations in pore water from the clay-rich basal Kirkwood Formation have been reported to be as much as 35 $\mu\text{g/L}$ (Szabo and others, 2006). Concentrations of As_f were less than 1 $\mu\text{g/L}$ in water from the clustered observation wells drilled in the GEHR watershed for the ongoing NAQWA study. These wells, finished in geologic materials of varying composition, range from about 7.6 to 36.6 m in depth. The highest concentrations of As (at, or slightly above 0.5 $\mu\text{g/L}$) were in water from a well cluster that penetrated organic-rich clays and silts containing pyrite.

Concentrations of As_u in shallow groundwater discharging to the GEHR, its tributaries, and to HAMM were similar to those in deep groundwater. At most GEHR sites, the As concentration was less than 1 $\mu\text{g/L}$, and little particulate As was present, although most of the As (0.3 and 0.5 $\mu\text{g/L}$) in HAMM shallow groundwater was particulate. Because virtually all of the Al and Fe in the HAMM samples also was in particulate form, it is likely that As in the groundwater was sorbed to Fe hydroxide coatings on clay particles (colloids) that commonly are found in CKKD groundwater (Ryan and Gschwend, 1994; Barringer and others, 2010a).

It also appears that, for filtered groundwater samples from Outer Coastal Plain sites, As and Fe are closely associated (regression analysis indicated a significant R^2 of 0.87 ($p < 0.05$). Insofar as there are no data collected during this study for particles less than 0.45 μm in diameter, it is not possible to determine how much As in filtered groundwater samples represents As on Fe colloids and how much As and Fe is actually dissolved. If dissolved As and Fe dominate the filtered samples, reducing conditions beneath the streambeds would be clearly indicated.

Concentrations of As_u exceeding the New Jersey MCL ($\text{As}_u = 6.0$ and 7.5 $\mu\text{g/L}$) were found in groundwater discharging to sites on two GEHR tributaries, GA (urban) and GC (mixed land-use with substantial urban component), respectively (see fig. 3 for locations). High concentrations of Cl^- , NH_4^+ , Fe_p , and DOC (79.9 mg/L, 0.37 mg/L as N, 29,600 $\mu\text{g/L}$, and 4.8 mg/L, respectively) and low DO concentrations (1.15 mg/L) at GA indicated reducing conditions and likely effects of wastewater on the groundwater chemistry. In slightly more oxidizing conditions at GC (DO = 2.94 mg/L), concentrations of $\text{NO}_2^- + \text{NO}_3^-$ were 7.7 mg/L as N, and

Cl^- and DOC concentrations also were elevated (17.8 and 3.52 mg/L, respectively; appendix 5), probably indicative of wastewater inputs at GC as well. In a recent USGS study, As concentrations in domestic septic-system effluent are reported to be low (less than or equal to 1 $\mu\text{g/L}$; Deluca and others, 2006), at least where groundwater concentrations of As are low. Consequently, it appears unlikely that the wastewater is the proximate source of the increased concentrations of As in the shallow groundwater at GA and GC. Rather, based on the USGS/NJDEP and Rutgers University studies at CRO (Barringer and others 2010b, 2011a), wastewater inputs apparently stimulated microbial activity, resulting in greater release of As from the geologic materials.

Relations between concentrations of As and DOC (and also total organic carbon (TOC)) indicate that it is not the amount of OC that is present in the groundwater that determines the amount of As that is released, however. There is a generally strong positive trend (R^2 greater than 0.95) shown for As concentration as a function of DOC concentration in shallow groundwater discharge; this was demonstrated at RAC (Barringer and others, 2010b), and the same As/DOC relation is seen for groundwater discharging to the GEHR tributaries (fig. 9a). This conclusion could not be drawn for the CRO watershed as there weren't enough samples collected to see a significant trend. However, at site C6 on CRO, where wastewater inputs were apparent, samples contained much higher As relative to the amount of DOC (which, at about 15 mg/L, was still high for groundwater) as compared to the other CRO sites (fig. 9b; Barringer and others, 2010b). The same As/DOC relation is seen for groundwater discharging to the GEHR at sites GA and GC (fig. 9a, and not shown, respectively).

Insofar as the chemistry of groundwater from anomalous sites GA and GC (with respect to the general As/DOC trend) is indicative of wastewater inputs, it appears that, as at CRO site C6, the concentration of OC is not as critical to microbial As release as is its composition. Wastewater OC generally (1) contains sulfide-bearing ligands (Hsu-Kim and Sedlak, 2005) and (2) is more aliphatic than naturally derived DOC (Sirivedhin and others, 2005). It appears that such OC provides greater stimulation to microbes within the shallow aquifer and beneath the streambed than does OC derived only from naturally decaying vegetation. Currently (2013), it is not clear whether elevated inputs of N also have a stimulatory effect on the microbes.

There was no apparent particulate As in groundwater at GA, whereas As (and Fe) in groundwater at GC was mostly in particulate form. Extrapolating from the study at CRO C6, it seems likely that, at GA and GC, microbes beneath the streambed released Fe by reducing Fe(II) in minerals such as ilmenite; sorbed As also would be released by this process. Further, microbes also may have actively respired mineral-bound or sorbed arsenate and reduced it to mobile arsenite. Insofar as groundwater at GC came from a slightly more oxic environment than that of GA, the As in groundwater at GC may have been in oxidized form. Any Fe released as Fe (II) at GC probably was oxidized, as concentrations were only

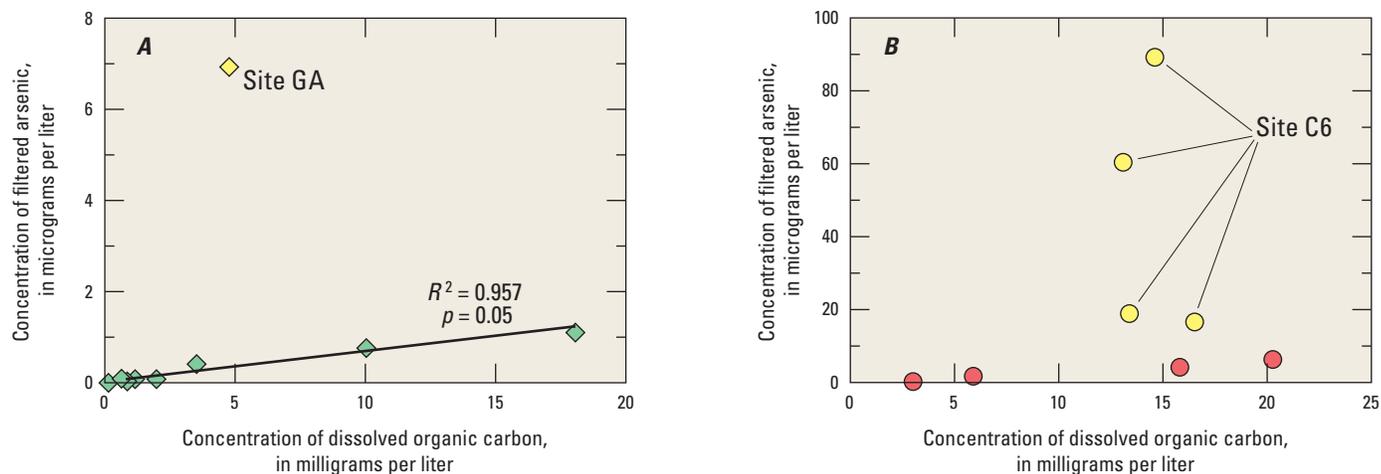


Figure 9. Relations of concentrations of arsenic in filtered samples to dissolved organic carbon in shallow groundwater from A, Great Egg Harbor River watershed and B, Crosswicks Creek, New Jersey.

139 µg/L in the unfiltered sample and 14.7 µg/L in the filtered sample, compared with 31,800 and 29,600 µg/L, respectively, in unfiltered and filtered samples of groundwater at GA.

The geochemical processes in these tributaries to the GEHR appear similar to those observed at RAC and CRO in the Inner Coastal Plain: Fe and As are released into solution in groundwater by microbial action in the shallow aquifer; upon discharge to the stream, the Fe and As become oxidized, the Fe precipitates as a hydroxide and the As co-precipitates with, or sorbs to, the Fe hydroxide. This process results in much of the As in the groundwater being sequestered by the streambed sediments; as a likely indication of this process, the total As content of the streambed sediments at GA was the third highest of the sampled sites in the GEHR watershed.

Conditions for As release in a wetlands environment appear to differ from those observed in the urbanized areas of the GEHR. At a transect of four piezometers installed at wetlands site G5, shallow soil water and groundwater with low concentrations of DO and the highest concentrations of DOC also contained the highest concentrations of As (fig. 10). Hydrogen sulfide odors detected during piezometer installation and Fe_f concentrations of 4,000 to 10,000 µg/L indicate that both sulfate- and iron-reducing bacteria are present in the anoxic to suboxic conditions that occur along the banks and in parts of the GEHR streambed at G5. Nevertheless, although Fe concentrations in pore waters and groundwater discharge at G5 were high, As concentrations were not, relative to concentrations seen in Inner Coastal Plain groundwater discharges or to the samples from GA and GC. Biogeochemical conditions at G5 appeared superficially like those at C6, where there was evidence for sulfate reducing and Fe-reducing bacteria, high concentrations of DOC, and high concentrations of Cl⁻. At G5, however, the high concentrations of Cl⁻ apparently arise from

roadsalt rather than from wastewater discharge, as there are only wetlands and no residential development immediately upgradient from site G5. In addition, the high DOC in pore waters at G5 derives from decaying vegetation, rather than from wastewater inputs. Given the data collected to date, our hypothesis is that greater release of As from geologic materials occurs when microbial communities are stimulated by wastewater inputs rather than by naturally occurring DOC. Studies of DOC composition at C6, GA, and G5 would be useful in testing this hypothesis, as would a study of the microbial communities at GA and G5.

Stream-water Chemistry and Arsenic Concentrations

Inner Coastal Plain

The pH of streams in the Inner Coastal Plain tends to be slightly acidic to neutral. In the three streams (CRO, RAC, and OLD) studied during the USGS/NJDEP investigation, stream-water pH ranged from 5.9 to 7.3. There was relatively little variation in pH as a function of hydrologic condition, in part because the streams are lacking extensive wetlands from which low-pH water is flushed to the stream following rainfall—a feature typical of the Outer Coastal Plain streams such as the GEHR (Barringer and others, 2010a).

Concentrations of As_f tended to be lower in stream water collected from CRO, RAC, and OLD at high base flow in March and April 2007 than at low base flow in May and July 2007. Lower concentrations of As and other trace elements in springtime samples have been observed in other streams in

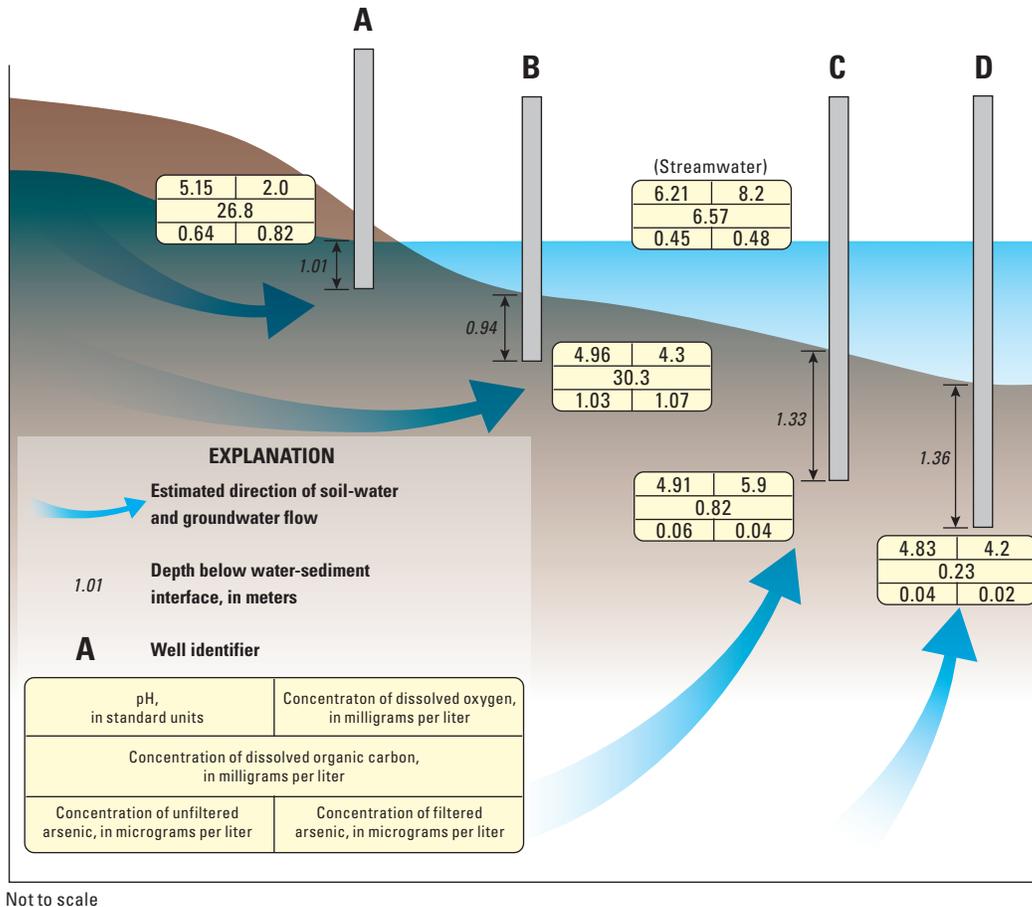


Figure 10. Piezometer depth, pH, and concentrations of dissolved oxygen, dissolved organic carbon, and arsenic in unfiltered and filtered samples of stream water and groundwater from piezometers A, B, C, and D, Great Egg Harbor River at site G5, Outer Coastal Plain, New Jersey, June 2007.

New Jersey (Barringer and others, 2007a) and elsewhere (for example, Neal and others, 2000), and may represent dilution of solutes during early spring high water levels.

In water from all three Inner Coastal Plain streams, concentrations of As_p , regardless of geologic substrate, rarely exceeded 1 $\mu\text{g/L}$ (appendix 6) because, where groundwater discharge contained elevated concentrations of Fe and As, these constituents became oxidized in the stream, Fe hydroxides precipitated, and arsenate either co-precipitated with or sorbed to the Fe hydroxides, as described above. These hydroxides typically form as orange flocs and coatings on streambed sediments (Barringer and others, 2010b). A sample of floc from C7 at CRO contained 49.6 mg/kg of As (total digestion) (appendix 4; Barringer and others, 2011a).

Sampling at CRO during the current study indicated that, during high-flow conditions, As_v concentrations in stream water increased with distance downstream and could approach or exceed 5 $\mu\text{g/L}$ at C8—the farthest downstream sampling site. At CRO, most of the As was particulate at high flow, and As_f concentrations generally remained about 1 $\mu\text{g/L}$ or less

(Barringer and others, 2010b). Although runoff carrying As-rich soil particles undoubtedly contributes to the total As load in CRO during high flow, fine-grained As-bearing streambed sediments become suspended and form a substantial part of the As load, as reported by Barringer and others (2011a).

Particulate As and Fe were present in stream water at RAC and OLD during early and late spring samplings under moderate- and low-flow conditions, respectively. The particles were more apparent at low flow during warm weather, as Fe-hydroxide particles were forming in the stream water and sequestering As that entered the stream from shallow groundwater discharge (fig. 11); the particulate As at low flow could not be ascribed to runoff carrying soil particles, but, rather, to in-stream processes.

Whether the As in runoff to the Inner Coastal Plain streams includes residues from past pesticide use has proved difficult to ascertain. Agriculture in the Inner Coastal Plain has constituted primary land use in the past and, in some areas, is still widespread. In the OLD watershed, agricultural land contains predominantly fields of row crops and a few orchards.

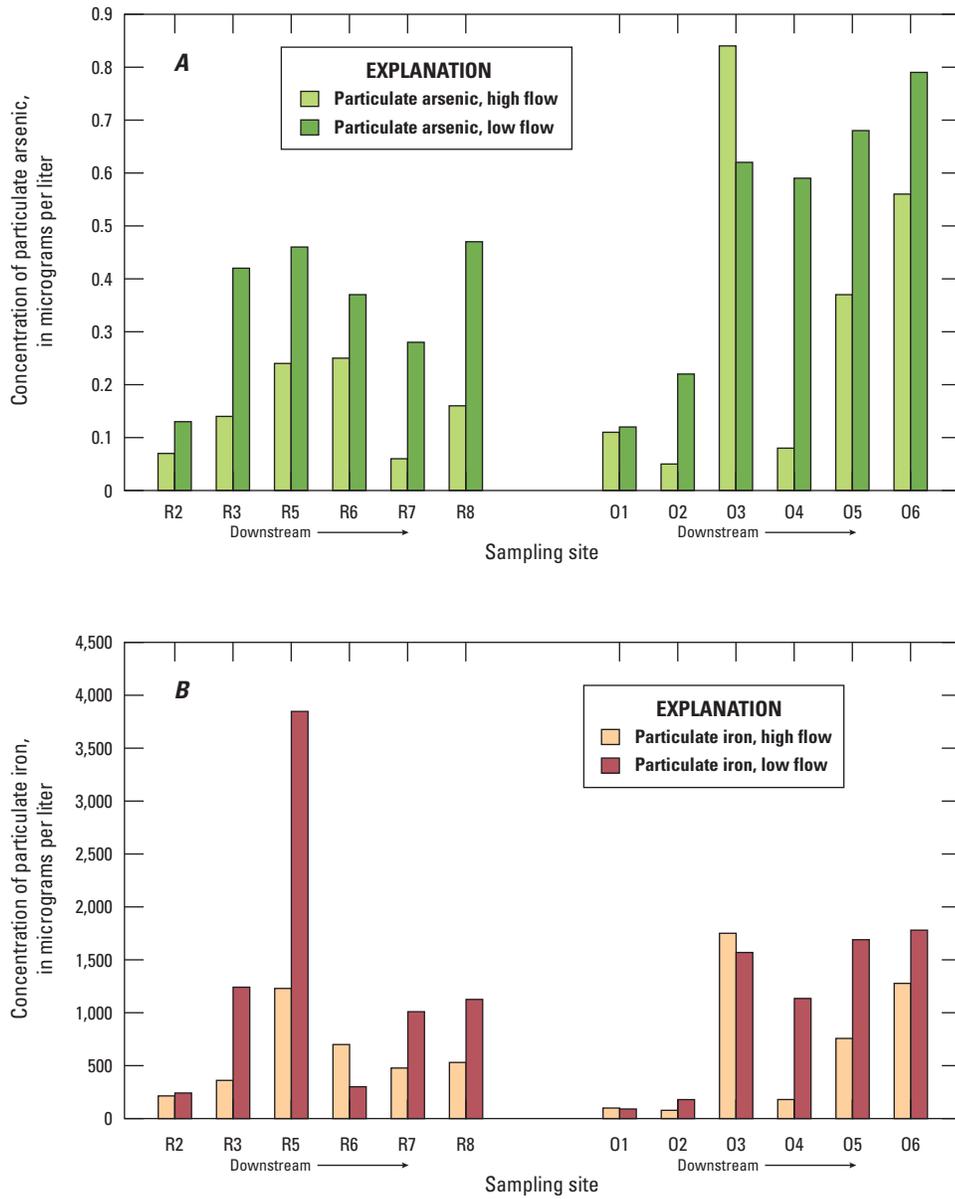


Figure 11. Concentrations of *A*, particulate arsenic and *B*, particulate iron under different flow regimes from Raccoon Creek and Oldmans Creek, Inner Coastal Plain, New Jersey, 2007.

The CRO watershed also contains relatively few orchards, mostly apples, whereas peach orchards previously have dominated agriculture in the RAC watershed. Historically, apples and pears received larger applications of arsenical pesticides than did other fruit trees (Jones and Hatch, 1937); acid lead arsenate (PbHAsO_4) was most commonly used during the early to mid-20th century (Wagner and others, 2003).

Possible effects of pesticide residues on runoff to the RAC were seen at the outfalls of two detention basins in residential areas recently developed during the 1990s and early 2000s; one basin (at R1), underlain by quartz-rich sediments, was on former orchard land, and the other (at R4), underlain by glauconitic sediments, was on former farm fields. Runoff at R1 would be likely to contain relatively little geogenic As, compared to the runoff at R4, but the As_d concentration in runoff from the basin at R1 during a storm was $2.45 \mu\text{g/L}$, possibly indicating contributions from former orchards. The As concentration at R4, where geogenic As inputs likely would be high, was $3.17 \mu\text{g/L}$ (Barringer and others, 2011b). Nearly all of the As issuing from the detention basins was in either dissolved or fine colloidal form; the basins apparently trapped most particles carried in by runoff. As a result of the study's design and scope, no measurements of runoff water entering the basins were made, although calculation of particulates in the stream water was made by determining the difference between unfiltered and filtered concentrations of As and other constituents. Consequently, the identification of soil

particles in runoff-bearing-pesticide residues remains tentative for RAC, as it does for runoff at CRO, where soil and stream-water chemistry are suggestive of pesticide residues, but not definitive (Barringer and others, 2011a).

Outer Coastal Plain

Like the groundwater, surface water in the Outer Coastal Plain tends to be acidic, and, in wetlands-rich watersheds such as the GEHR, the pH varies depending largely on hydrologic conditions. During wet periods, as acidic wetlands pore waters are washed into the streams, the pH declines to below 5, but during dry periods, stream-water pH may exceed 6. Despite these variations, the stream water is sufficiently acidic that large variations in As_f concentration caused by pH-controlled sorption and desorption reactions are unlikely to occur, unlike As in waters of neutral or alkaline pH (for example: Nimick and others, 1998; Barringer and others, 2007b). Bihourly measurements of As for 22 hours at wetlands site G8 during a drought indicated concentrations of about $0.3 \mu\text{g/L}$ that varied little, and pH varied between 6.04 and 6.17 during the same period. Particulate As appeared to increase slightly during the night in concert with an increase in particulate Fe (fig. 12) and particulate Mn. Increases in particulate As and metals have been reported elsewhere (Brick and Moore, 1996; Barringer and others, 2007b) and may be attributed to the nocturnal activity of benthic organisms within the streambed sediments.

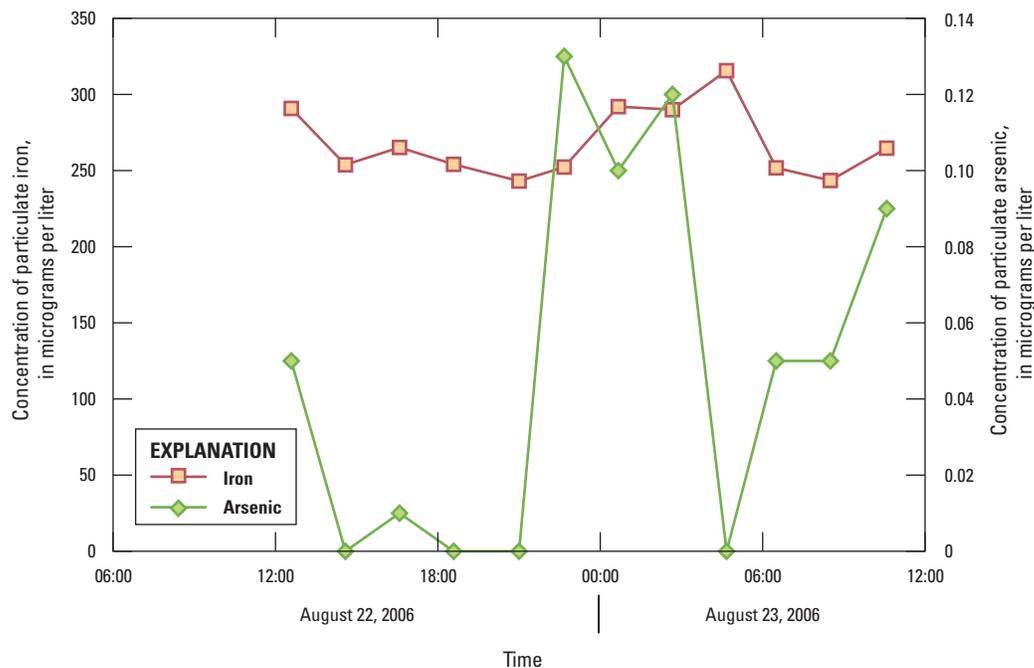


Figure 12. Variations in concentrations of particulate arsenic and iron in samples from site G8, Great Egg Harbor River, New Jersey, August 2006. (Some As concentrations were close to the laboratory reporting limit; therefore, some small variations in concentration shown may be affected by the imprecision in the measurement.)

In the GEHR, concentrations of As_u (generally 0.40 to 0.65 $\mu\text{g/L}$) varied little with downstream distance in the watershed or with flow regime. Increased As_u concentrations were found in samples from the urban sites G1 and G2 at the headwaters, where concentrations were 1 $\mu\text{g/L}$ at high flow and 0.76 $\mu\text{g/L}$ at low flow; much of this As was particulate. The concentrations of As_p generally constituted a greater proportion of the As in unfiltered samples of stream water from the urban and mixed sites on the GEHR than in stream water from sites with mostly forest and wetlands (fig. 13). The same phenomenon was seen with Hg in waters of the GEHR and its tributaries; particulate Hg constituted a greater proportion of the unfiltered samples from urban and mixed land-use sites than from most forest and wetlands sites (Barringer and others, 2010a).

Concentrations of As_u and As_f in stream water from HAMM were generally less than 1 $\mu\text{g/L}$, and much of the As in the water samples from urban sites on the HAMM was particulate. In stream water at the outlet of Hammonton Lake (H1), from 20 to 49 percent of As_u also was particulate. Additionally, As_u and As_f concentrations at H1 varied seasonally, being lowest in December; increased in May; and greatest in September after a dry period (fig. 14). This seasonal variation is similar to, but at concentrations smaller than, the seasonal variations found in a lake in northwestern New Jersey where summer stratification and anoxic bottom conditions promoted As reduction and release by microbial activity (Barringer and others, 2010c). Elsewhere on the HAMM, concentrations of As_u were similar to those seen in stream water from the GEHR watershed.

As with the Inner Coastal Plain watersheds, runoff in the Outer Coastal Plain watersheds has the potential to contribute anthropogenic As to the streams, in addition to geogenic As; thus the distribution of agricultural land with respect to the two Outer Coastal Plain streams needed to be considered. Orchards formerly were present in the GEHR and HAMM watersheds. In the HAMM watershed, most of the former orchard land is still in agricultural use, but much of the orchard and other agricultural land in the GEHR watershed has been residentially developed as of 2011. As mentioned above, elevated As contents of bankside soils upstream from GEHR site GD, Squankum Branch, indicate inputs of As from pesticide residues, but these did not appear to have affected stream-water As concentrations, which were similar to most As concentrations in stream water elsewhere in the GEHR watershed—about 0.5 to 0.6 $\mu\text{g/L}$. Stream-water As_u concentrations in HAMM ranged from 0.24 to 0.60 $\mu\text{g/L}$ at sites downstream from H2 with the lowest concentrations being measured in treated water discharged from the STP outfall. Although the HAMM runs past former orchard land (now mainly farm fields) on the left bank, no spike in As concentration in the stream water was observed at the two downstream sampling sites (H4 and H5) bordered by farm fields. In-stream processes such as sorption and sediment deposition probably move most As from the water column to the streambed sediments.

Effects of Geologic Sources and Anthropogenic Inputs on Arsenic Mobilization Processes

Between and within the Inner and Outer Coastal Plain physiographic sub-provinces of New Jersey there are differences in geology, hydrology, and land-use distributions that affect the chemistry of Coastal Plain waters and sediments and the amount of As that is present to be mobilized and transported in the environment. A summary of selected geochemical characteristics and constituents found in waters and sediments of the Inner and Outer Coastal Plain provinces, New Jersey, are presented in table 8.

In the Inner Coastal Plain, the low concentrations of As and metals in shallow groundwater and the As and metals contents of soils and sediments tend to occur in those parts of the watersheds that are underlain by the quartz-rich geologic formations, and high concentrations and contents are associated with the parts of the watersheds underlain by glauconitic formations. The increased concentrations of Cl^- and DOC in groundwater, however, appear in some instances to be associated with anthropogenic inputs. In the Outer Coastal Plain, with fairly uniform geologic substrate, the greater As concentrations/contents tend to be in developed, mainly urban, parts of the watersheds, demonstrating the importance of land use in affecting the overall chemistry of an Outer Coastal Plain watershed. Several examples illustrate where the data collected during the current study are indicative of the potential for past and present land use to affect the processes occurring below and within the streambeds and thus to As inputs to streams in the Coastal Plain and, ultimately, to As loads.

Comparing As loads and yields in two watersheds—CRO and RAC—of substantially differing size and degree of development illustrates the apparent effect of development on delivery of As to the respective streams. Sampling waters from these two streams throughout a storm event was beyond the scope of the individual watershed studies, as was sampling both streams during the same event. Nevertheless, data from both streams at near peak flow during a storm event indicate comparable As concentrations, with concentrations at RAC greater than those at CRO (table 9). The samples from CRO were collected when flow was about 6 times the streamgage period of record median daily flow, and the samples from RAC were collected when flow was about 4 times the streamgage period of record median daily flow. The As in stream water from RAC during the storm was mostly (about 70 percent) in particulate form, which is similar to findings at CRO during high-flow events (Barringer and others, 2011a). The data for the storm events represent As concentrations (1) from a small part of the RAC watershed, from R1 to R4, and (2) from almost the entire sampled drainage area in the much larger CRO watershed, from C3 to C8. Given that As concentrations would be anticipated to vary during the course of a storm and that data from two different storms are being compared here, it

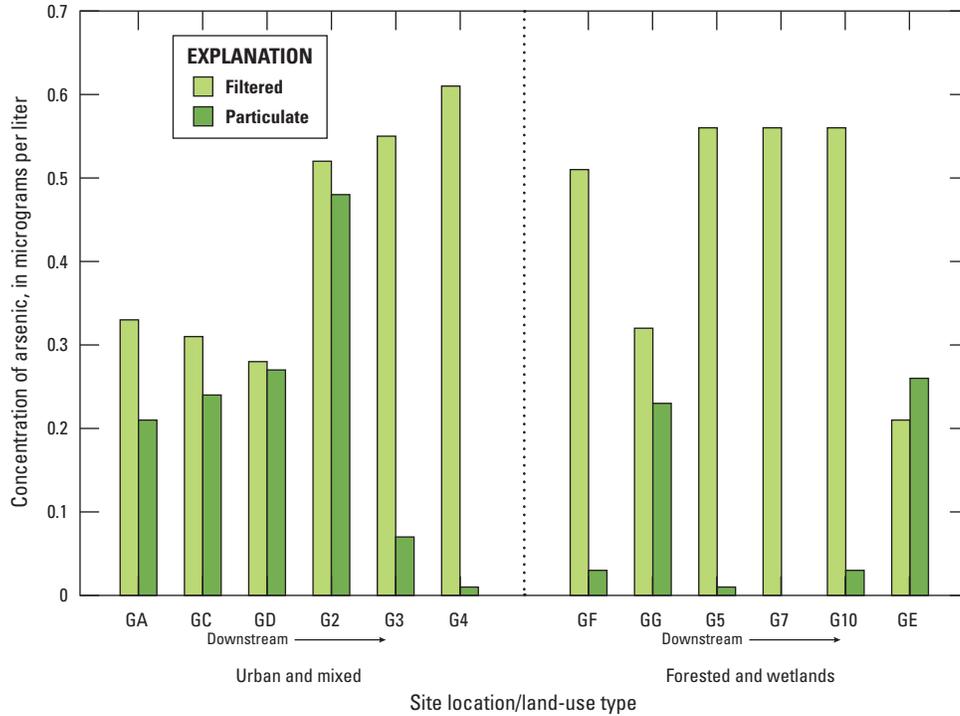


Figure 13. Concentrations of particulate and filtered arsenic in stream water in different land uses, Great Egg Harbor River and tributaries, Outer Coastal Plain, New Jersey, 2006.

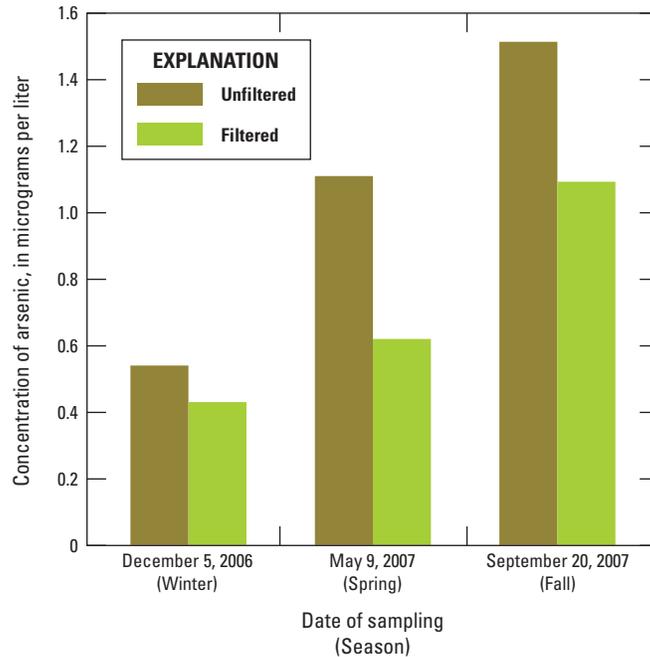


Figure 14. Seasonal variation in arsenic in filtered and unfiltered samples of stream water from site H1 at the outlet of Hammonton Lake, New Jersey.

Table 8. Summary of selected geochemical characteristics and constituents in waters and sediments of the New Jersey Coastal Plain sub-provinces.

[Total digestion results for As and metals usually were greater than recoverable results but less precise; in highly organic soils/sediments, recoverable results usually were greater than total; DOC, dissolved organic carbon; Cl⁻, chloride; Fe, iron; As, arsenic; subscripts u and f indicate unfiltered and filtered sample, respectively; mg/L, milligrams per liter; µg/L, micrograms per liter; mg/kg, milligrams per kilogram; <, less than]

Characteristic/constituent	Inner Coastal Plain	Outer Coastal Plain
pH—shallow groundwater	6.15–7.36	4.61–6.04
pH—stream water	5.9–7.3	¹ 4.5–7.5
DOC—shallow groundwater	0.36–20.3 mg/L	0.18–30.3 mg/L
DOC—stream water	0.92–8.5 mg/L	1.88–20.5 mg/L
Cl ⁻ —shallow groundwater	3.94–102 mg/L	2.47–287 mg/L
Cl ⁻ —stream water	9.62–78.1 mg/L	6.58–82.9 mg/L
Fe content—streambed sediments	² 5,100–143,000 mg/kg	² 494–8,300 mg/kg
Fe _f concentration—shallow groundwater	636–108,000 µg/L	9.6–29,600 µg/L
Fe _u concentration—stream water	179–25,000 µg/L	208–4,461 µg/L
Fe _f concentration—stream water	39.1–3,862 µg/L	104–912 µg/L
As content—streambed sediment	² <1–34.7 mg/kg	² <1–2.4 mg/kg
As _f concentration—shallow groundwater	<0.12–89.2 µg/L	<0.12–6.92 µg/L
As _u concentration—stream water	0.28–5.95 µg/L	³ 0.24–1.51 µg/L
As _f concentration—stream water	0.18–1.27 µg/L	0.2–1.09 µg/L
As content—near-stream soil/sediment	² 12–110 mg/kg	² <1–13.3 mg/kg
Total As content—aquifer sediment	⁴ 7–136 mg/kg	² <1–7.7 mg/kg

¹Measurements of pH greater than 6.6 were made at Hammonton Lake outlet (H1) and discharge from a sewage treatment plant (H2); pH values of all other Outer Coastal Plain stream waters were 6.6 or less (appendix 6).

²Total digestion.

³As_u concentrations in stream water greater than 1.0 µg/L were found at Hammonton Lake outlet (H1). All other As_u concentrations in Outer Coastal Plain stream waters were less than 1.0 µg/L.

⁴Dooley, 1998; 2001.

Table 9. Concentrations and instantaneous loads of arsenic and yields of total arsenic (normalized to drainage area) in water from Crosswicks and Raccoon Creeks, New Jersey, following storms.

[km², square kilometer; Q, instantaneous discharge; m³/s, cubic meter per second; As, arsenic; µg/L, microgram per liter; mg/s, milligram per second; mg/s/km², milligrams per second per square kilometer]

Site number	Date	Drainage area (km ²)	Q (m ³ /s)	Unfiltered As (µg/L)	Filtered As (µg/L)	Particulate As (mg/L)	Total As load (mg/s)	Total As yield (mg/s/km ²)
Crosswicks Creek								
C3	10/12/07	107	3.20	1.31	0.588	0.722	4.18	0.039
C7	10/12/07	211	11.0	2.35	0.591	1.76	25.8	0.122
Raccoon Creek								
R1	09/07/08	16.7	0.241	2.28	0.663	1.62	0.544	0.033
R4	09/07/08	33.1	1.13	3.10	1.00	2.10	3.51	0.106

is interesting to note that a small drainage area for one stream (RAC) can generate as much or more As in stream water during a less severe event than can a much larger drainage area during a more severe event (CRO).

To explore the comparison further, instantaneous As yields (instantaneous loads normalized to drainage area) indicate a similarity in As yields for the small part of the RAC watershed and the large part of the CRO watershed. The sampled part of the CRO watershed included in the yield calculation is underlain by a substantially greater areal extent of glauconite-bearing marine sediments than is the sampled area of the RAC watershed, where site R1 is underlain by quartz-rich sediments of the Kirkwood Formation rather than older glauconitic sediments. Consequently, geogenic inputs of As could be expected to be greater in the CRO watershed than in the RAC watershed, yet the As yields at high flow for both streams are similar. The land at site R1 of the RAC was formerly orchards, however. The geologic and land-use differences between these two watersheds, yet the similarities of As yields at high flow, likely indicate that type of agricultural land use and degree of land-use change are important factors affecting the amount of total As that is carried in runoff and that is present and mobile in stream water at high flow. Although the geogenic inputs of As to the RAC (from site R4 and farther downstream) likely are not small, Gloucester County, through which the RAC flows, had the largest amount of agricultural As applied (cumulatively, 1,247,400 kg) from 1900 to 1980 (Murphy and Aucott, 1998) of any Coastal Plain county. Thus it appears plausible that arsenical pesticide residues in runoff contribute to the total As present in RAC stream water during high-flow events.

In addition to effects from pesticide use, there are other plausible anthropogenic effects on groundwater and stream-water chemistry and As mobilization. In the Inner and Outer Coastal Plain sub-provinces, the highest pH values (greater than 7) in groundwater and stream water were mainly in developed areas with primarily urban and agricultural land use. One of these areas included the Hammonton STP site, which discharges to the HAMM. At neutral pH or higher, As (as arsenate) is less tightly bound to Fe oxides and clays than at acidic pH (Goldberg, 2002), and therefore, more prone to desorption. Consequently, if an effect of development is to raise the pH of water within, or discharging to, the streams, this could affect the mobility of As by causing desorption and increasing the amount in solution.

Arsenic concentrations in shallow groundwater discharging to the streams tended to be greater in developed (agricultural and urban) areas and were particularly high at those sites where the quality of groundwater appeared degraded by inputs of septic-system effluent, such as at C6 on the CRO and GA and GC on tributaries to the GEHR. The microbiological and geochemical studies at site C6 on the CRO demonstrate that microbial activity appears responsible for the release of As from aquifer materials to the groundwater and, further, that

inputs of DOC associated with wastewater appear to stimulate such activity (Barringer and others, 2010b; Mumford and others, 2012). Extrapolating from the results of the study at CRO to other instances of elevated As concentrations in groundwater where inputs of wastewater OC occur, it appears that where degradation of that OC results in a reducing environment below the streambed, conditions are optimal for the microbial activity that leads to extraction of trace elements such as Fe and As from the minerals beneath the streambed.

The current USGS/NJDEP study has examined only the chemistry of groundwater that discharges to the Coastal Plain streams (appendix 5); instances where streams lose to groundwater were not investigated. In Coastal Plain areas undergoing residential development, increases in withdrawals of groundwater, either by groups of domestic wells or by large-volume public-supply wells, have the potential for reversing flow whereby formerly gaining stream reaches now lose water to the saturated zone. Insofar as Coastal Plain stream waters can contain substantial amounts of naturally occurring DOC, it may be that such flow reversal would bring DOC into shallow parts of the aquifers that were formerly poor in OC content and thus could affect the redox status of groundwater near the stream, as indicated in a review of bank filtration issues (Farnsworth and Hering, 2011). Whether such re-routed stream-water DOC would have a stimulatory effect on the microbial communities of the shallow aquifers and result in reducing conditions is not known. Nor is it known whether OC from petroleum and organic solvents [common contaminants in CKKD groundwater (Barringer and Szabo, 2006)] also would stimulate microbial communities such that extraction and mobilization of trace elements, such as As, from geologic materials would occur. These possibilities warrant further investigation.

Although the process of microbial release and mobilization of As apparently occurs in watersheds of both Inner and Outer Coastal Plain sub-provinces, the effect of such biogeochemical processes on Inner Coastal Plain groundwater is greater than on Outer Coastal Plain groundwater because of the differing amounts of As that are present in the geologic materials underlying the streams. The greater the groundwater input of As to a given stream in the Inner Coastal Plain, the more As is then sorbed or precipitated on the streambed sediments. The net result is that, irrespective of runoff inputs, the total As load of an Inner Coastal Plain stream is substantially increased by the As on suspended streambed sediments at high flow (Barringer and others, 2011a) and, based on current data, exceeds that of an Outer Coastal Plain stream.

A summary of the As content and concentrations found in various media from the Inner and Outer Coastal Plain provinces, New Jersey, as determined in an earlier study (Dooley, 2001) and observed in this study, are presented in table 10. The range of stream-water concentrations shown in table 10 do not include the HAMM STP effluent discharge samples and are considered ambient concentrations. Despite groundwater

Table 10. Summary of arsenic contents and concentrations in various media from the sub-provinces Inner Coastal Plain and Outer Coastal Plain, New Jersey.

[mg/kg, milligrams per kilogram; <, less than; µg/L, micrograms per liter; NA, not available]

Medium	Inner Coastal Plain			Outer Coastal Plain		
	Range of concentrations	Median	Number of samples	Range of concentrations	Median	Number of samples
Arsenic (mg/kg)						
Soils	¹ 13–131	29.5	NA	² <1–13.3	3.9	12
Streambed sediments	² <1–34.7	14.1	25	² <1–2.4	<1	16
Aquifer sediments	¹ 7–136	24	NA	² <1.0–7.7	3.4	11
Arsenic, filtered samples (µg/L)						
Groundwater	<0.12–89.2	6.31	16	<0.12–6.92	0.10	21
Stream water	0.18–1.27	0.59	48	³ 0.21–1.09	0.46	³ 31

¹From Dooley, 2001.²Total digestion.³Range of concentrations does not include sewage-treatment-plant discharge site H2. Median As value of 0.33 µg/L for diurnal sampling at G8 used in calculation of Outer Coastal Plain median As concentration.

inputs to the streams that may include As released as a result of human activities, in-stream redox processes sorb As to sediments and produce comparatively low stream-water concentrations. When As enters the stream, through runoff or groundwater infiltration, there is currently no way to distinguish geogenic from anthropogenic arsenic due to the multitude of in-stream oxidation and precipitation processes that take place.

Summary and Conclusions

In the Inner Coastal Plain, Arsenic (As) is released from glauconite and probably from other minerals below the streambed by microbial activity, and enters streams through groundwater discharge. Runoff also can contribute As, as soils developed on the glauconitic marine sediments are enriched in As. In the Outer Coastal Plain, geologic materials (mainly quartz sands) generally contribute relatively little As to groundwater and runoff as compared to the Inner Coastal Plain geologic materials. In the Inner and Outer Coastal Plain watersheds, where a biogeochemical setting conducive to microbial release of As is created by septic-effluent inputs, As release to groundwater and then to the stream is enhanced. Legacy pesticide residues may contribute to the geologically derived As in the Coastal Plain watersheds, but the effect is difficult to see in the Inner Coastal Plain setting because geologic inputs of As are large. Human-induced additions or changes to the biogeochemical environment appear to result

in greater amounts of As entering groundwater, runoff, soils and streambed sediments. Because of in-stream processes of oxidation and precipitation/sorption, the concentrations of As in the Inner and Outer Coastal Plain stream waters, except on suspended particles, remain low—about 1 microgram per liter (µg/L) or less, although even these low concentrations exceed the State's surface water quality standard (SWQS).

There are, potentially, other factors arising from human activities that can alter the biogeochemical environments such that As is mobilized to the waters of Coastal Plain watersheds. In the watersheds included in the current investigation, increases in the pH of shallow groundwater and stream water were associated with residential development. For pHs that are near-neutral or neutral, As, as arsenate, is sorbed less strongly to soil particles and sediments, and thus can desorb, becoming a mobile solute. Whether increases in groundwater withdrawals associated with development could cause loss of dissolved organic carbon rich stream water to groundwater, thus potentially stimulating microbes to release As from geologic materials, as described above, is not known. Such a scenario is worthy of future investigation.

Overall, the inputs of geologically derived As are greater in Inner Coastal Plain streams than in Outer Coastal Plain streams; consequently, under high-flow conditions, the contributions by the As-enriched suspended sediments to the total As load is greater in Inner Coastal Plain streams than in Outer Coastal Plain streams. The data collected during 2006–09 indicate the potential, however, for various anthropogenic inputs to the environment to increase the amount of As that becomes mobile within Coastal Plain watersheds.

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Appendix 1. Short site names, U.S. Geological Survey site numbers and age, and description of underlying geologic formations for three Inner Coastal Plain streams.

[Geology summarized from Owens and Sohl, 1969]

Short site name	U.S. Geological Survey site number ¹	Geologic formation ²	Age	Geologic description
Crosswicks Creek				
C1	01464290	Kirkwood	Miocene	Quartz sand, gravel, clayey silt, micaceous, carbonaceous.
C2	01464330	Manasquan	Eocene	Quartz sand, glauconite sands locally, silty, clay.
C3	01464400	Vincetown	Paleocene	Calcareous, quartz sand, glauconite sand.
C4	01464430	Homerstown	Paleocene	Massive glauconite sands.
C5	01464480	Navesink/Mt. Laurel	Cretaceous	Clayey glauconite sand, mica/quartz sand, glauconite (reworked).
C6	01464485	Navesink/Mt. Laurel	Cretaceous	Clayey glauconite sand, mica/quartz sand, glauconite (reworked).
C7	01464500	Marshalltown/Englishtown	Cretaceous	Glauconite sand, mica, wood/quartz sand, carbon-rich silt, clay.
C8	01464504	Merchantville	Cretaceous	Glauconite sand, mica, carbon-rich silt.
Raccoon Creek				
R1	01477081	Kirkwood	Miocene	Quartz sand, gravel, clayey silt, micaceous, carbonaceous.
R2	01477100	Kirkwood	Miocene	Quartz sand, gravel, clayey silt, micaceous, carbonaceous.
R3	01477102	Kirkwood	Miocene	Quartz sand, gravel, clayey silt, micaceous, carbonaceous.
R4	01477105	Homerstown/Navesink	Paleocene/Cretaceous	Massive glauconite sands/clayey glauconite sands, mica.
R5	01477109	Navesink/Mt. Laurel	Cretaceous	Clayey glauconite sand, mica/quartz sand, glauconite (reworked).
R6	01477110	Navesink/Mt. Laurel	Cretaceous	Clayey glauconite sand, mica/quartz sand, glauconite (reworked).
R7	01477118	Navesink/Mt. Laurel	Cretaceous	Clayey glauconite sand, mica/quartz sand, glauconite (reworked).
R8	01477120	Mt. Laurel	Cretaceous	Quartz sand, glauconite (reworked).
Oldmans Creek				
O1	01477440	Cohansey	Miocene	Quartz sand, silt, gravel, clay lenses.
O2	01477445	Cohansey	Miocene	Quartz sand, silt, gravel, clay lenses.
O3	01477480	Mt. Laurel	Cretaceous	Quartz sand, glauconite (reworked).
O4	01477488	Kirkwood	Miocene	Quartz sand, gravel, clayey silt, micaceous, carbonaceous.
O5	01477509	Mt. Laurel	Cretaceous	Quartz sand, glauconite (reworked).
O6	01477510	Mt. Laurel	Cretaceous	Quartz sand, glauconite (reworked).

¹U.S. Geological Survey site numbers from the National Water Information System database at <http://waterdata.usgs.gov/nj/nwis>.

²Slash (/) indicates sampling site close to formations' contact.

Appendix 2. Composition of anaerobic medium used in microcosm experiments using Crosswicks Creek groundwater and streambed sediments.

[g/L, grams per liter; mg/L, milligrams per liter; µg/L, micrograms per liter]

Compound	Concentration
Sodium chloride (NaCl)	1 g/L
Magnesium chloride dihydrate (MgCl ₂ ·2H ₂ O)	400 mg/L
Calcium chloride dihydrate (CaCl ₂ ·2H ₂ O)	100 mg/L
Monopotassium phosphate (KH ₂ PO ₄)	200 mg/L
Potassium chloride (KCl)	500 mg/L
Disodium phosphate (Na ₂ HPO ₄)	0.19 g/L
Monosodium phosphate (NaH ₂ PO ₄)	0.06 g/L
Ammonium chloride (NH ₄ Cl)	0.27 g/L
3-(N-morpholino) propanesulfonic acid (MOPS)	1.05 g/L
Nitrilotriacetic acid (C ₆ H ₉ NO ₆)	1.5 mg/L
Ferrous ammonium sulfate (Fe(NH ₄) ₂ (SO ₄) ₂)	0.8 mg/L
Sodium selenite (Na ₂ SeO ₃)	0.2 mg/L
Cobalt chloride hexahydrate (CoCl ₂ ·6H ₂ O)	0.1 mg/L
Manganese sulfate monohydrate (MnSO ₄ ·H ₂ O)	0.1 mg/L
Sodium molybdate monohydrate (Na ₂ MoO ₄ ·H ₂ O)	0.1 mg/L
Sodium tungstate monohydrate (NaWO ₄ ·H ₂ O)	0.1 mg/L
Nickel chloride hexahydrate (NiCl ₂ ·6H ₂ O)	0.1 mg/L
Boric acid (H ₃ BO ₃)	0.01 mg/L
Copper sulfate pentahydrate (CuSO ₄ ·5H ₂ O)	0.01 mg/L
Nicotinic acid (C ₆ H ₅ NO ₂)	0.1 µg/L
Calcium pantothenate	0.1 µg/L
Pyridine HCl	0.1 µg/L
Riboflavin	0.1 µg/L
Thiamine HCl	0.1 µg/L
Biotin	0.05 µg/L
Folic acid	0.05 µg/L
α-lipoic acid	0.05 µg/L
Vitamin B-12	0.05 µg/L

Appendix 3. Replicates and blanks for water samples from five watersheds in the New Jersey Coastal Plain.

(Available online at: <http://pubs.usgs.gov/sir/2013/5107/>)

Appendix 4. Total and recoverable contents, major and trace elements, streambed sediments, five Coastal Plain streams, 2007, 2009.

(Available online at: <http://pubs.usgs.gov/sir/2013/5107/>)

Appendix 5. Field properties and concentrations of selected constituents in groundwater discharging to streams in five watersheds in the New Jersey Coastal Plain.

(Available online at: <http://pubs.usgs.gov/sir/2013/5107/>)

Appendix 6. Field properties, discharge, and concentrations of constituents in stream waters of five watersheds in the New Jersey Coastal Plain.

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