

The Presence and Distribution of Polycyclic Aromatic Hydrocarbons and Inorganic Elements in Water and Lakebed Materials and the Potential for Bioconcentration in Biota at Established Sampling Sites on Lake Powell, Utah and Arizona



Open-File Report 2013–1299

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

COVER

Aerial photograph above Padre Bay of Lake Powell, Utah and Arizona
(U.S. Geological Survey photograph by Jon Mason).

The Presence and Distribution of Polycyclic Aromatic Hydrocarbons and Inorganic Elements in Water and Lakebed Materials and the Potential for Bioconcentration in Biota at Established Sampling Sites on Lake Powell, Utah and Arizona

By Kurt T. Schonauer, Robert J. Hart, and Ronald C. Antweiler

Open-File Report 2013–1299

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

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment, visit
<http://www.usgs.gov> or call 1-888-ASK-USGS

For an overview of USGS information products, including maps, imagery, and publications, visit
<http://www.usgs.gov/pubprod>

To order this and other USGS information products, visit *<http://store.usgs.gov>*

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this information product, for the most part, is in the public domain, it also may contain copyrighted materials as noted in the text. Permission to reproduce copyrighted items must be secured from the copyright owner.

Suggested citation:

Schonauer, K.T., Hart, R.J., and Antweiler, R.C., 2014, The presence and distribution of polycyclic aromatic hydrocarbons and inorganic elements in water and lakebed materials and the potential for bioconcentration in biota at established sampling sites on Lake Powell, Utah and Arizona: U.S. Geological Survey Open-File Report 2013–1299, 28 p., *<http://dx.doi.org/10.3133/ofr20131299>*.

Contents

Abstract.....	1
Introduction.....	2
Description of Lake Powell	3
Purpose and Scope	3
Sampling Conditions.....	3
Field and Laboratory Methods.....	6
Field Methods	6
Laboratory Methods.....	8
Quality Assurance	9
Polycyclic Aromatic Hydrocarbons in SPMDs	9
Dissolved Inorganic Elements	12
Polycyclic Aromatic Hydrocarbons in Lakebed Material	12
Total Inorganic Elements in Lakebed Material	14
Data Results and Observations	17
Concentrations of Polycyclic Aromatic Hydrocarbons in SPMDs	17
Dissolved Inorganic Elements	18
Polycyclic Aromatic Hydrocarbons in Lakebed Material	19
Total Inorganic Elements in Lakebed Material	21
Sediment Size of Lakebed Material.....	22
Considerations for Future Monitoring	22
Summary.....	23
Acknowledgments.....	25
References Cited.....	25

Appendixes

[Available online only as .xlsx workbooks at <http://pubs.usgs.gov/of/2013/1299>]

- A. Bin averaged data of depth profile measurements of depth, water temperature, specific conductance, pH, dissolved oxygen, fluorescence, and turbidity for the sampling sites, Lake Powell, 2010 deployment.
- B. Bin averaged data of depth profile measurements of depth, water temperature, specific conductance, pH, dissolved oxygen, fluorescence, and turbidity for the sampling sites, Lake Powell, 2011 deployment.
- C. Bin averaged data of depth profile measurements of depth, water temperature, specific conductance, pH, dissolved oxygen, fluorescence, and turbidity for the sampling sites, Lake Powell, 2010 retrieval.
- D. Bin averaged data of depth profile measurements of depth, water temperature, specific conductance, pH, dissolved oxygen, fluorescence, and turbidity for the sampling sites, Lake Powell, 2011 retrieval.
- E. Depth placement of semipermeable membrane devices in feet.
- F. Concentrations of polycyclic aromatic hydrocarbon compounds detected in the semipermeable membrane devices, original data in nanograms per ampule, 2010 and 2011.

- G. Concentrations of polycyclic aromatic hydrocarbon compounds detected in the semipermeable membrane devices, converted data in nanograms per liter, 2010 and 2011.
- H. Dissolved concentrations of inorganic elements detected at the sampling sites, Lake Powell, 2010 and 2011.
- I. Total concentrations of polycyclic aromatic hydrocarbons detected in lakebed material at the sampling sites, Lake Powell, 2010 and 2011.
- J. Percent weight and total concentrations of inorganic elements detected in lakebed material at the sampling sites, Lake Powell, 2010 and 2011.
- K. Sediment size of lakebed material detected at the sampling sites, Lake Powell, 2010 and 2011.

Figures

- 1. Location map showing the study area and sample points, Lake Powell, north-central Arizona and south-central Utah4
- 2. Graph of water-surface elevation of Lake Powell during this study5
- 3. Graph of temperature-depth profile, conductivity, temperature, and depth profiler, and placement of semipermeable membrane devices at Stateline Marina on Lake Powell.....6
- 4. Photographs showing examples of Lake Powell sampling sites at high-use site at Antelope Marina and low-use site at Farley Canyon.....7
- 5. Photographs of Lake Powell sample collection—semipermeable membrane device in shipping aluminum tin next to protective canister, retrieval of lakebed material with Ponar dredge sampler, and collection of subsample with Teflon spatula8
- 6. Graph comparing environmental samples collected at the Bullfrog Marina on Lake Powell. Individual zones are compared to their combined average and environmental sample13
- 7. Map showing sum of polycyclic aromatic hydrocarbon concentrations found in semipermeable membrane device samples found throughout Lake Powell.....17
- 8. Graph showing average concentrations of select inorganic elements from lower to upper Lake Powell22
- 9. Map showing sum of polycyclic aromatic hydrocarbon in lakebed material found in Lake Powell23
- 10. Graph showing average concentrations of cobalt found in lakebed material samples from Lake Powell24

Tables

- 1. Results of field blank analysis for semipermeable membrane devices used on Lake Powell during 2010 and 201110
- 2. Spike and surrogate recoveries for performance reference compounds added to samplers used on Lake Powell14
- 3. Percent relative standard deviations for Lake Powell field sample replicate, for those chemical species with concentrations greater than 10 times the detection limit15
- 4. Ratios of the median standard deviations between Lake Powell field sample replicates and the detection limit for those chemical species with concentrations between the detection limit and 10 times the detection limit15

5. Results of laboratory reagent blanks for lakebed material from Lake Powell in 2010 and 2011.....	16
6. Spike and surrogate recoveries for lakebed material from Lake Powell collected in 2010 and 2011.....	18
7. Certified values for National Institute of Standards and Technology Reference Material 8704, Buffalo River Sediment, along with the median value of 11 digestions, the median absolute deviation, and the percent relative median absolute deviation	20
8. Percent relative standard deviations for sample replicate digestions for those chemical species with concentrations greater than 10 times the detection limit	21
9. Absolute percentage difference between the published values and the median observed values for the sediment reference standard for those elements whose concentrations were at least 10 times the detection limit in Lake Powell.....	21

Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square foot (ft ²)	0.09290	square meter (m ²)
square mile (mi ²)	2.590	square kilometer (km ²)
Volume		
gallon (gal)	3.785	liter (L)
cubic foot (ft ³)	0.02832	cubic meter (m ³)
acre-foot (acre-ft)	1,233	cubic meter (m ³)
Flow rate		
acre-foot per year (acre-ft/yr)	1,233	cubic meter per year (m ³ /yr)
foot per second (ft/s)	0.3048	meter per second (m/s)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
mile per hour (mi/h)	1.609	kilometer per hour (km/h)
Concentration		
part per million (ppm)	1	milligram per liter (mg/L)
part per billion (ppb)	1	microgram per liter (µg/L)
part per trillion (ppt)	1	nanogram per liter (ng/L)
Mass		
ounce (oz)	28.4	gram (g)
pound (lbs)	0.4536	kilogram (kg)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Elevation, as used in this report, refers to distance above the vertical datum.

Abbreviated Water-Quality Units

Chemical concentration and water temperature are given only in metric units. Chemical concentration in water is given in milligrams per liter (mg/L), micrograms per liter ($\mu\text{g/L}$), or nanograms per liter (ng/L). Milligrams per liter is a unit expressing the solute mass (milligrams) per unit volume (liter) of water. One thousand micrograms per liter is equivalent to 1 milligram per liter. For concentrations less than 7,000 milligrams per liter, the numerical value is about the same as for concentration in parts per million. Specific conductance is given in microSiemens per centimeter at 25 degrees Celsius ($\mu\text{S/cm}$). Chemical concentration in bottom sediment is given in grams per kilogram (g/kg), micrograms per gram ($\mu\text{g/g}$), milligrams per kilogram (mg/kg), or micrograms per kilogram ($\mu\text{g/kg}$). Grams per kilogram is equal to parts per thousands (ppt). Milligrams per kilogram and micrograms per gram are equal to parts per million (ppm). Micrograms per kilogram are equal to parts per billion (ppb).

Datums

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)

Elevation, as used in this report, refers to the distance above the vertical datum

Acronyms and Symbols

EPA	U.S. Environmental Protection Agency
GC/MS	gas chromatography/mass spectrometry
GLCA	Glen Canyon National Recreation Area
GPS	Global Positioning System
ICP-AES	inductively coupled plasma-emission spectrometry
ICP-MS	inductively coupled plasma-mass spectrometry
MDL	method detection limit
MPN	most probable number
NIST	National Institute of Standards and Technology
NRP	National Research Program of the U.S. Geological Survey
NPS	National Park Service
NWQL	U.S. Geological Survey National Water Quality Laboratory
PAH	polycyclic aromatic hydrocarbon
PRC	performance reference compounds
PWC	personal watercraft
REE	rare earth element
SPMD	semipermeable membrane device
USGS	U.S. Geological Survey

Al	aluminum	Na	sodium
As	arsenic	NH ₄	ammonium
B	boron	Ni	nickel
Ba	barium	NO ₂	nitrite
Br	bromine	NO ₃	nitrate
Ca	calcium	Nd	neodymium
Cd	cadmium	P	phosphorus
Ce	cerium	Pb	lead
Cl	chloride	PO ₄	phosphate
Co	cobalt	Pr	praseodymium
Cr	chromium	Rb	rubidium
Cs	cesium	Re	rhenium
Cu	copper	S	sulfur
Dy	dysprosium	Sb	antimony
Er	erbium	Se	selenium
Eu	europium	SiO ₂	silica
Fe	iron	SO ₄	sulfate
Ga	gallium	Sm	samarium
Gd	gadolinium	Sn	tin
HCl	hydrochloric acid	Sr	strontium
Hg	mercury	Te	tellurium
HNO ₃	nitric acid	Th	thorium
Ho	holmium	Tl	thallium
K	potassium	Tm	thulium
K ₂ CrO ₇	potassium dichromate	U	uranium
La	lanthanum	V	vanadium
Li	lithium	W	tungsten
Lu	lutetium	Y	yttrium
Mg	magnesium	Yb	ytterbium
Mn	manganese	Zr	zirconium
Mo	molybdenum	Zn	zinc

The Presence and Distribution of Polycyclic Aromatic Hydrocarbons and Inorganic Elements in Water and Lakebed Materials and the Potential for Bioconcentration in Biota at Established Sampling Sites on Lake Powell, Utah and Arizona

By Kurt T. Schonauer, Robert J. Hart, and Ronald C. Antweiler

Abstract

The National Park Service is responsible for monitoring the effects of visitor use on the quality of water, lakebed material (bottom sediments), and biota, in Lake Powell, Utah and Arizona. A sampling program was begun in 2010 to assess the presence, distribution, and concentrations of organic and inorganic compounds in the water column and bottom sediment. In response to an Environmental Impact Statement regarding personal watercraft and as a continuation from previous studies by the U.S. Geological Survey and the National Park Service, Glen Canyon National Recreation Area, water samples were collected and analyzed for polycyclic aromatic hydrocarbons (PAHs) using semipermeable membrane devices and inorganic elements using a fixed-bottle sampler deployed at established monitoring sites during 2010 and 2011. Lakebed material samples were also analyzed for polycyclic aromatic hydrocarbons and inorganic elements, some of which could be harmful to aquatic biota if present at concentrations above established aquatic life criteria.

Of the 44 PAH compounds analyzed, 26 individual compounds were detected above the censoring limit in the water column by semipermeable membrane devices. The highest number of compounds detected were at Lone Rock Beach, Wahweap Marina, Rainbow Bridge National Monument, and Antelope Marina which are all located in the southern part of Lake Powell where visitation and boat use is high. Because PAHs can remain near their source, the potential for bioconcentration is highest near these sites. The PAH compound found in the highest concentration was phenol (5,902 nanograms per liter), which is included in the U.S. Environmental Protection Agency's priority pollutants list.

The dissolved inorganic chemistry of water samples measured at the sampling sites in Lake Powell defined three different patterns of elements: (1) concentrations were similar

between sites in the upper part of the lake near Farley Canyon downstream to Halls Crossing Marina, a distance of about 36 lake miles, (2) concentrations varied depending on the element between Halls Crossing Marina downstream to the mouth of the Escalante River, a distance of about 33 lake miles, and (3) concentrations were similar between sites from below the mouth of the Escalante River to Glen Canyon Dam, a distance of about 68 lake miles.

Analysis of lakebed bottom sediment material samples detected PAH compounds at all sampling sites except at Halls Crossing Marina, Stanton Creek, and Forgotten Canyon. Twenty-four of 44 PAHs analyzed in lakebed material were detected above the reporting limit. Perylene was the most prevalent compound detected above the reporting limit in lakebed material and was detected at three sampling sites. Concentrations of perylene ranged from an estimate of 24.0 to 47.9 micrograms per kilogram ($\mu\text{g}/\text{kg}$). Fluoranthene had the highest concentration of any PAH and was detected at the Wahweap Marina with a concentration of 565 $\mu\text{g}/\text{kg}$. The highest sum of concentrations for all compounds found in lakebed material samples at one site was at the Wahweap Marina, which had concentrations five times higher than the next highest site.

The three major tributaries to Lake Powell—the Colorado, Escalante, and San Juan Rivers—all showed elevated concentrations of inorganic elements in their delta sediments for most elements relative to the majority of the sediment samples taken from the lake itself. However, there were four lake sites that had concentrations for most inorganic elements that equaled or exceeded those of the tributaries. Two of these sites were at the northeast part of the lake, nearest to the Colorado River as it enters Lake Powell (Farley Canyon and Blue Notch Canyon), one was at the Escalante River below 50-Mile Canyon, and other was at Antelope Marina.

Introduction

Lake Powell, located in north-central Arizona and south-central Utah, is the second largest reservoir in the United States. The National Park Service (NPS) as part of Glen Canyon National Recreation Area (GLCA) manages the lands around the lake, use of the lake, and monitors the water quality. Lake Powell is used for flood control, storage, power generation, and recreation. The use of personal watercraft (PWC), many of which rely on two-stroke carbureted engines, on Lake Powell is popular among recreationalists. Beginning in May 1998, a petition brought by a nonprofit organization, Bluewater Network, urged the NPS to prohibit PWC throughout the national park system (National Park Service, 2003). Two concerns addressed by this petition are PWC impacts on (1) visitors and (2) natural resources. Because Lake Powell is the predominant feature in GLCA, water quality for aquatic biota in the lake and visitors who choose to recreate on and around the lake is a high priority. It is estimated that PWC with two-stroke carbureted engines discharge as much as 30 percent of their fuel and oil unburned into the water column (Asplund, 2000). This discharge contains polycyclic aromatic hydrocarbons (PAHs) and other contaminants.

In 2001, a settlement with the Bluewater Network was negotiated requiring the NPS to develop an Environmental Impact Statement (EIS) concerning the use of PWC specifically on Lake Powell. The NPS completed the EIS in 2003. Although a complete ban was not imposed by the Record of Decision, special regulations were established (alternative B from the EIS). One feature of this alternative includes development of a water-quality monitoring program for hydrocarbon contamination (National Park Service, 2003). Twenty sentinel sampling sites throughout the lake were established in 2004 for monitoring including marinas, bays, beaches, and side canyons (Hart and others, 2012).

Previous investigations of water and lakebed material quality in Lake Powell (Hart and others, 2005 and 2012) focused on specific areas or contaminants. Vernieu (2009) compiled historical physical and chemical water quality characteristics dating back to 1964. In 2001, the NPS collected water samples and had them analyzed to determine hydrocarbon concentrations at four locations. Samples were collected at three high-use areas and one control area that was closed to gasoline-powered water vessels. Water samples were collected at two depths (20 inches and 10 feet, ft) at each site to characterize vertical distribution of hydrocarbons (National Park Service, 2003). In 2001 and 2002, the U.S. Geological Survey (USGS) collected water chemistry and lakebed material samples at three side canyons and documented PAHs and inorganic elements in addition to other contaminants (Hart and others, 2005). Also in 2001, the USGS collected and analyzed sediment core samples collected from the Colorado River bed near Hite, Utah, for organic and inorganic compounds (Hart and others, 2005). From 2004 to 2006, the USGS in cooperation with the NPS established 20 sentinel sites for monitoring

and collected discrete water and lakebed material samples (Hart and others, 2012). Routinely scheduled sampling for nutrients and major ions in addition to measurements of physical and chemical properties is done by the USGS's Grand Canyon Research and Monitoring Center (Vernieu, 2009). Presently, no systematic or routine sampling is being done for hydrocarbons or other contaminants associated with visitor use.

A study completed by Lico and Johnson (2007) on lakes Mead and Mohave found that high concentrations of PAH compounds found in semipermeable membrane devices (SPMDs) were associated with high-traffic boating areas. They also found that PAH concentrations were generally low in lakebed material. These findings are similar to those found in this study conducted on Lake Powell.

PAHs can be found naturally in the environment but a majority of sources are manmade from the incomplete burning of fuel (fossil fuels or biomass), use of asphalt and parking lot sealants, and waste incinerators (Agency for Toxic Substances and Disease Registry, 1995, Mahler and others, 2005). The U.S. Environmental Protection Agency (EPA) has currently designated 32 PAH compounds as priority pollutants (<http://water.epa.gov/scitech/methods/cwa/pollutants.cfm>, accessed February 4, 2012) that the EPA regulates. The fate of PAHs is of significant environmental concern because of their carcinogenic effects and other negative health impacts to humans and aquatic organisms (Eisler, 1987; Agency for Toxic Substances and Disease Registry, 1995; Albers, 2003). PAHs tend to accumulate in sediments because of their hydrophobic character. They also can be found partitioned between the water column and aquatic organisms (Tuvikene, 1995). Watercraft exhaust and fuel/oil spills can be a significant contributor of PAHs to the environment particularly near marinas, but also in other areas where high use of recreational watercraft occur. PAH compounds can degrade through photochemical processes, which may be a controlling factor in the euphotic zone of Lake Powell; however, light is limited or nonexistent at depth in the hypolimnion of Lake Powell, where PAH compounds can accumulate in lakebed material.

Discrete water samples collected for PAHs during previous studies are considered point-in-time samples and most likely do not characterize the range in concentrations at each site. Also, the potential for bioconcentration of PAHs in aquatic biota and the presence and distribution of PAHs and inorganic elements found in the water column and sediments in Lake Powell is not completely understood. A long-term monitoring program for organic and inorganic contaminants is needed to provide representative data to the NPS. To address this need, the USGS in cooperation with the NPS-GLCA through the USGS/NPS Water-Quality Partnership Program (http://water.usgs.gov/nps_partnership, accessed June 6, 2012) began a two-year sampling program in 2010 to assess the presence of PAHs and other contaminants in Lake Powell. Data collected during this study for PAHs in the water column and lakebed material, along with inorganic elements in lake bed material, will be used as a baseline for future monitoring.

The recently completed study described in this report used SPMDs to assess the potential for bioconcentration of PAHs in aquatic organisms. SPMDs collect time-weighted average concentrations of chemicals, therefore avoiding the potential of collecting maximum or minimum contaminant concentrations when using a point-in-time sampling method. Although aquatic organisms have the ability to metabolize and excrete PAHs, bioconcentration can still occur based on characteristics of the species and compound (Spacie and others, 1983; Tuvikene, 1995; Sun and others, 2006). Therefore SPMDs have been selected to be a standardized proxy for these organisms. In addition, the use of SPMDs allowed for the collection of depth-integrated samples from each of the stratified zones of the lake. Also presented in this report are data for inorganic elements found in water, PAHs, and inorganic elements in lakebed material and sediment size distribution. These data will be used to build on previous sampling efforts to inform the NPS-GLCA of contaminant levels at sentinel sites.

Description of Lake Powell

Lake Powell was created by impoundment of the Colorado River by Glen Canyon Dam in 1963. Because of the capacity of the reservoir, it took 17 years for Lake Powell to completely fill. Full pool elevation is 3,700 ft, whereas the elevation at the top of Glen Canyon Dam is 3,715 ft. Inlets to the penstocks for power generation are at an elevation of 3,470 ft (Bureau of Reclamation, 1970). On completion of the dam, lake levels rose filling what was once Glen Canyon. This canyon is narrow and deep with vertical walls reaching several hundred feet. The many narrow side canyons give the lake a dendritic shape (fig. 1). The water-surface area is 266 square miles and the shoreline length is 1,960 miles (Bureau of Reclamation, 2008).

At full pool elevation, the average depth of the lake is 167 ft. The highest percentage of streamflow entering Lake Powell is from the Colorado River (85 percent) followed by the San Juan (14 percent), Dirty Devil (0.6 percent), and Escalante Rivers (0.1 percent). Lake Powell is a warm monomictic lake with some vertical mixing during the winter. Convective mixing does not always reach the bottom of the lake due to its depths. Advective mixing occurs as flow enters the lake and sinks due to the higher inflow density. This advective mixing inhibits the formation of anaerobic conditions near the lake bottom only in the upstream region of the reservoir (Potter and Drake, 1989).

Purpose and Scope

The purpose of this report is to present data on the presence, concentration, and distribution of PAHs and on selected inorganic elements in Lake Powell. Water and lakebed material (environmental) samples were collected during the summers of 2010 and 2011 at 20 sites throughout the

lake. These data will be used as a baseline for future monitoring of water in Lake Powell. The scope of the report includes all data collected during the study—field parameters, PAHs and inorganic elements in water and in lakebed material, and sediment-size distribution. Description of sampling and laboratory methods, and data analysis and observations are also discussed.

Sampling Conditions

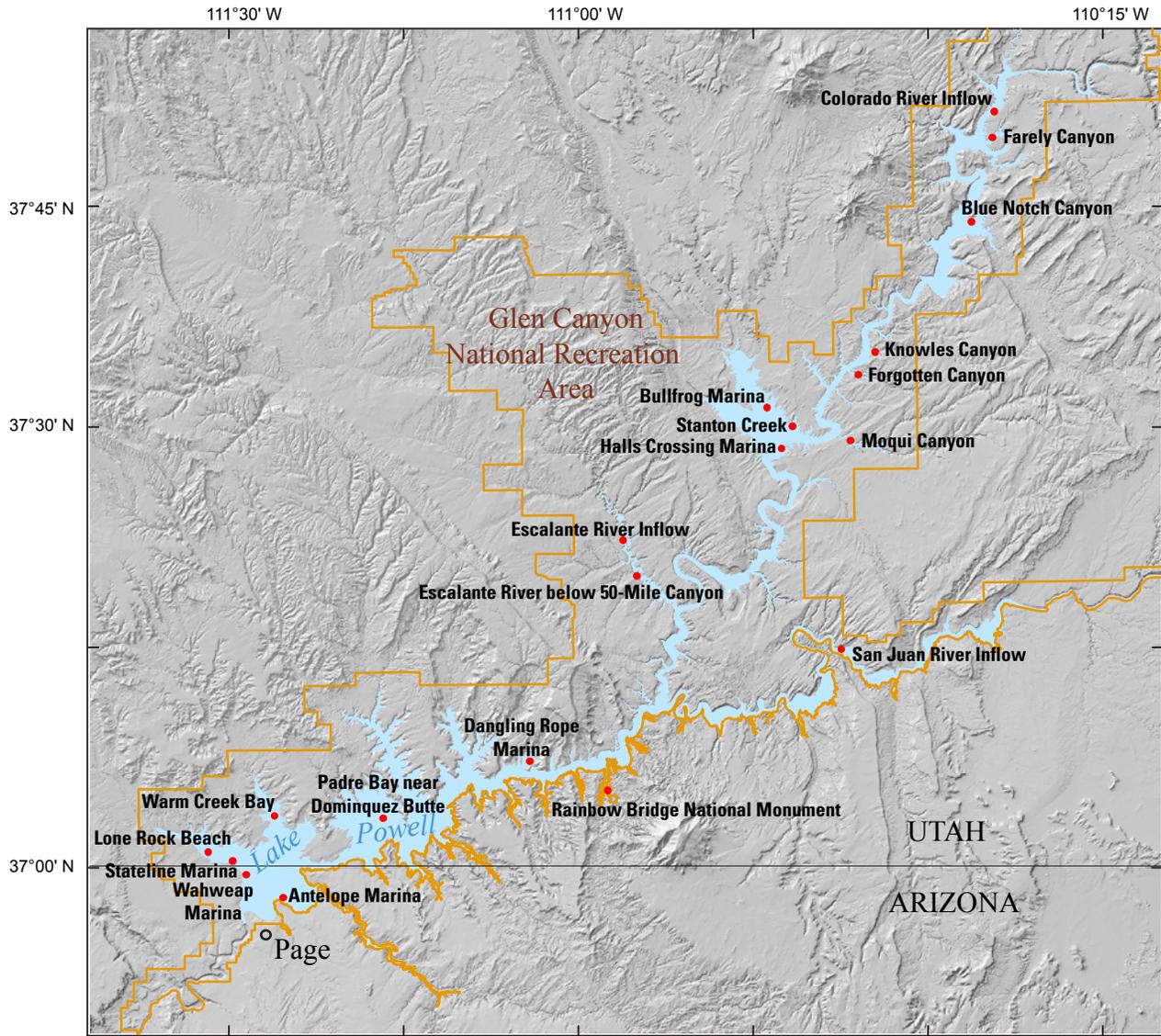
Sampling visits were made in 2010 and 2011 during summer months to coincide with high-visitor use. Sampling during this period will ascertain annual high concentrations of contaminants as well as provide information about the potential exposure to those contaminants by recreationalists and park employees. The popular boating season on Lake Powell begins on Memorial Day (the end of May) and continues through Labor Day (the beginning of September), a period of about 3 months. Facilities that support recreation (marinas, fuel docks, concessionaires, and rental shops) are operating at full capacity during the summer months. However, boating occurs year round even during the winter months when visitation is lower. The average visitation for 2010 and 2011 during the summer (June through August) was 1.1 million visitors and in the winter (December through February) it was 95,000 visitors (National Park Service, 2013).

Elevated streamflow resulting from snowmelt in the upper Colorado River watershed reaches Lake Powell in late spring and early summer. As a result of this and regulation of the lake level for power generation, downstream use, and flood control, lake elevation is normally at its highest level of the year during the summer. During the 2 years of this study, annual lake level fluctuation continued in a typical cycle. During the first year of sampling, lake elevation was on average 14 ft below the 30-year average. In the second year of the study, significant spring runoff, primarily from the Colorado River, increased the reservoir elevation to its highest level in more than 9 years. During the sampling period in 2011, the water surface elevation was on average 8 ft above the 30-year average (fig. 2).

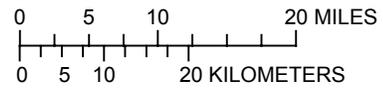
During the summer months, an interflow-density current prevails because of warm, clear, and high salinity inflows to the lake (Hart and Sherman, 1996). This advective process vertically stratifies Lake Powell (fig. 3). The stratification of the lake controls the distribution of living and nonliving materials, dissolved or suspended in the lake (Marzolf and others, 1998). Because of this process, the depths where stratification breaks occurred were considered in water sampling and deployment of the SPMDs.

Twenty sentinel sites were established in 2004 (Hart and others, 2012) to serve as locations for long-term monitoring. These are the sites used to conduct the research presented here and are distributed throughout the lake representing a range of conditions in regards to use, depth, boat traffic, and adjacent land use (fig. 4).

4 Polycyclic aromatic hydrocarbons and inorganic elements in water and lakebed materials in Lake Powell, Utah and Arizona



Base from U.S. Geological Survey digital data, 1:100,000, 2009 Universal Transverse Mercator projection, Zone 12



EXPLANATION

- Recreational Area boundary
- Sentinel sampling point

Figure 1. Location map showing the study area and sample points, Lake Powell, north-central Arizona and south-central Utah.

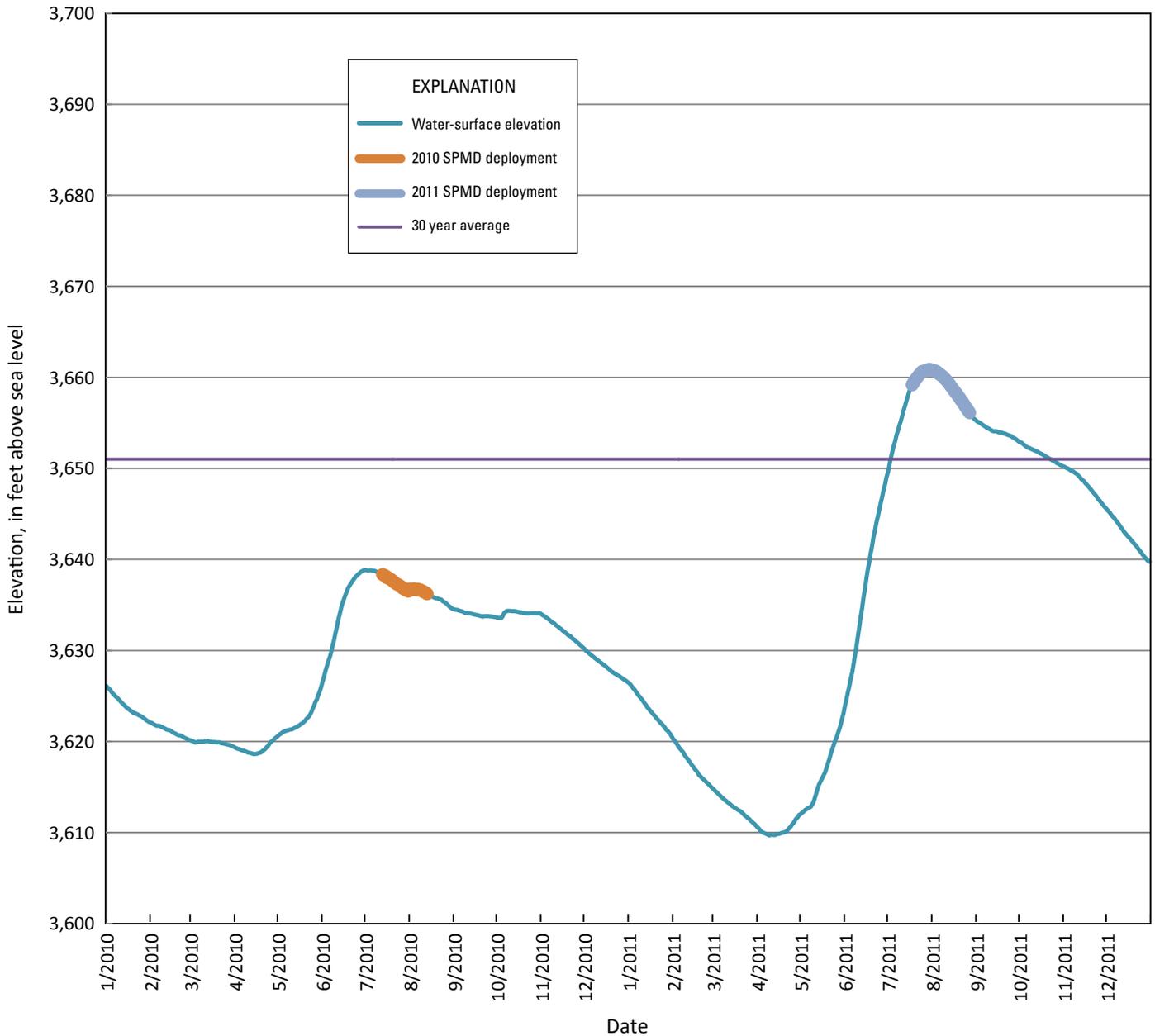


Figure 2. Graph of water-surface elevation of Lake Powell during this study (data source, Bureau of Reclamation, 2012). Date format is month/year. SPMD, semipermeable membrane device.

Marinas, popular beaches, and sight-seeing destinations such as Rainbow Bridge National Monument are accessible and heavily used by visitors with various types of watercraft including PWCs, ski boats, and houseboats during the peak visitation period. Low-use sites are located mostly in the northern part of the lake in side canyons not frequently visited. There are sites located in each of the main tributaries, that are positioned to be representative of the tributaries contribution

to the lake. On the basis of the physical features and boat traffic at each site, precise sample location was adjusted to optimize quality control. Sample sites were modified when necessary to ensure watercraft would not make physical contact with samplers and to avoid fumes from refueling or engine exhaust. Sampling was done from boats, beaches, docks, or rock ledges only after safety, effectiveness, and efficiency were evaluated.

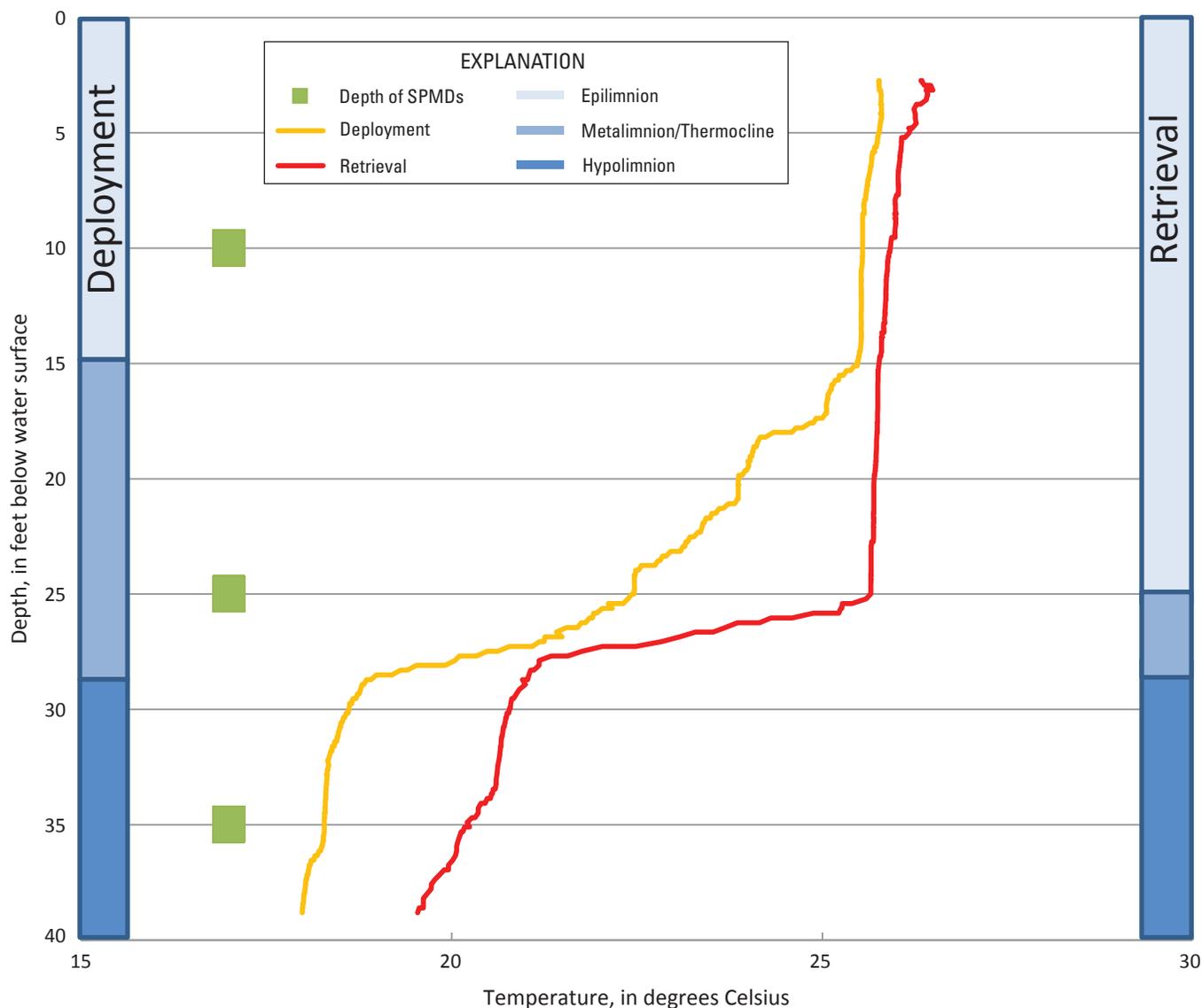


Figure 3. Graph of temperature-depth profile from Sea-Bird Electronics, Inc., conductivity, temperature, and depth (CTD) profiler, model SBE 25™ and placement of semipermeable membrane devices (SPMD) at Stateline Marina on Lake Powell (see fig. 1).

Field and Laboratory Methods

Field Methods

A Sea-Bird Electronics, Inc., conductivity, temperature, and depth (CTD) profiler, model SBE 25™, was used to make depth-profile measurements for field parameters (depth, water temperature, specific conductance, pH, dissolved oxygen, fluorescence, and turbidity). Each of the field parameters were collected at a rate of 8 hertz. The SBE 25 was lowered and raised using a capstan at an average rate of 1.0 foot per second (ft/s). All sensors of the SBE 25 were calibrated before each year's sample collection by the manufacturer. Calibration

coefficients were updated in the Sea-Bird software following calibration. Post processing of SBE 25 data immediately after profiling provided information about the stratification at each site. Use of the SBE 25 resulted in a well-defined profile of the thermocline. Based on water depth, input sources, and mixing, it was found that the thermocline can range in thickness from 5 to 60 ft with an average of about 30 ft. An example profile is provided in figure 3. The 8 hertz depth profile data was averaged into 1-foot bins and are shown in appendices A–D.

A series of three SPMDs were set at preselected depths (appendix E; note that appendixes A–K are available online only as .xlsx workbooks at <http://pubs.usgs.gov/of/2013/1299>) and deployed in the water column at each sampling site to document the presence and concentration of PAHs. SPMDs mimic the uptake of organic contaminants in fatty tissue of



Figure 4. Photographs showing examples of Lake Powell sampling sites at (left) high-use site at Antelope Marina and (right) low-use site at Farley Canyon.

organisms. SPMDs consist of a neutral lipid, ultra-high-purity triolein, encased in a thin-walled layflat polyethylene membrane tube (Petty and others, 2000). The dimensions of the SPMDs used in this study are 91.4 centimeters (cm) by 2.5 cm containing 1 milliliter (mL) of triolein, with a total surface area of about 460 square centimeters (cm²). The membrane allows nonpolar chemicals to pass through to the lipid where the chemicals are concentrated (Alvarez, 2010). Performance reference compounds (PRC) (fluoranthene-d10, fluorine-d10, and anthracene-d10) were added by Environmental Sampling Technologies, Inc., to the samplers during manufacturing. PRCs are added to the samplers to account for temperature, biofilm, and water flow which can all affect the performance of the SPMD (Alvarez, 2010). SPMDs are shipped to the field chilled from the laboratory in solvent-rinsed gallon tins filled with argon gas. During deployment in the field, a single SPMD is housed in a protective canister to prevent impact damage (fig. 5). To deploy the SPMDs, lids on the deployment canister and the gallon tin are removed, SPMDs are removed from the tin, mounted into the canister, lids are replaced, and SPMDs are slowly lowered into the water. At the end of deployment, SPMDs are placed back into the tins and chilled.

Because vertical water chemistry and physical properties control the distribution of living or nonliving materials, the SBE 25 profile data for temperature was reviewed onsite to determine the placement of SPMDs in the water column to target the epilimnion, metalimnion, and hypolimnion (fig. 3). If it was determined that the water column at a site was well mixed, the samplers were placed at a single depth, deep enough to ensure they would remain submerged during deployment. Samplers were anchored to available dock structures, trees, rocks, or buoys. At three sites, the depth of water, water clarity, and (or) the depth of the euphotic zone required the use of a shade structure over the top-most SPMD to prevent photodegradation of PAHs. These shade structures did not restrict water passage and were completely open on

the bottom. SPMDs were deployed for an average of 35 days, after which they were retrieved and put on ice for shipment. On retrieval of SPMDs, an additional SBE 25 profile was made to evaluate change in water chemistry during the deployment period.

At each site water samples for major ions, nutrients, organic carbon, and inorganic elements were collected using a polytetrafluoroethylene (PTFE) fixed-bottle sampler, which was suspended by a calibrated line to determine sampling depth. Samples were taken within 3 feet of the surface of the lake. If there was a thermocline in the lake at the site, an additional sample was collected at a depth below this layer. Samples were immediately filtered on site through a Gelman™ 0.45-micrometer (μm) pore-size cartridge filter into aliquots for analysis. In addition to and concurrent with the filtration, an unfiltered aliquot was taken for the immediate determination of pH, specific conductance, and water temperature. The metals and mercury samples were preserved as appropriate, whereas the other samples were kept chilled until analysis. Additional information regarding sampling protocol can be obtained in Hart and others (2012).

In addition to water samples, a lakebed material sample was collected at each sample location using a Ponar dredge following protocols described by Hart and others (2012) for the determination of PAHs and inorganic elements (fig. 5). Because of their generally low water solubility and affinity for organic carbon, PAHs adhere to sediment particles in the water column and often settle to the bottom (Agency for Toxic Substances and Disease Registry, 1995). The Ponar dredge sampler was lowered through the water column until it reached the lakebed, the sampler was then triggered and retrieved. Subsamples taken from sediments not in direct contact with the metallic sampler were collected with a Teflon-coated spatula and deposited in a precleaned glass jar. Approximately 100 grams (g) of wet sediment was collected for each subsample and stored on ice.

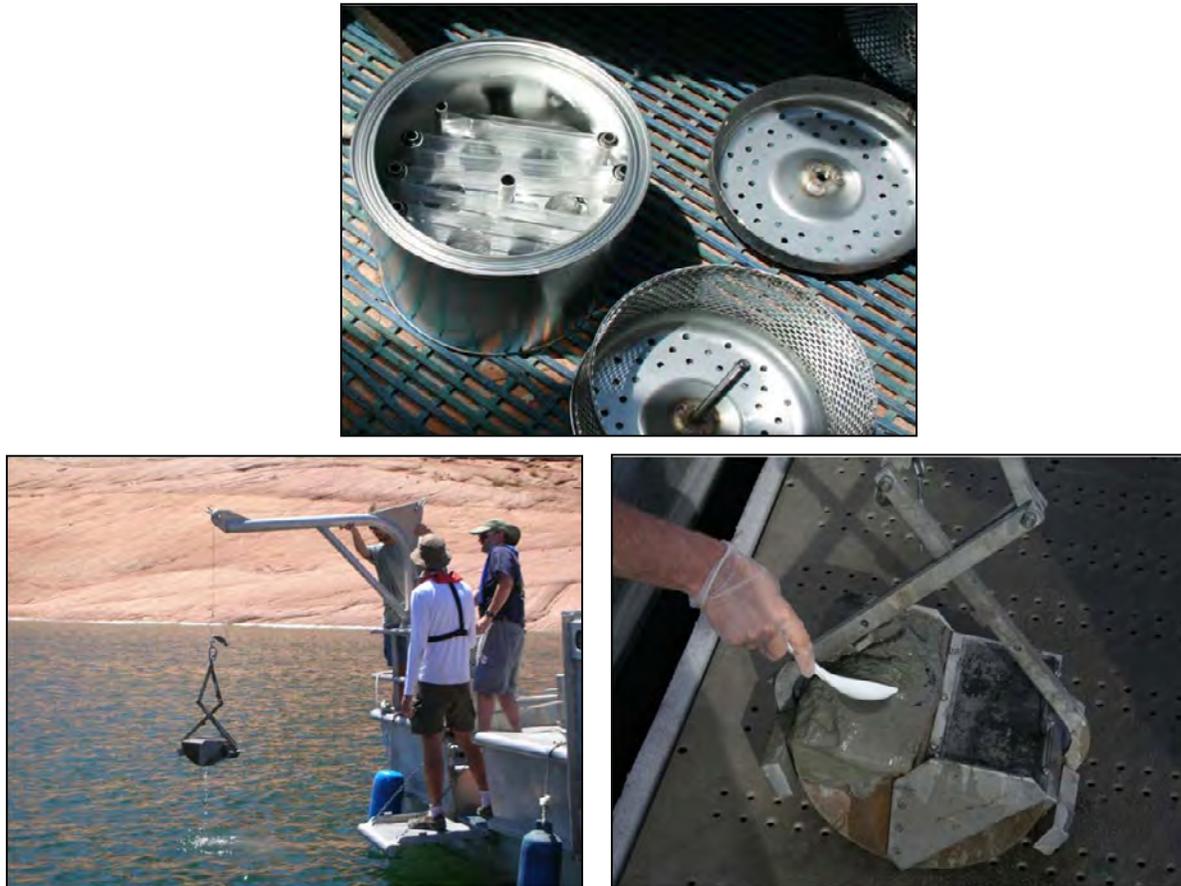


Figure 5. Photographs of Lake Powell sample collection—(top) semipermeable membrane device (SPMD) in shipping aluminum tin next to protective canister, (left) retrieval of lakebed material with Ponar dredge sampler, and (right) collection of subsample with Teflon spatula.

Laboratory Methods

Four laboratories were used during this study. Environmental Sampling Technologies, Inc. (EST), Saint Joseph, Missouri, was contracted to manufacture and supply the SPMDs and canisters and to complete the extractions from the SPMDs after deployment. The USGS National Water Quality Laboratory (NWQL) in Lakewood, Colorado, was used for analysis of PAHs from the SPMD's extract and in lakebed material. The USGS National Research Laboratory (NRP) in Boulder, Colorado, analyzed dissolved inorganic elements and also total inorganic elements in lakebed material. The USGS Cascade Volcano Observatory Laboratory (CVO) in Vancouver, Washington, was used to determine sediment sizes and breaks of lakebed material.

SPMDs were shipped on ice after retrieval from the sampling sites to EST for dialytic extraction. This post-processing step recovers chemical residues and sequesters the chemicals in an organic solvent. The three SPMDs for each site were composited, concentrated, and filtered through glass filter paper using a dichloromethane with methanol solution.

The samples were again concentrated and purified through gel permeation chromatography (GPC) using the dichloromethane with methanol solution. This GPC clean-up step is necessary for gas chromatography-mass spectroscopy (GC-MS). It removes carry-over contamination such as water, sulfur, lipid, and biofouling not removed during the pre-dialysis clean up (Terri Spencer, manager, EST, written commun., November 3, 2009).

Following processing at EST, the SPMD sample extracts were sent to the NWQL for analysis of PAH compounds. The instrumental analysis of the SPMD sample extract is described by Furlong and others, 1996, with the exception of the solvent dichloromethane, which is described by Zaugg and others, 2006. Concentrations of PAHs provided by the NWQL are in nanograms/ampule (ng/ampule). Conversion of this concentration into nanograms per liter (ng/L) was calculated using SPMD Water Concentration Estimator version 5.1, described by Huckins and others (2006) and Alvarez (2010). This model uses PRC loss rates, original compound values (in ng/ampule), and the octanol-water partition coefficient (K_{ow}) for each compound. K_{ow} is the ratio of solubility of a compound in

octanol to its solubility in water and for the compounds identified in this study range from 1.5 to 8.2. By using this model, estimated concentrations can be calculated for comparison to other sampling methods and media concentrations.

The sample set analyzed by NWQL included a laboratory blank and a spike. The spike was fortified at 4,000 ng/ampule with the analytes of interest. To each blank, spike, and SPMD sample, a surrogate mixture consisting of nitrobenzene-d5, 2-fluorobiphenyl, and terphenyl-d14 was added.

Dissolved concentrations of inorganic elements (trace elements and major cations) were determined by both inductively coupled plasma-atomic emission spectrometry (ICP-AES; Mitko and Bebek, 1999) and inductively coupled plasma-mass spectrometry (ICP-MS; Garbarino and Taylor, 1994; Taylor, 2001); dissolved mercury was determined by cold-vapor atomic fluorescence spectrometry (Roth and others, 2001); anions were determined by ion chromatography (Brinton and others, 1996); and dissolved organic carbon was determined by infrared absorption spectrophotometry (Wershaw and others, 1987).

PAH compounds in lakebed material samples were extracted using accelerated solvent extraction (ASE) with a mixture of distilled water and isopropyl alcohol. A surrogate mixture of nitrobenzene-d5, 2-fluorobiphenyl, and terphenyl-d14 compounds were added to the samples before extraction to verify method recoveries. Solid phase extraction cartridges consisting of polystyrene divinylbenzene and florasil were used for analyte isolation and extract clean up. The extracts were concentrated and solvent exchanged to dichloromethane. The internal standard mixture was added prior to analysis. The extracts were analyzed by full scan on a GC-MS system. Zaugg and others (2006) describe the method for determining semivolatile organic compounds and polycyclic aromatic hydrocarbons in solids by gas chromatography/mass spectrometry.

Lakebed sediment samples were dewatered by freeze-drying, and approximately 100 milligrams (mg) of dried sample was completely digested into a mixture of hydrofluoric, hydrochloric, and nitric acids according to protocols described in Hart and others (2005). The digested sample was subsequently analyzed for inorganic element and major cations by ICP-AES and ICP-MS.

Particle-size analysis of each lakebed material sample was conducted for grain size analysis at 62, 31, 16, 8, 4, and 2 μm . A subsample of sediment was placed into a pie tin and dried until semisolid. Deionized water was added to the sediment and was passed through 2.0, 1.0, 0.50, 0.25, 0.125, and 0.063 millimeter (mm) sieves. Each of these particle sizes were put into a pre-tared crucible with glass microfiber filters seated in them. The remainder (less than 0.063 mm) was put into a pre-tared glass dish. All of the crucibles and dishes were placed on racks in an oven at 103 degrees Celsius ($^{\circ}\text{C}$) for 2 hours. The racks were placed in an enclosure with desiccant to cool for 1 hour. A second subsample was passed thru a 0.063 mm sieve to isolate the silt and clay portion, and the sand portion was discarded. This silt and clay was poured

into a sedigraph cup with deionized water and 1 to 3 mL of dispersant (sodium hexametaphosphate). The sample was poured into a sedigraph for analysis using x-rays. A description of methods and quality-assurance plan can be found in Guy (1969) and Matthes and others (1992).

Quality Assurance

Precautions were taken to minimize contamination during sampling, processing, and transportation. Water- and lakebed-material-chemistry sampling was done following standard USGS procedures as documented in the "National field manual for the collection of water quality data: U.S. Geological Survey Techniques of Water-Resources Investigations" (variously dated). Quality-Assurance (QA) samples were collected to determine any bias and variability associated with field and laboratory methods.

Polycyclic Aromatic Hydrocarbons in SPMDs

Bias was evaluated through the analysis of laboratory and field blank samples (table 1). To assess potential bias in SPMD samples introduced during laboratory analysis, two laboratory blanks were analyzed by the NWQL in 2010 and 2011; all compounds were below the reporting limit of 50 ng/ampule. Five field blanks (3 composite and 2 site-specific) were collected to assess potential bias introduced during SPMD deployment and (or) retrieval (table 1). Each field blank was a single SPMD of the same lot number as the environmental SPMDs. Collection of a field blank is completed by removing the lid from the tin can exposing the SPMD to the atmosphere at the same location and for the same duration as the environmental SPMDs. To determine general contamination, one composite field blank was collected during deployment and retrieval at every site in 2010. In 2011, two additional composite blanks were collected; one for deployment and one for retrieval. Also in 2011, two field blanks were collected during deployment and retrieval, one at a high-use site (Bullfrog Marina) and one at a low-use site (Escalante River below 50-Mile Canyon). Finally, two fabrication (day zero) laboratory blanks were processed, one for each year of the study. These blanks consisted of SPMDs manufactured by EST at the same time as the field SPMDs, but they remained at their laboratory during the field deployment period. The fabrication blanks were then processed and analyzed in series with the environmental samples and field blanks.

An upper confidence limit was determined for each compound using the two fabrication and five field blanks; there is a 92-percent chance that contamination is no greater than the highest blank concentration detected for any given compound in at least 70 percent of the samples. For compounds with no detections in the fabrication and the field blanks, there is a 92-percent chance that contamination is no greater than the reporting limit in at least 70 percent of the

10 Polycyclic aromatic hydrocarbons and inorganic elements in water and lakebed materials in Lake Powell, Utah and Arizona

Table 1. Results of field blank analysis for semipermeable membrane devices used on Lake Powell during 2010 and 2011.

[ng, nanograms; <, actual value is known to be less than the value shown; E, estimated value; ND, no detection]

Compound name	Reporting limit (ng/ampule)	Censoring level two times the highest blank concentration (ng/ampule)	2010		
			Lab Blank (ng)	Day zero (ng/ampule)	Field composite (ng/ampule)
1,2,4-Trichlorobenzene	50	ND	ND	ND	ND
1,2-Dimethylnaphthalene	50	30	ND	E14.6	E14.9
1,6-Dimethylnaphthalene	50	99	ND	E46.7	E49.6
1-Methyl-9H-fluorene	50	19	ND	<250	E9.6
1-Methylphenanthrene	50	36	ND	E17.8	E9.1
1-Methylpyrene	50	52	ND	E25.9	E5.9
2,3,6-Trimethylnaphthalene	50	56	ND	E28.0	E26.4
2,6-Dimethylnaphthalene	50	161	ND	E75.9	E80.4
2-Ethyl-naphthalene	50	66	ND	E30.8	E33.2
2-Methylanthracene	50	ND	ND	ND	ND
4,5-Methylenephenanthrene	50	10	ND	E4.8	ND
9H-Fluorene	50	40	ND	E17.4	E20.0
Acenaphthene	50	18	ND	E7.5	E8.9
Acenaphthylene	50	11	ND	ND	E5.5
Anthracene	50	ND	ND	ND	ND
Anthraquinone	50	ND	ND	<250	<250
Benz[a]anthracene	50	ND	ND	<250	<250
Benzo[a]pyrene	50	8	ND	E3.9	ND
Benzo[b]fluoranthene	50	27	ND	E13.5	ND
Benzo[e]pyrene	50	86	ND	E43.1	ND
Benzo[ghi]perylene	50	81	ND	E40.4	ND
Benzo[k]fluoranthene	50	ND	ND	ND	ND
Bis[2-ethylhexyl]phthalate	50	2,180	ND	323	241
Butylbenzyl phthalate	50	250	ND	E125	E118
Carbazole	50	ND	ND	ND	ND
Chrysene	50	33	ND	E16.6	ND
Coronene	50	734	ND	E367	ND
Dibenz[a,h]anthracene	50	ND	ND	<250	ND
Dibenzothiophene	50	25	ND	E12.3	E9.5
Diethyl phthalate	50	1,214	ND	588	607
Dimethyl phthalate	50	71	ND	<250	E4.7
Di-n-butyl phthalate	50	244	ND	<250	<250
Di-n-octyl phthalate	50	ND	ND	<330	<330
Fluoranthene	50	99	ND	E49.4	E26.0
Hexachlorobenzene	50	ND	ND	ND	ND
Indeno[1,2,3-cd]pyrene	50	39	ND	E19.5	ND
Naphthalene	50	316	ND	E158	E107
Pentachloroanisole	50	ND	ND	<250	<250
Pentachloronitrobenzene	50	ND	ND	<250	<250
Perylene	50	ND	ND	ND	ND
Phenanthrene	50	296	ND	E148	E112
Phenanthridine	50	ND	ND	ND	ND
Phenol	50	93	ND	E39.2	E46.6
Pyrene	50	230	ND	E115	E20.3

Table 1. Results of field blank analysis for semipermeable membrane devices used on Lake Powell during 2010 and 2011.—Continued

[ng, nanograms; <, actual value is known to be less than the value shown; E, estimated value; ND, no detection]

Compound name	2011					
	Lab blank (ng)	Day zero (ng/ampule)	Deployment composite (ng/ampule)	Retrieval composite (ng/ampule)	Site ID 373057110442300 (ng/ampule)	Site ID 371938110553700 (ng/ampule)
1,2,4-Trichlorobenzene	ND	ND	ND	ND	ND	ND
1,2-Dimethylnaphthalene	ND	E7.24	ND	ND	ND	ND
1,6-Dimethylnaphthalene	ND	E19.3	E25.6	ND	ND	E19.5
1-Methyl-9H-fluorene	ND	ND	ND	ND	ND	ND
1-Methylphenanthrene	ND	ND	ND	ND	ND	ND
1-Methylpyrene	ND	ND	ND	ND	ND	ND
2,3,6-Trimethylnaphthalene	ND	E14.4	ND	E26.1	ND	E17.5
2,6-Dimethylnaphthalene	ND	E28.0	E45.5	E35.2	ND	E42.4
2-Ethyl-naphthalene	ND	E12.1	E22.3	E19.6	ND	E19.1
2-Methylanthracene	ND	ND	ND	ND	ND	ND
4,5-Methylenephenanthrene	ND	ND	ND	ND	ND	ND
9H-Fluorene	ND	ND	ND	ND	ND	ND
Acenaphthene	ND	ND	ND	ND	ND	ND
Acenaphthylene	ND	ND	ND	ND	ND	ND
Anthracene	ND	ND	ND	ND	ND	ND
Anthraquinone	ND	ND	ND	ND	ND	ND
Benz[a]anthracene	ND	ND	ND	ND	ND	ND
Benzo[a]pyrene	ND	ND	ND	ND	ND	ND
Benzo[b]fluoranthene	ND	ND	ND	ND	ND	ND
Benzo[e]pyrene	ND	ND	ND	ND	ND	ND
Benzo[ghi]perylene	ND	ND	ND	ND	ND	ND
Benzo[k]fluoranthene	ND	ND	ND	ND	ND	ND
Bis[2-ethylhexyl]phthalate	ND	1,090	739	639	219	183
Butylbenzyl phthalate	ND	ND	ND	ND	ND	ND
Carbazole	ND	ND	ND	ND	ND	ND
Chrysene	ND	ND	ND	ND	ND	ND
Coronene	ND	ND	ND	ND	ND	ND
Dibenz[a,h]anthracene	ND	ND	ND	ND	ND	ND
Dibenzothiophene	ND	ND	ND	ND	ND	ND
Diethyl phthalate	ND	345	246	252	E129	219
Dimethyl phthalate	ND	E15.0	ND	E35.6	ND	ND
Di-n-butyl phthalate	ND	122	<100	<80	ND	<55
Di-n-octyl phthalate	ND	ND	ND	ND	ND	ND
Fluoranthene	ND	E20.8	NC	ND	<55	<55
Hexachlorobenzene	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-cd]pyrene	ND	ND	ND	ND	ND	ND
Naphthalene	ND	108	E63.6	E73.1	E41.9	E79.6
Pentachloroanisole	ND	ND	ND	ND	ND	ND
Pentachloronitrobenzene	ND	ND	ND	ND	<60	ND
Perylene	ND	ND	ND	ND	ND	ND
Phenanthrene	ND	59.5	E82.4	103	E103	108
Phenanthridine	ND	ND	ND	ND	ND	ND
Phenol	ND	ND	ND	ND	ND	ND
Pyrene	ND	E12.2	NC	ND	ND	ND

samples. However, contamination is unknown in the remaining 30 percent of the samples. Therefore, based on the objective of this project, it was decided that a critical concentration, below which the environmental data will be censored, should be set at two times the highest blank concentration for each compound (table 1).

All field blank values greater than the reporting limit of 50 ng/ampule corresponded with fabrication (day zero) blank values greater than 50 ng/ampule. There were two fabrication blank values greater than the reporting limit, but they were associated with either a non-detect or a field blank value less than the reporting limit. In general, presence and concentrations of fabrication and field blank values were similar. Values for composite blanks are usually averaged based on the number of sites at which the blank was exposed to the atmosphere. However, blank data was not divided because contamination is thought to have occurred during manufacturing or post processing and not as the result of cumulative exposure from each site.

A comparison sample was collected at the Bullfrog Marina site to characterize variability and evaluate the sampling approach that targeted each stratified layer with an individual SPMD. At each of the three depths at this site, three additional SPMDs were placed next to the environmental SPMDs. The three replicates at each depth were then composited and analyzed to give a vertical depth profile of PAH concentrations. These data were used to evaluate variability related to stratification and subsequent chemical-compound accumulation. In addition, the average for all three depths was compared to the environmental sample. For all compounds found at this site, a vertical stratification of concentrations is apparent (fig. 6).

To evaluate bias associated with recovery and matrix interference, the NWQL analyzed laboratory reagent spikes and surrogate data. A laboratory spike was done each year of the study for all compounds of interest, and a surrogate mixture (nitrobenzene-d₅, 2-fluorobiphenyl, and terphenyl-d₁₄) was added to each environmental and QC sample. Environmental samples have not been adjusted based on spike recoveries. To account for the effects of membrane biofouling, flow-turbulence, and temperature differences on the uptake rates and losses, the PRCs Anthracene-d₁₀, Fluoranthene-d₁₀, and Fluorene-d₁₀ were added to SPMDs during manufacturing. A sample of spiking compound was sent to the NWQL with environmental samples.

Dissolved Inorganic Elements

Three inorganic field blanks were collected to evaluate bias associated with the inorganic environmental data. Aluminum (Al) and calcium (Ca) were the only two elements detected in all three blanks. The values of the blanks (0.007 mg/L) for Ca were more than three orders of magnitude less than the minimum value of all samples (35 mg/L), whereas the blank values for Al (0.28 micrograms per liter,

µg/L) were almost a factor of three less than the minimum value of the samples (0.79 µg/L). Concentrations of this magnitude indicate that contamination was very minimal and inorganic concentrations determined in the environmental samples, including Al and Ca, are considered valid.

Establishment of variability for the dataset was done by examining the field replicate samples collected during the study. Seven samples represent sequential field replicates since they were collected in different containers as close in time as possible to their pairs, and they were filtered, processed and analyzed as completely different samples than their partners.

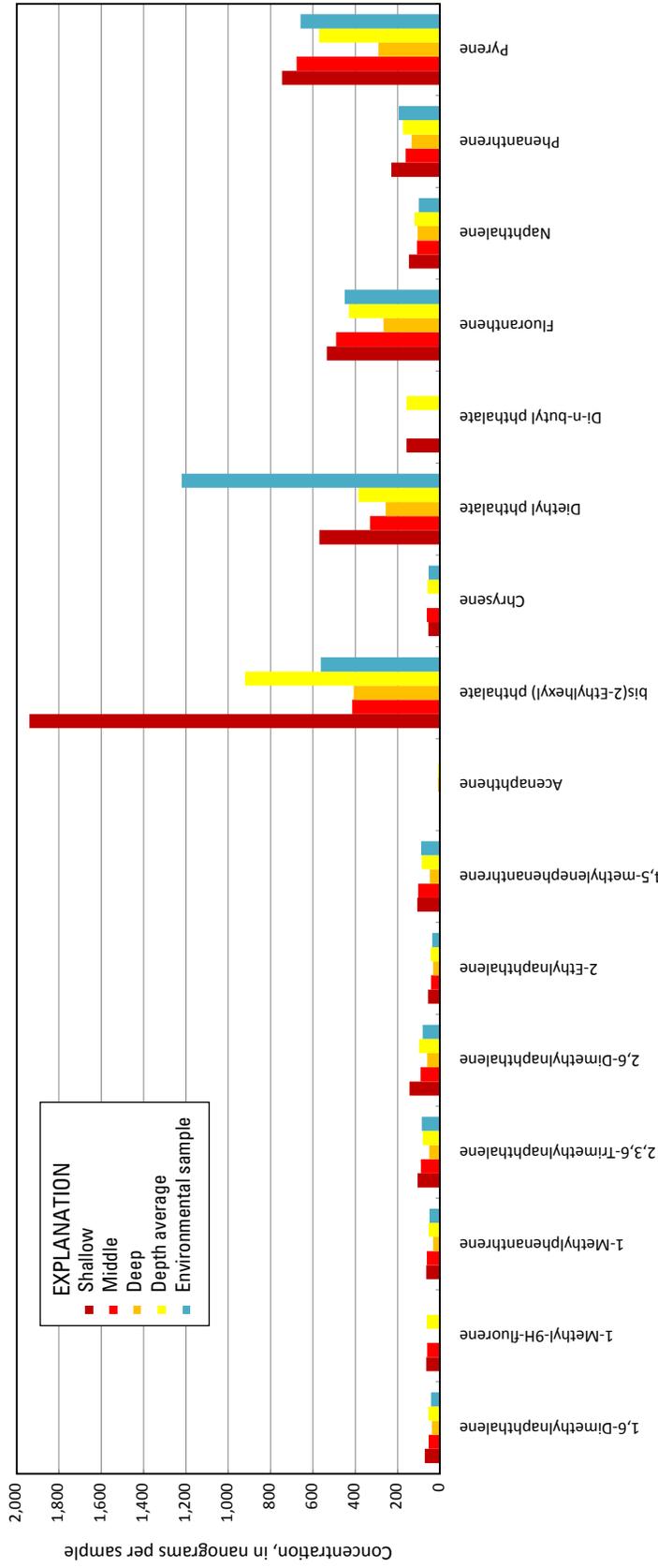
For samples with sufficiently high concentrations (greater than 10 times the detection limit), the measure used to establish variability was the percent relative standard deviation (PRSD). Table 3 shows the median PRSD for those chemical species whose replicate values were greater than 10 times the detection limit. For most inorganic elements, the median value is less than 5 percent, and only cerium (Ce, 6.9 percent), neodymium (Nd, 5.6 percent), and selenium (Se, 5.6 percent) were marginally greater than 5 percent.

For samples with concentrations near the detection limit (but still above it), the PRSD is not an adequate measure. As concentrations approach the detection limit, one would expect the uncertainty in an individual measurement or replicate to approach 100 percent. Thus, the measure used for these chemical species is to compare the standard deviation of the replicate pair against the detection limit as a ratio. Table 4 shows this ratio for the low concentration elements. Only praseodymium (Pr, 4.0), thorium (Th, 3.0), zinc (Zn, 4.0), and zirconium (Zr, 2.7) are substantially above 2.

Polycyclic Aromatic Hydrocarbons in Lakebed Material

Detection limits for lakebed material samples are dependent on the dried weight of the sample aliquots that were selected for analysis and can vary considerably from sample to sample (appendix I). Values of detection limits for PAHs are for the median dried weight of all samples.

Laboratory reagent blanks were analyzed each year of the study (table 5). Only blank values for benzo[a]pyrene, bis[2-ethylhexyl]phthalate, butylbenzylphthalate, diethylphthalate, di-n-butylphthalate, and phenol were above the average method detection levels. Benzo[a]pyrene was only slightly above detection and is 14 times less than the minimum environmental sample. The blank values for compounds bis[2-ethylhexyl]phthalate and butylbenzylphthalate were above the detection limit; however, there were no environmental samples with these compound present. The diethylphthalate blank value was more than six times less than the only environmental sample above the detection limit. di-n-butylphthalate and phenol were above the detection limit but were 1.9 and 2.6 times less than the highest environmental sample, respectively.



Select PAH compounds

Figure 6. Graph comparing environmental samples collected at the Bullfrog Marina on Lake Powell. Individual zones are compared to their combined average and environmental sample. PAH, polycyclic aromatic hydrocarbon.

Table 2. Spike and surrogate recoveries for performance reference compounds (PRCs) added to samplers used on Lake Powell. [NWQL, U.S. Geological Survey National Water Quality Laboratory; %, percent]

Compound name	2010 NWQL spike % recovered	2011 NWQL spike % recovered	Compound name	2010 NWQL spike % recovered	2011 NWQL spike % recovered
1,2,4-Trichlorobenzene	63.81	104.08	Carbazole	67.95	107.04
1,2-Dimethylnaphthalene	63.71	106.69	Chrysene	64.31	112.23
1,6-Dimethylnaphthalene	64.72	109.50	Coronene	80.85	108.18
1-Methyl-9H-fluorene	65.77	111.00	Dibenz[a,h]anthracene	72.02	111.80
1-Methylphenanthrene	64.71	107.77	Dibenzothiophene	66.03	110.66
1-Methylpyrene	65.92	110.83	Diethyl phthalate	68.68	114.76
2,3,6-Trimethylnaphthalene	63.66	110.43	Dimethyl phthalate	64.92	110.33
2,6-Dimethylnaphthalene	64.30	108.44	Di-n-butyl phthalate	65.34	110.11
2-Ethyl-naphthalene	64.87	109.86	Di-n-octyl phthalate	69.71	118.06
2-Methylanthracene	66.68	113.21	Fluoranthene	65.14	110.75
4,5-Methylenephenanthrene	65.53	108.22	Hexachlorobenzene	64.09	111.56
9H-Fluorene	64.68	111.82	Indeno[1,2,3-cd]pyrene	70.19	113.86
Acenaphthene	63.42	107.48	Naphthalene	63.69	106.63
Acenaphthylene	65.92	109.59	Pentachloroanisole	64.50	109.01
Anthracene	66.86	111.41	Pentachloronitrobenzene	69.55	117.71
Anthraquinone	72.10	117.64	Perylene	65.51	112.54
Benz[a]anthracene	65.91	115.12	Phenanthrene	64.36	109.05
Benzo[a]pyrene	68.65	114.48	Phenanthridine	67.98	113.28
Benzo[b]fluoranthene	66.36	111.89	Phenol	68.04	105.4
Benzo[e]pyrene	65.43	113.91	Pyrene	65.44	109.95
Benzo[ghi]perylene	69.23	113.71	2-Fluorobiphenyl (surrogate)	51.89	104.31
Benzo[k]fluoranthene	67.22	115.16	Nitrobenzene-d5 (surrogate)	55.12	99.03
Bis[2-ethylhexyl]phthalate	64.76	117.22	Terphenyl-d14 (surrogate)	52.59	108.57
Butylbenzyl phthalate	66.08	115.61			

A replicate sample was collected in 2011 at the Escalante River below 50-Mile Canyon. No compounds were above the detection limit for the sample and replicate. Four spikes were analyzed to examine matrix interference and analytical performance (table 6). In 2010, a lakebed material sample was sent to the NWQL for a laboratory spike to determine PAH compound recovery in the matrix sampled. This native material was spiked with each of the compounds analyzed in this project. One laboratory reagent spike in 2010 and two in 2011 were completed during analytical runs. The matrix for the laboratory reagent spike is 25 g of Ottawa sand. Surrogate compounds were added to all environmental and laboratory reagent spikes and were used to evaluate analytical method performance. Surrogate standards have similar physiochemical properties to targeted compounds but are not expected to be in the environment (Zaugg and others, 2006). Spike recoveries ranged from a low of 32.8 to a high of 106.9 percent.

Total Inorganic Elements in Lakebed Material

Detection limits for inorganic elements in lakebed material samples are also dependent on the dried weight of the sample aliquots that were selected for digestion and analysis. The values of the detection limits listed in appendix J are for the median dried weight of all samples. For most elements, the digestion blank values were less than the detection limit. Of those that were above the limit, only bismuth (Bi) had a value that was greater than the minimum value of all the samples.

The variability of the lakebed material data is more difficult to assess than that of the dissolved data because lakebed material, by its very nature, consists of many discrete particles. Therefore heterogeneities within the samples can generate imprecision that is not a function of the digestion or analysis of those samples. For this reason, it is appropriate to consider two types of variability for lakebed material data: digestion variability, which includes analytical variability, and field variability.

Table 3. Percent relative standard deviations (PRSD) for Lake Powell field sample replicate, for those chemical species with concentrations greater than 10 times the detection limit.

[Entries that are italicized had a proportion of the replicates with concentrations less than 10 times. Values in the table represent the median value of all replicates; DOC, dissolved organic carbon; element and chemical symbols are explained in the front matter of this report]

Chemical	PRSD	Chemical	PRSD
Al	2.1	<i>Mn</i>	<i>2.2</i>
As	0.4	Mo	0.9
B	1.7	Na	0.5
Ba	0.6	<i>Nd</i>	<i>5.6</i>
Ca	0.5	Rb	0.3
Ce	6.9	S	0.6
Cl	0.8	Se	5.6
Co	4.1	SiO ₂	0.6
Cu	0.5	SO ₄	0.5
DOC	1.0	Sr	0.4
<i>F</i>	<i>4.4</i>	U	0.4
K	0.6	V	0.6
Li	0.4	Y	3.0
Mg	0.5		

Digestion variability is determined by an examination of replicate digestions of reference materials that are generally considered to be homogeneous for most elements. The reference material used for the lakebed material digestions was National Institute of Standards and Technology Reference Material 8704, Buffalo River Sediment (National Institutes of Standards and Technology, 2012). Table 7 contains the certified values for this standard (Rousseuw, 1990) along with the median and median absolute deviation (MAD) and the percent relative MAD (RMAD). Of the elements listed in the table, only molybdenum (Mo), rhenium (Re), sulfur (S), selenium and tellurium (Te) had concentrations less than ten times the detection limit (these are italicized), and excluding these, the RMAD ranged from 1.6 percent (for magnesium, Mg) to 22 percent (for Tin, Sn). Forty five of the 54 elements had RMADs less than 9 percent.

Field variability is measured by comparing the replicate sample digestions to each other. In this study, there were eight replicate pairs, and as with the dissolved data, the RSDs for those elements with concentrations greater than 10 times the detection limit are tabulated (table 8). There were 41 elements whose median concentrations were greater than 10 times the detection limit, and of these, the median RSD was 6.6 percent.

Table 4. Ratios of the median standard deviations between Lake Powell field sample replicates and the detection limit for those chemical species with concentrations between the detection limit and 10 times the detection limit.

[Element and chemical symbols are explained in the front matter of this report. The majority of all concentrations for Cr, P, Sn, and Te were less than the detection limit and were not included. SD_{rep} represents the standard deviation from the recoveries obtained of the replicate analyses; DL, detection limit]

Chemical	SD _{rep} /DL	DL
Be	0.7	0.002
Bi	1.0	0.007
Cd	0.6	0.001
Cs	1.0	0.0008
Dy	2.2	0.0003
Er	1.4	0.0003
Eu	1.8	0.0001
F	0.4	0.02
Fe	0.2	3
Gd	1.2	0.0002
Hg	1.3	0.1
Ho	1.7	0.00004
La	1.9	0.0002
Lu	1.1	0.00005
Ni	0.1	0.5
NO ₃	0.3	0.02
Pb	2.3	0.002
Pr	4.0	0.00008
Sb	0.4	0.07
Sm	0.8	0.0005
Tb	0.6	0.0001
Th	3.0	0.001
Tl	0.2	0.003
Tm	0.6	0.0001
W	0.4	0.003
Yb	1.7	0.00008
Zn	4.0	0.08
Zr	2.7	0.008

Following what was done for the dissolved data, table 9 shows the absolute percentage differences between the median observed (or reported) value of the reference standard and the published value for those elements with concentrations at least 10 times the detection limit. Percentages varied from near zero for cadmium (Cd), manganese (Mn), and Sodium (Na) to near 15 percent for cerium (Ce) and cesium (Cs). The median PRSD value for all elements was 5.3 percent.

Table 5. Results of laboratory reagent blanks for lakebed material from Lake Powell in 2010 and 2011.

[µg/kg, micrograms per kilogram; average method detection limit is equal to 11.9 µg/kg; E, estimated value; <, actual value is known to be less than the value shown]

Compound	2010a blank value (µg/kg)	2010b blank value (µg/kg)	2011a blank value (µg/kg)	2011b blank value (µg/kg)
1,2,4-Trichlorobenzene	<25	<25	<25	<25
1,2-Dimethylnaphthalene	<25	<25	<25	<25
1,6-Dimethylnaphthalene	<25	<25	<25	<25
1-Methyl-9H-fluorene	<25	<25	<25	<25
1-Methylphenanthrene	<25	<25	<25	<25
1-Methylpyrene	E1.27	E1.27	<25	<25
2,3,6-Trimethylnaphthalene	<25	<25	<25	<25
2,6-Dimethylnaphthalene	<25	<25	<25	<25
2-Ethyl-naphthalene	E1.36	E1.36	<25	<25
2-Methylantracene	<25	<25	<25	<25
4,5-methylenepheneanthrene	<25	<25	<25	<25
9H-Fluorene	<25	<25	<25	<25
Acenaphthene	<25	<25	<25	<25
Acenaphthylene	<25	<25	<25	<25
Anthracene	<25	<25	<25	<25
Anthraquinone	E3.63	E3.63	<25	<25
Benz[a]anthracene	E2.69	E2.69	<25	E1.5
Benzo[a]pyrene	E4.50	E4.50	<25	E14.0
Benzo[b]fluoranthene	E4.84	E4.84	<25	<25
Benzo[e]pyrene	E3.84	E3.84	<25	<25
Benzo[ghi]perylene	E6.75	E6.75	<25	<25
Benzo[k]fluoranthene	E3.86	E3.86	<25	<25
Bis[2-ethylhexyl]phthalate	E95.0	E95.0	27.8	39.6
butylbenzylphthalate	28.1	32.5	10.0	36.2
Carbazole	<25	<25	<25	<25
Chrysene	E2.49	E2.49	<25	<25
Coronene	11.8	3.0	<25	<25
Dibenz[a,h]anthracene	E6.59	E6.59	<25	<25
Dibenzothiophene	<25	<25	<25	<25
Diethyl phthalate	E14.1	E14.1	9.1	64.7
Dimethylphthalate	0.64	0.68	<25	<25
Di-n-butylphthalate	<25	15.0	6.52	12.1
Di-n-octylphthalate	7.1	5.7	4.73	<25
Fluoranthene	E6.26	E6.26	<25	<25
Hexachlorobenzene	<25	<25	<25	<25
Indeno[1,2,3-cd]pyrene	E7.06	E7.06	<25	<25
Naphthalene	E2.85	E2.85	4.5	E3.5
Pentachloroanisole	<25	<25	<25	<25
Pentachloronitrobenzene	<25	<25	<25	<25
Perylene	E2.38	E2.38	<25	<25
Phenanthrene	E2.96	E2.96	1.3	<25
Phenanthridine	<25	<25	<25	<25
Phenol	32.6	31.9	37.8	39.7
Pyrene	E4.81	E4.81	<25	<25

Data Results and Observations

Concentrations of Polycyclic Aromatic Hydrocarbons in SPMDs

Only one site (Farley Canyon) had zero compounds detected in the SPMD sample (in ng/ampule). The rest of the sites contained between 2 and 21 PAH compounds from the 44 that were analyzed and were higher than the censoring limit (2 times the highest blank compound). The highest number of compounds that exceeded the censoring limit were found at Lone Rock Beach, Wahweap Marina, Rainbow Bridge National Monument, and Antelope Marina (21, 20, 20, and 19, respectively). The greatest potential for exposure and bioconcentration for the majority of PAH compounds is in the southern part of the lake near high boat traffic areas (fig. 7).

On the other hand, the single highest PAH value detected in the SPMDs was for diethyl phthalate (29,672 ng/L). This sample was reanalyzed after a dilution at the laboratory verifying the original value. This concentration was detected at the Moqui Canyon site, which is located in the upper half of the lake. Diethyl phthalate is used in cosmetics, fragrances, plasticizers, detergent bases, and aerosol sprays and is ubiquitous in the environment. Without this compound included in the sum of concentrations for Moqui Canyon, it would reduce the concentration to one of the lowest sums of any site. Phenol had the second highest concentration above the censoring limit (5,902 ng/L). The highest concentrations of PAHs were also found in the upper part of the water column in Lake Powell, which is consistent with a study conducted on Lake Mead by Rosen and others (2010). All PAH data for raw and converted concentrations are in appendixes E and F.

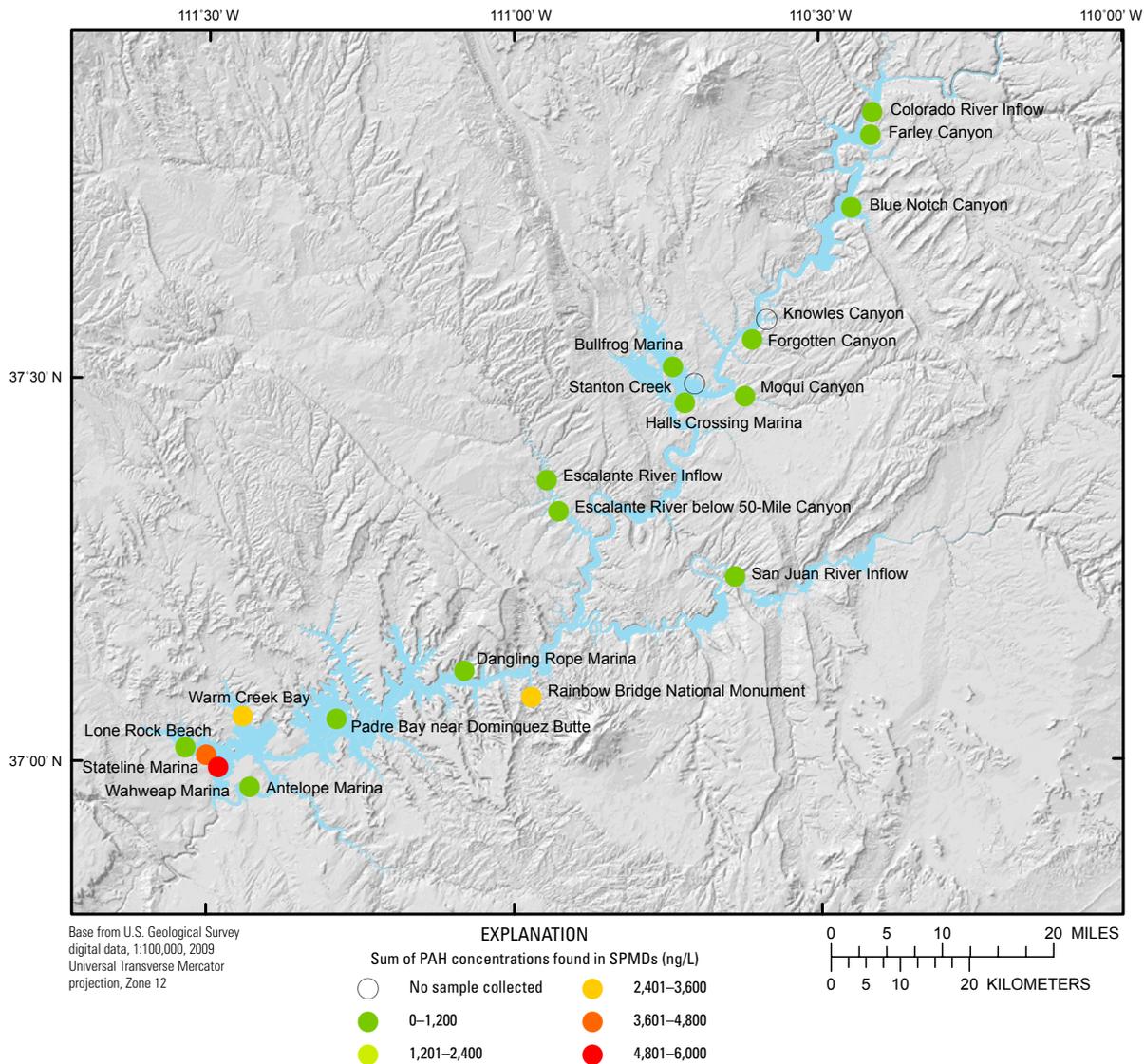


Figure 7. Map showing sum of polycyclic aromatic hydrocarbon (PAH) concentrations found in semipermeable membrane device (SPMD) samples found throughout Lake Powell. ng/L, nanograms per liter.

Table 6. Spike and surrogate recoveries for lakebed material from Lake Powell collected in 2010 and 2011.

[% , percent]

Compound name	2010 lakebed spike % recovered	2010 reagent spike % recovered	2011 lakebed spike % recovered	2011 reagent spike % recovered
1,2,4-Trichlorobenzene	62.8	62.0	75.6	70.4
1,2-Dimethylnaphthalene	76.8	75.2	92.8	77.6
1,6-Dimethylnaphthalene	74.5	69.5	92.5	75.3
1-Methyl-9H-fluorene	92.8	79.8	87.5	93.6
1-Methylphenanthrene	93.0	76.3	87.6	89.4
1-Methylpyrene	97.3	74.9	95.1	93.0
2,3,6-Trimethylnaphthalene	76.5	72.8	91.9	78.0
2,6-Dimethylnaphthalene	73.7	68.7	87.3	76.5
2-Ethyl-naphthalene	75.2	70.1	87.7	77.1
2-Methylantracene	77.5	71.6	98.5	95.4
4,5-Methylenephenanthrene	92.7	78.1	95.9	88.8
9H-Fluorene	91.4	82.3	91.9	95.5
Acenaphthene	87.7	75.1	84.5	91.8
Acenaphthylene	65.5	71.0	81.1	89.5
Anthracene	76.3	72.2	93.9	88.6
Anthraquinone	76.2	71.8	101.9	99.4
Benz[a]anthracene	96.6	71.3	91.6	100.4
Benzo[a]pyrene	86.2	72.1	88.8	88.9
Benzo[b]fluoranthene	119.1	84.3	92.1	87.4
Benzo[e]pyrene	125.1	83.3	100.4	89.0
Benzo[ghi]perylene	104.0	76.5	87.8	83.2
Benzo[k]fluoranthene	119.3	79.6	94.7	87.8
Bis[2-ethylhexyl]phthalate	94.0	78.2	90.8	98.9
Butylbenzyl phthalate	44.8	44.8	67.0	84.5

Dissolved Inorganic Elements

The dissolved inorganic chemistry (appendix H) for water samples can be broken into three sections within the lake—(1) for most elements, the inorganic chemistry of the lake was similar between the upper lake sampling sites (Farley Canyon to Halls Crossing Marina), a distance of about 36 lake miles; (2) between Halls Crossing Marina and the mouth of the Escalante River, a distance of about 31 lake miles, the chemistry varied (depending on the element), and (3) from the mouth of the Escalante River near constant concentrations were found to Glen Canyon Dam, a distance of about 68 lake miles (fig. 8).

Samples taken in consecutive years at the Padre Bay sampling site had similar concentrations for nearly all elements, indicating that the chemistry of the lake during the two sampling years, at least at that site, was constant. Two

tributaries entering the lake, the Escalante, and San Juan Rivers had chemistries for some elements that were different than the main body of lake. The flows of these are small in comparison with the Colorado River, so it is assumed that their effect on the lake chemistry is negligible.

A few elements from the EPA's maximum contaminant levels (MCL) list were found, but are all below the maximum level. Arsenic is a constituent of interest for wildlife and human health. The arsenic concentration was highest at the Escalante River inflow (2.6 µg/L), but decreased in concentration to 1.6 µg/L at the Escalante River below 50-Mile Canyon. Cu concentrations in the surface water ranged from 1.0 to 1.4 µg/L; Hg concentrations ranged from 0.5 to 1.5 ng/L; and Zn concentrations were variable, but always less than 3.5 µg/L; Pb concentrations within the lake were uniformly less than 0.035 µg/L, although there was one anomalously high value from Padre Bay near Dominguez Butte, 0.13 µg/L.

Table 6. Spike and surrogate recoveries for lakebed material from Lake Powell collected in 2010 and 2011.—Continued

[% , percent]

Compound name	2010 lakebed spike % recovered	2010 reagent spike % recovered	2011 lakebed spike % recovered	2011 reagent spike % recovered
Carbazole	87.8	79.7	106.9	95.6
Chrysene	99.6	73.7	89.8	99.5
Coronene	75.9	75.9	87.1	75.5
Dibenz[a,h]anthracene	102.8	76.4	88.7	85.8
Dibenzothiophene	95.4	84.7	92.6	99.6
Diethyl phthalate	77.6	57.0	69.0	91.8
Dimethyl phthalate	32.8	32.8	45.6	59.0
Di-n-butyl phthalate	59.0	59.0	88.5	88.1
Di-n-octyl phthalate	72.6	72.6	87.5	83.9
Fluoranthene	99.5	78.3	101.9	91.7
Hexachlorobenzene	87.6	74.1	80.1	91.8
Indeno[1,2,3-cd]pyrene	97.1	72.4	87.1	84.5
Naphthalene	69.4	69.5	85.2	75.2
Pentachloroanisole	92.5	77.3	86.9	91.8
Pentachloronitrobenzene	67.2	54.3	86.7	85.8
Perylene	88.7	68.8	80.9	80.0
Phenanthrene	90.8	79.4	96.1	92.3
Phenanthridine	87.0	77.2	95.3	88.9
Phenol	76.2	76.2	74.5	64.9
Pyrene	98.3	77.4	97.2	91.8
2-Fluorobiphenyl (surrogate)	68.5	66.1	77.8	71.9
Nitrobenzene-d5 (surrogate)	57.5	61.9	75.3	68.3
Terphenyl-d14 (surrogate)	86.3	74.4	86.8	89.4

Arsenic (As) and tungsten (W) were slightly higher at the Escalante River below 50-Mile Canyon (1.6 µg/L and 0.027 µg/L, respectively) and Rainbow Bridge National Monument (1.4 µg/L and 0.04 µg/L, respectively), Cd at Lone Rock Beach (0.017 µg/L), and lead (Pb) at Antelope Marina (0.035 µg/L). None of these concentrations exceeded the EPA MCL. In addition, Moqui Canyon concentrations were higher than surrounding sites for As, Cd, Se, thallium (Tl), and uranium (U); and Rainbow Bridge National Monument concentrations were higher than other nearby sites for As, boron (B), lithium (Li), Mn, Mo, U, and W.

At most lake sites, the chemistries of dissolved inorganic samples collected at the surface tended vary from their counterparts collected at depth, but compared with the spatial differences between the upper lake and the lower lake, these differences with depth were minor.

Polycyclic Aromatic Hydrocarbons in Lakebed Material

Analysis of lakebed material samples detected PAH compounds at all sampling sites except at Halls Crossing Marina and Forgotten Canyon (appendix I). Twenty-four of 44 PAHs analyzed were detected in lakebed material. Concentrations overall were generally low, but there were a few exceptions. At Rainbow Bridge National Monument, diethyl phthalate was detected at 446 µg/kg. Fluoranthene exhibited the highest concentration of any PAH and was detected at Wahweap Marina with a concentration of 565 µg/kg. Also at the Wahweap Marina site, 23 PAH compounds exceeded the laboratory MDL, with 12 compounds ranging from 109 to 565 µg/kg. This site is shallow compared to most other sites that were sampled, and resuspension of lakebed material and associated PAHs into the water column due to water-level

Table 7. Certified values for National Institute of Standards and Technology Reference Material 8704, Buffalo River Sediment (National Institutes of Standards and Technology, 2012), along with the median value of 11 digestions, the median absolute deviation (MAD, Rousseeuw, 1990) and the percent relative MAD (RMAD).

[Element symbols are explained in the front matter of this report. Italicized entries are elements with concentrations less than 10 times the detection limit. na, not available]

Element	Certified value	Median	MAD	RMAD	Element	Certified value	Median	MAD	RMAD
Al	6.10	5.55	0.31	5.60	Nd	na	27.00	2.00	6.30
As	17.00	15.00	1.00	3.40	Ni	42.90	40.00	2.00	4.60
B	na	102.00	9.00	8.50	P	na	1,033.00	88.00	8.50
Ba	413.00	397.00	8.00	1.90	Pb	150.00	142.00	11.00	7.70
Be	na	1.60	0.00	2.70	Pr	na	6.90	0.40	5.10
Bi	na	0.59	0.10	16.10	Rb	na	93.00	5.00	4.90
Ca	2.64	2.51	0.09	3.50	Re	na	0.00	0.00	31.20
Cd	2.94	2.90	0.20	6.10	S	na	0.43	0.02	4.20
Ce	66.50	56.00	2.00	4.00	Sb	3.07	2.70	0.20	8.00
Co	13.60	12.00	1.00	5.40	Sc	11.30	12.00	1.00	11.00
Cr	122.00	117.00	4.00	3.60	Se	na	1.20	0.30	23.10
Cs	5.83	5.00	0.10	3.00	Sm	na	5.60	0.40	7.60
Cu	na	87.00	7.00	8.10	Sn	na	10.00	2.00	21.80
Dy	na	4.50	0.20	5.50	Sr	na	130.00	5.00	3.60
Er	na	2.50	0.20	6.00	Tb	na	0.77	0.06	7.80
Eu	na	1.10	0.00	3.10	Te	na	0.11	0.02	16.30
Fe	3.97	3.92	0.26	6.60	Th	9.10	8.40	0.50	5.50
Gd	na	4.70	0.30	5.40	Ti	0.46	0.44	0.03	7.50
Ho	na	0.88	0.05	5.90	Tl	na	0.99	0.06	6.50
K	2.00	1.92	0.11	5.50	Tm	na	0.38	0.02	5.10
La	na	27.00	1.00	4.50	U	3.09	2.70	0.10	4.00
Li	na	42.00	3.00	6.20	V	95.00	89.00	5.00	5.70
Lu	na	0.39	0.01	3.10	W	na	1.50	0.20	12.20
Mg	1.20	1.16	0.02	1.60	Y	na	24.00	1.00	4.90
Mn	544.00	543.00	28.00	5.10	Yb	2.80	2.60	0.20	6.70
Mo	na	3.80	0.50	14.40	Zn	408.00	395.00	18.00	4.50
Na	0.55	0.55	0.03	6.30	Zr	na	204.00	40.00	19.70

fluctuation is a concern for aquatic and human health at this site. Perylene was the most prevalent compound detected above the reporting limit in lakebed material and was detected at three sampling sites. Concentrations of perylene ranged from an estimate of 24.0 to 47.9 $\mu\text{g}/\text{kg}$ (fig. 9).

Comparison of PAH results for this study to previous USGS studies on Lake Powell in 2001 to 2002 and 2004 to 2006 show the persistence of some PAH compounds in Lake Powell sediments. A similar study on Lake Mead also showed the presence of PAH compounds in sediments at sites that were sampled (Lico and Johnson, 2007). Nine PAH compounds detected during 2010 and 2011 on Lake Powell were also detected during 2004 to 2006 (Hart and others, 2012), including 2,6-dimethylnaphthalene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[e]pyrene, benzo[ghi]perylene, benzo[k]fluoranthene, fluoranthene, phenanthrene, and pyrene.

Sites sampled during 2004 to 2006 were limited to Bullfrog and Wahweap Marinas, Lonerock Beach, and the San Juan River inflow. Concentrations of those compounds ranged from 10 to 40 $\mu\text{g}/\text{kg}$. During 2001 to 2002 (Hart and others, 2004), only benzyl-n-butyl-phthalate and bis[2-ethylhexyl]phthalate were detected in lakebed material at sites in Knowles, Forgotten, and Moqui Canyons. However, method detection limits were considerably higher (about 5 times) during this study which may account for the few detections that were observed. On Lake Mead, Lico and Johnson (2007), found PAH compounds at every site sampled during 2004 to 2006. Also, highest concentrations were detected at high-use sites including marinas and popular boating areas. They attributed the presence of PAH compounds to motorized watercraft.

The highest sum of all PAHs in lakebed material was found at Wahweap Marina (3,477 $\mu\text{g}/\text{kg}$) and was 5 times

Table 8. Percent relative standard deviations (PRSD) for sample replicate digestions for those chemical species with concentrations greater than 10 times the detection limit.

[Element symbols are explained in the front matter of this report. Entries that are italicized had a proportion of the replicates with concentrations less than 10 times the detection limit. Values in the table represent the median value of all replicates. wt%, weight percent; $\mu\text{g/g}$, micrograms per gram]

Element	Units	PRSD	Element	Units	PRSD
Al	wt%	5.9	Mn	$\mu\text{g/g}$	5.1
As	$\mu\text{g/g}$	2.6	Na	wt%	6.8
B	$\mu\text{g/g}$	10.9	Nd	$\mu\text{g/g}$	8.8
Ba	$\mu\text{g/g}$	5.8	Ni	$\mu\text{g/g}$	7.1
Be	$\mu\text{g/g}$	2.3	Pb	$\mu\text{g/g}$	1.9
Ca	wt%	11.6	Pr	$\mu\text{g/g}$	7.0
Ce	$\mu\text{g/g}$	6.8	Rb	$\mu\text{g/g}$	4.8
Co	$\mu\text{g/g}$	5.8	Sm	$\mu\text{g/g}$	10.0
Cs	$\mu\text{g/g}$	8.8	Sr	$\mu\text{g/g}$	4.4
Cu	$\mu\text{g/g}$	5.2	Tb	$\mu\text{g/g}$	8.3
Dy	$\mu\text{g/g}$	8.7	Th	$\mu\text{g/g}$	3.7
Er	$\mu\text{g/g}$	10.8	Ti	wt%	6.0
Eu	$\mu\text{g/g}$	6.6	Tl	$\mu\text{g/g}$	3.7
Fe	wt%	6.5	Tm	$\mu\text{g/g}$	11.8
Gd	$\mu\text{g/g}$	6.4	U	$\mu\text{g/g}$	10.4
Ho	$\mu\text{g/g}$	9.5	W	$\mu\text{g/g}$	6.7
K	wt%	4.9	Y	$\mu\text{g/g}$	8.9
La	$\mu\text{g/g}$	6.2	Yb	$\mu\text{g/g}$	8.9
Li	$\mu\text{g/g}$	3.9	Zn	$\mu\text{g/g}$	5.2
Lu	$\mu\text{g/g}$	11.9	Zr	$\mu\text{g/g}$	7.2
Mg	wt%	4.8			

higher than the next highest site. This site is fairly shallow, and resuspension of PAHs from bed material into the water column due to water-level fluctuation could increase the risk of exposure to aquatic organisms and potentially humans.

Total Inorganic Elements in Lakebed Material

The inorganic chemistry of lakebed material showed several consistent features across nearly all inorganic elements (appendix J). The three major tributaries to Lake Powell—the Colorado, Escalante, and San Juan Rivers—all showed elevated concentrations of inorganic elements in their deltas for virtually all of elements. Of the three, the San Juan River site, the concentrations tended to be higher than the Escalante River sites, which in turn was almost always higher than the Colorado River. For example, cobalt (Co) concentration in the San Juan River lakebed material was 12.3 $\mu\text{g/g}$, in the Escalante lakebed material, the concentration was 9.7 $\mu\text{g/g}$,

Table 9. Absolute percentage difference between the published values and the median observed (reported) values for the sediment reference standard for those elements whose concentrations were at least 10 times the detection limit in Lake Powell.

[Element symbols are explained in the front matter of this report. %, percent]

Element	Certified value	Median	Median absolute % difference
Al	6.10	5.55	9.00
As	17.00	15.0	10.6
Ba	413	397	4.00
Ca	2.64	2.51	4.80
Cd	2.94	2.90	0.70
Ce	66.50	56.0	15.5
Co	13.60	12.0	9.50
Cr	122.00	117	4.40
Cs	5.83	5.00	14.4
Fe	3.97	3.92	1.30
K	2.00	1.92	4.20
Mg	1.20	1.16	3.60
Mn	544	543	0.20
Na	0.55	0.55	0.10
Ni	42.90	40.0	7.70
Pb	150	142	5.10
Sb	3.07	2.70	11.7
Sc	11.30	12.0	8.00
Th	9.10	8.40	7.30
Ti	0.46	0.44	3.10
U	3.09	2.70	12.6
V	95.0	89.0	5.50
Yb	2.80	2.60	8.60
Zn	408	395	3.20

and in the Colorado River site, the concentration was 6.1 $\mu\text{g/g}$; compared to the median value of the lakebed material, which was 2.0 $\mu\text{g/g}$ (fig. 10).

Although these three tributaries had elevated concentrations of inorganic elements, there were four lake sites which consistently had concentrations for most elements that equaled or exceeded those of the tributaries. Two of these sites were nearest the Colorado River (Farley Canyon and Blue Notch Canyon), the Escalante River below 50-Mile Canyon, and at Antelope Marina. For Farley Canyon and Blue Notch Canyon, it is possible the high concentrations originate from the Colorado River. The higher concentrations found at the Escalante River below 50-Mile Canyon could originate from the mainstem Colorado River, or from the Escalante River inflows. The high concentrations at Antelope Marina could be due in part to the small sediment particle size in combination with its significant depth which inhibits resuspension. None

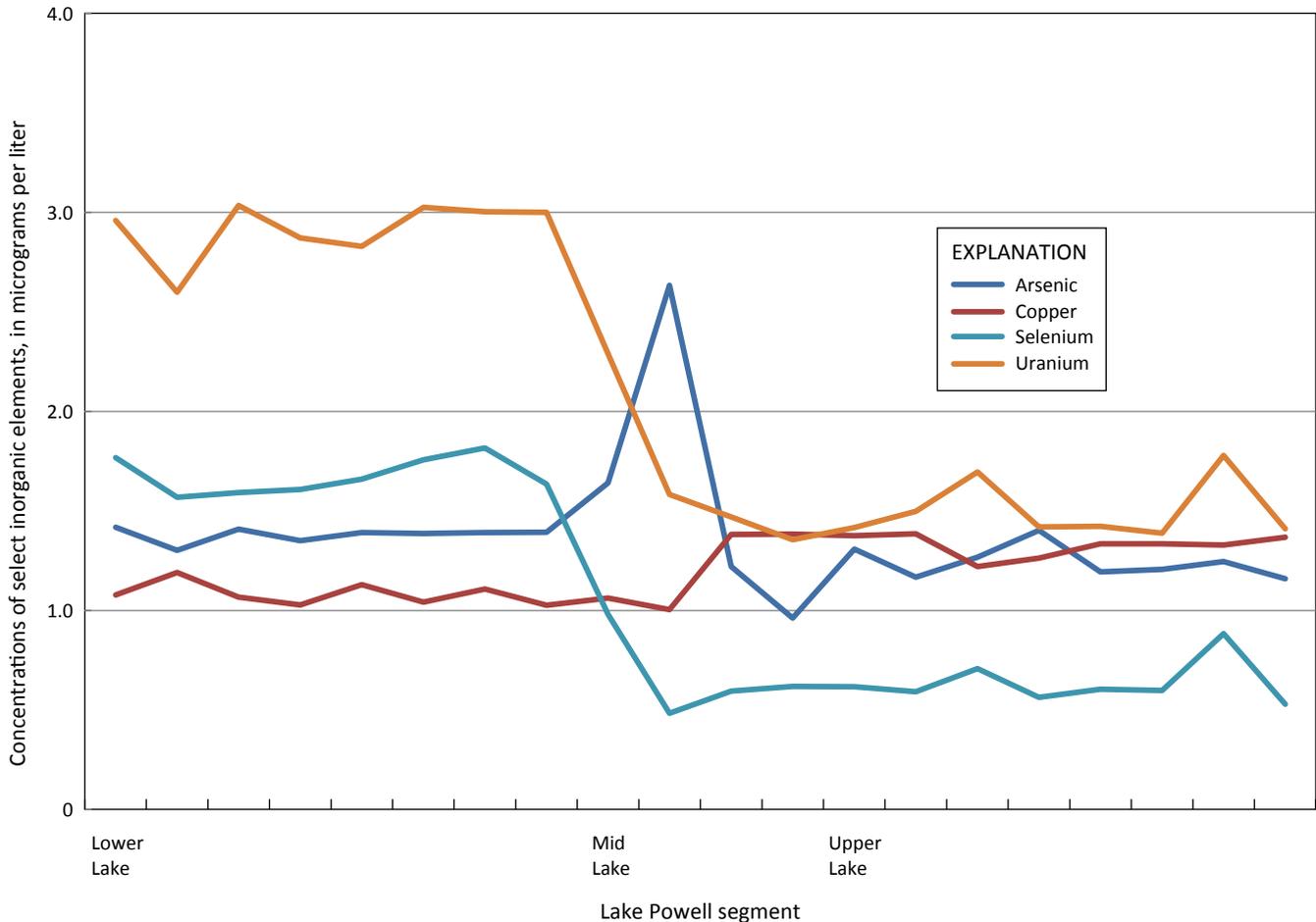


Figure 8. Graph showing average concentrations of select inorganic elements from lower to upper Lake Powell.

of the lakebed material samples from any of the other marinas showed elevated concentrations for any of the environmentally relevant inorganic elements (those that impair the health of biota; such as arsenic, lead, and mercury); this is also true of Rainbow Bridge National Monument, Lone Rock Beach, Warm Creek Bay, and Stanton Creek, the highest use nonmarina sites that were sampled.

Sediment Size of Lakebed Material

The affinity of contaminants to sorb to sediment is a function of the surface area and electrical charge. Clay particles have the highest surface area, and therefore it can be assumed that the highest concentration of contaminants will be found at sites with the highest percentage of clay. The four sites mentioned previously (Farley Canyon, Blue Notch Canyon, Escalante River below 50-Mile Canyon, and Antelope Marina) all have the highest percentage of clay particles (an average of 71 percent of the particles are less than 0.004 mm (coarse clay; appendix K)). In contrast, the average for the other sites is about 13 percent. Overall the highest sediment-class percentage found at all sites was for the 0.063–0.125-mm size class, coarse silt to fine sand (26.4 percent).

Considerations for Future Monitoring

Even though concentrations of PAH compounds found on Lake Powell in this study are generally low, continued monitoring will be needed to determine if concentrations remain low or increase. Information gathered could be used to determine if management actions concerning PWC have reduced PAHs. On the basis of findings from this study and previous USGS studies, a routinely scheduled monitoring approach could be strategically planned to focus on areas of greater concern (marinas and other areas that experience high visitation) and where high concentrations of select organic compounds and inorganic elements have been detected. Results of the SPMD method for evaluating the potential for bioconcentration suggests that this method would be useful in future monitoring. SPMD comparison samples from this study suggest that future studies might deploy SPMDs at different depths and analyze them based on the stratification of the lake to capture the vertical distribution of hydrocarbon compounds. New methods for determining bioconcentration also could be evaluated and used in concert with the SPMDs. To assess whether organic compounds are found in carbon-rich sediments organic carbon analysis should be included. Other

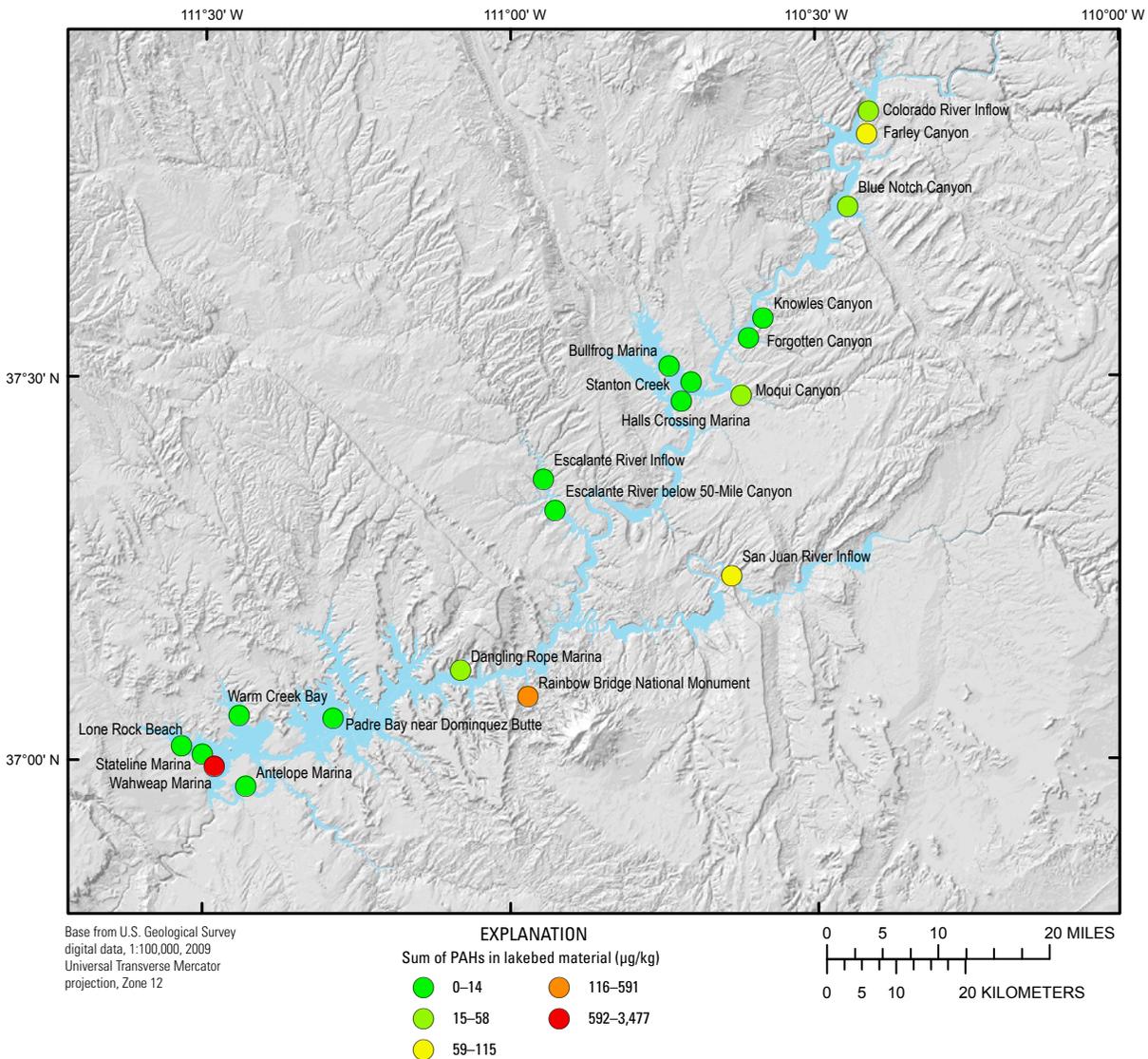


Figure 9. Map showing sum of polycyclic aromatic hydrocarbon (PAH compounds) in lakebed material found in Lake Powell. µg/kg, micrograms per kilogram.

contaminants associated with anthropogenic activities, including contaminants of emerging concern (pharmaceuticals and chemicals in personal hygiene products) might be considered in future monitoring.

Summary

In response to the National Park Service’s requirement to monitor contaminants in Lake Powell, the U.S. Geological Survey collected water and lakebed material samples during the annual high-visitation periods of 2010 and 2011 for analysis of polycyclic aromatic hydrocarbons and inorganic elements. Semipermeable membrane devices (SPMDs) were deployed at established sites to assess the potential for bioconcentration of polycyclic aromatic hydrocarbons.

Depth-profile measurements of physical and chemical water properties were made at each site. Information from these profiles was used to identify depths for placement of SPMDs and collection of water samples for inorganic elements. During the deployment of SPMDs and the collection of water samples, lakebed material samples were also collected. These lakebed material samples were analyzed for PAH compounds, inorganic elements, and particle-size distribution.

Results from this study indicate that PAH exposure may be greatest in the southern part of the lake. The highest concentrations and largest number of compounds in SPMDs were found near marinas and recreation destinations (high-use visitation). Although the value for diethyl phthalate found in Moqui Canyon was verified, it does not coincide with the concurrent lakebed material sample or with results from a previous study (Hart and others, 2004) and is considered suspect.

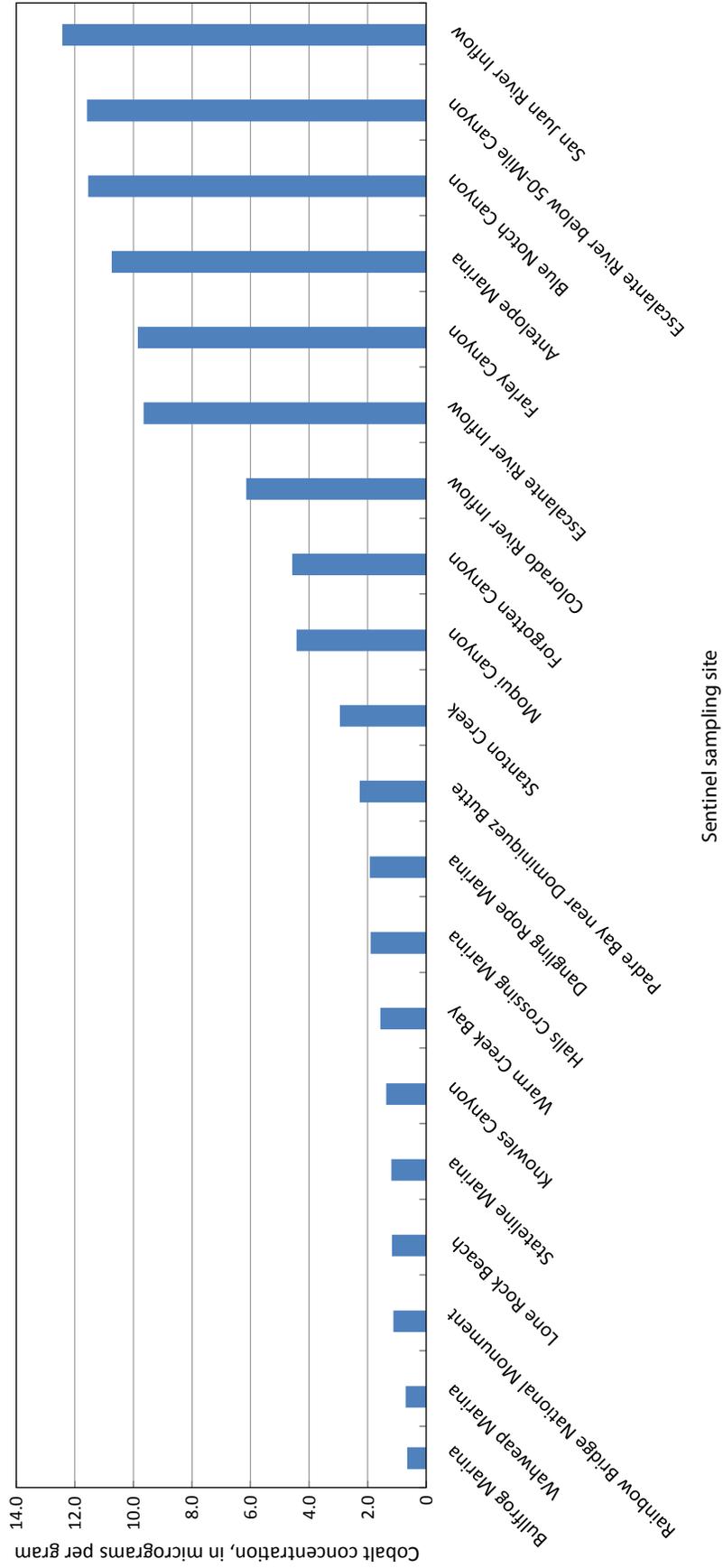


Figure 10. Graph showing average concentrations of cobalt (Co) found in lakebed material samples from Lake Powell.

Concentrations of dissolved inorganic constituents within the lake tended to follow consistent features most likely related to natural processes and dominated by the inputs from the Colorado River and other major tributaries. However, there were two sites which tended to show high dissolved concentrations for various elements relative to neighboring sites, Moqui Canyon and Rainbow Bridge National Monument. In addition, Lone Rock Beach, the Escalante River below 50-Mile Canyon and Antelope Marina showed high concentrations for particular environmentally relevant elements. None of the values observed in this study approached the U.S. Environmental Protection Agency's maximum contaminant level drinking water standards.

PAH concentrations in lakebed material were generally low and differed from SPMD samples by having fewer compounds detected at each site. The site with the highest combined concentration for all compounds was found at Wahweap Marina in the southern part of the lake.

Lakebed material concentrations of inorganic elements were high (relative to median lakebed material values) for seven sites—the inflows of the Colorado, Escalante and San Juan Rivers, Farley Canyon, Blue Notch Canyon, the Escalante River below 50-Mile Canyon, and Antelope Marina. None of the other marinas or high-use sites showed high concentrations for any environmentally relevant inorganic-elements.

Acknowledgments

The authors would like to thank Mark Anderson, Carolyn Hackbarth, and Dave Goodman from the NPS-GLCA for their navigational support, hard work, and precision boat handling. We are also thankful to Howard Taylor, and Dave Roth from the USGS National Research Program for their expertise in the field and laboratory. Appreciation is extended to Greg Fisk, Nancy Hornewer, and Chris Smith from the USGS. The authors are also thankful to our volunteers Kendra Hart and Austin Smith for their energy and strong work ethic.

References Cited

- Agency for Toxic Substances and Disease Registry, 1995, Toxicological profile for polycyclic aromatic hydrocarbons (PAHs), Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service, p. 6-244.
- Albers, P.H., 2003, Petroleum and individual polycyclic aromatic hydrocarbons, in Hoffman, D.J., Rattner, B.A., Burton, G.A., Jr., and Cairns, J., Jr., eds., *Handbook of ecotoxicology*—Second edition: CRC Press, Boca Raton, Fla., p. 341–371.
- Alvarez, D.A., 2010, Guidelines for the use of the semipermeable membrane device (SPMD) and the polar organic chemical integrative sampler (POCIS) in environmental monitoring studies: U.S. Geological Survey, Techniques and Methods 1-D4, 28 p.
- Asplund, T., 2000, The effects of motorized watercraft on aquatic ecosystems: Wisconsin Department of Natural Resources, PUBL-SS-948-00, 5 p.
- Brinton, T.I., Antweiler, R.C., and Taylor, H.E., 1996, Method for the determination of dissolved chloride, nitrate and sulfate in natural water using ion chromatography: U.S. Geological Survey Open-File Report 95–426A, 16 p.
- Bureau of Reclamation, 1970, Glen Canyon dam and powerplant, technical record of design and construction—A water resources technical publication: Bureau of Reclamation, 658 p.
- Bureau of Reclamation, 2006, Upper Colorado River Region—Lake Powell: Bureau of Reclamation Web site, accessed March 6, 2012, at <http://www.usbr.gov/uc/crsp/charts/displaysites.jsp>.
- Bureau of Reclamation, 2008, Upper Colorado River Region—Lake Powell: Bureau of Reclamation Web site, accessed July 8, 2012, at <http://www.usbr.gov/uc/rm/crsp/gc/lakepowell.html>.
- Bureau of Reclamation, 2012, Upper Colorado Reservoir Operations—Lake Powell [data from January 2010 through December 2011]: Bureau of Reclamation Web site, accessed March 6, 2012, at <http://www.usbr.gov/uc/crsp/GetSiteInfo>.
- Eisler, R., 1987, Polycyclic aromatic hydrocarbon hazards to fish, wildlife, and invertebrates—A synoptic review: U.S. Fish and Wildlife Service Biological Report 85(1.11), 4 p.
- Furlong, E.T., Vaught, D.G., Merten, L.M., Foreman, W.T., and Gates, P.M., 1996, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of semivolatile organic compounds in bottom sediment by solvent extraction, gel permeation chromatographic fractionation, and capillary-column gas chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 95–719, 67 p.
- Garbarino, J.R., and Taylor, H.E., 1994, Inductively coupled plasma-mass spectrometric method for the determination of dissolved trace elements in water: U.S. Geological Survey Open-File Report 94–358, 92 p.
- Guy, H.P., 1969, Laboratory theory and methods for sediment analysis: U.S. Geological Survey, Techniques of Water-Resources Investigations, book 5, chapter C1, 58 p.

- Hart, R.J., and Sherman, K.M., 1996, Physical and chemical characteristics of Lake Powell at the forebay of Glen Canyon dam, Northeastern Arizona, 1990–91: U.S. Geological Survey Water-Resources Investigations Report 96-4016, 78 p.
- Hart, R.J., Taylor, H.E., Antweiler, R.C., Graham, D.D., Fisk, G.G., Riggins, S.G., and Flynn, M.E., 2005, Sediment chemistry of the Colorado River delta of Lake Powell, Utah, 2001: U.S. Geological Survey Open-File Report 2005–1178, 33 p., available at <http://pubs.usgs.gov/of/2005/1178/>.
- Hart, R.J., Taylor, H.E., Antweiler, R.C., Fisk, G.G., Anderson, G.M., Roth, D.A., Flynn, M.E., Peart, D.B., Truini, M., and Barber, L.B., 2005, Physical and chemical characteristics of Knowles, Forgotten, and Moqui Canyons, and effects of recreational use on water quality, Lake Powell, Arizona and Utah: U.S. Geological Survey Scientific Investigations Report 2004–5120, 43 p., available at <http://pubs.usgs.gov/sir/2004/5120/>.
- Hart, R.J., Taylor, H.E., and Anderson, G.M., 2012, Establishment of sentinel sampling sites to monitor changes in water and sediment quality and biota related to visitor use at Lake Powell, Arizona and Utah, 2004–2006: U.S. Geological Survey Open-File Report 2012–1237, 25 p., available at <http://pubs.usgs.gov/of/2012/1237/>.
- Huckins, J.N., Petty, J.D., and Booij, K., 2006, Monitors of organic chemicals in the environment—semipermeable membrane devices: Springer, New York, 223 p.
- Lico, M.S., and Johnson, B.T., 2007, Gasoline-related compounds in Lakes Mead and Mohave, Nevada, 2004–06: U.S. Geological Survey Scientific Investigations Report 2007–5144, 28 p., available at <http://pubs.usgs.gov/sir/2007/5144/>.
- Mahler, B.J., Van Metre, P.C., Bashara, T.J., Wilson, J.T., and Johns, D.A., 2005, Parking lot sealcoat—An unrecognized source of urban PAHs: *Environmental Science and Technology*, v. 39, no. 15, p. 5560–5566.
- Marzolf, G.R., Hart, R.J., and Stephens, D.W., 1998, Depth profiles of temperature, specific conductance, and oxygen concentration in Lake Powell, Arizona-Utah, 1992–95: U.S. Geological Survey Open-File Report 97–835, 119 p.
- Matthes, W.J., Sholar, C.J., and George, J.R., 1992, Quality-assurance plan for the analysis of fluvial sediment by laboratories of the U.S. Geological Survey: U.S. Geological Survey Open-File Report 91–467, 31 p.
- Mitko, K., and Bebek, M., 1999, ICP-OES determination of trace elements in salinated water: *Atomic Spectroscopy*, v. 20, p. 217–223.
- National Institutes of Standards and Technology, 2012, Report of Investigation, reference material 8704, Buffalo River sediment: National Institutes of Standards and Technology, accessed June 13, 2012, at <https://www-s.nist.gov/srmors/reports/8704.pdf?CFID=2111649&CFTOKEN=a40f235ae02c9261-E72D8616-FEB3-CDCC-B94F284367A2A111&jsessionid=f030697366de4b9a90e26c1e61301e16225e>.
- National Park Service, 2003, Environmental impact statement, personal watercraft rulemaking, final: National Park Service, Glen Canyon National Recreation Area, Page, Ariz., May 2003, v. 1–2.
- National Park Service, 2013, National Park Service visitor use statistics: National Park Service Web site, accessed July 18, 2013, at <https://irma.nps.gov/Stats/Reports/Park>.
- Petty, J.D., Jones, S.B., Huckins, J.N., Cranor, W.L., Parris, J.T., McTague, T.B., and Boyle, T.P., 2000, An approach for assessment of water quality using semipermeable membrane devices (SPMDs) and bioindicator tests: *Chemosphere*, v. 41, p. 311–321.
- Potter, L.D., and Drake, C.L., 1989, Lake Powell—Virgin flow to dynamo: University of New Mexico Press, 328 p.
- Rosen, M.R., Alvarez, D.A., Goodbred, S.L., Leiker, T.J., and Patino, R., 2010, Sources and distribution of organic compounds using passive samplers in Lake Mead National Recreation Area, Nevada and Arizona, and their implications for potential effects on aquatic biota: *Journal of Environmental Quality*, v. 39, p. 1161–1172.
- Roth, D.A., Taylor, H.E., Domalgalski, J., Dileanis, P., Peart, D.B., Antweiler, R.C., and Alpers, C.N., 2001, Distribution of inorganic mercury in Sacramento River water and suspended colloidal sediment material: *Archives of Environmental Contamination and Toxicology*, v. 40, p. 161–172.
- Rousseeuw, P.J., 1990, Robust estimation and identifying outliers, in Wadsworth, H.M., ed., *Handbook of statistical methods for engineers and scientists*, p. 16.1–16.24.
- Spacie, A., Landrum, P.F., Leversee, G.J., 1983, Uptake, depuration and biotransformation of anthracene and benzo(a)pyrene in Bluegill Sunfish: *Ecotoxicology and Environmental Safety*, v. 7, p. 330–341.
- Sun, Y., Yu, H., Zhang, J., Yin, Y., Shi, H., Wang, X., 2006, Bioaccumulation, depuration and oxidative stress in fish *Carassius auratus* under phenanthrene exposure: *Chemosphere*, v. 63, p. 1319–1327.
- Tuvikene, A., 1995, Responses of fish to polycyclic aromatic hydrocarbons PAHs: *Annales Zoologici Fennici*, v. 35, p. 295–309.

- U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, available at <http://pubs.water.usgs.gov/twri9A>.
- Vernieu, W.S., 2009, Physical and chemical data for water in Lake Powell and from Glen Canyon dam releases, Utah-Arizona, 1964–2008: U.S. Geological Survey Data Series 471, 23 p., available at <http://pubs.usgs.gov/ds/471/>.
- Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., 1987, Methods for the determination of organic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A3, 80 p.
- Zaugg, S.D., Burkhardt, M.R., Burbank, T.L., Olson, M.C., Iverson, J.L., and Schroeder, M.P., 2006, Determination of semivolatile organic compounds and polycyclic aromatic hydrocarbons in solids by gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, chap. B3, 44 p.

Menlo Park Publishing Service Center, California
Manuscript approved for publication December 20, 2013
Edited by James W. Hendley II
Layout and design by Ronald S. Spencer

