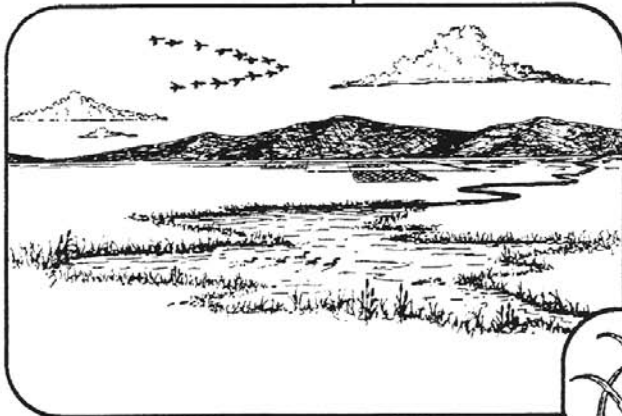
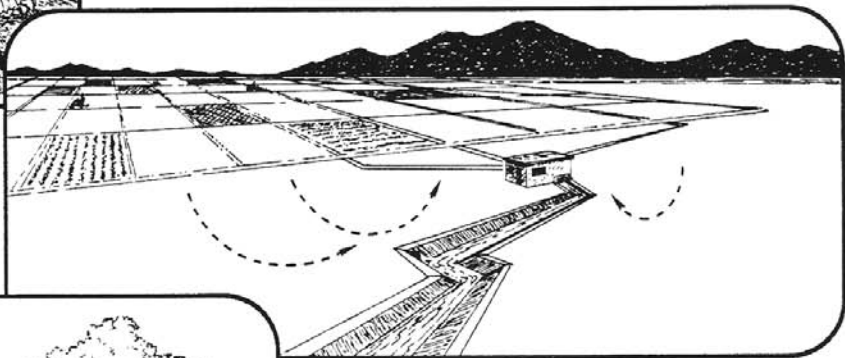
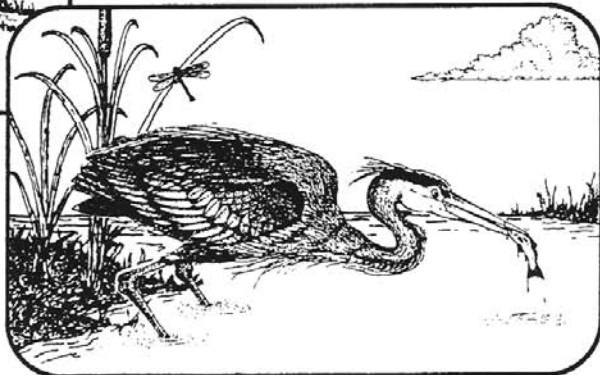




Irrigation-Induced Contamination of Water, Sediment, and Biota in the Western United States—Synthesis of Data from the National Irrigation Water Quality Program



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Irrigation-Induced Contamination of Water, Sediment, and Biota in the Western United States— Synthesis of Data from the National Irrigation Water Quality Program

By RALPH L. SEILER, JOSEPH P. SKORUPA, DAVID L. NAFTZ, *and* B. THOMAS NOLAN

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CONVERSION FACTORS, VERTICAL DATUM, AND WATER-QUALITY UNITS

Multiply	By	To obtain
acre	4,047	square meter
bar	100	kilopascal
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second
foot (ft)	0.3048	meter
inch (in.)	25.40	millimeter
inch per year (in/yr)	25.40	millimeter per year
mile (mi)	1.609	kilometer
pint	0.4732	liter
pound per day (lb/d)	0.4536	kilogram per day
square mile (mi ²)	2.590	square kilometer

Abbreviated water-quality units used in this report:

mg/L, milligram per liter
 µg/L, microgram per liter
 ng/L, nanogram per liter
 pg/L, picograms per liter

Additional abbreviated units used in this report:

µg/g, microgram per gram
 µm, micrometer
 mm, millimeter
 µg/kg, microgram per kilogram
 mg/kg, milligram per kilogram
 EC_x, Concentration that has an effect on x percent of the organisms tested. The EC₅₀, is the concentration that affects 50 percent of the organisms tested.

Unless otherwise noted, all trace-element concentrations in biological samples are in dry weight. Dry-weight and wet-weight concentrations in biological tissue can be converted from one to the other by using these equations:

$$\text{Dry-weight concentration} = (\text{wet-weight concentration}) / [1 - (\text{percent moisture}/100)]$$

$$\text{Wet-weight concentration} = (\text{dry-weight concentration}) \times [1 - (\text{percent moisture}/100)]$$

Sea level: In this report, "sea level" refers to the National Geodetic vertical Datum of 1929 (NGVD of 1929, formerly called Sea-Level Datum of 1929), which is derived from a general adjustment of the first-order leveling networks of the United States and Canada.

Irrigation-Induced Contamination of Water, Sediment, and Biota in the Western United States—Synthesis of Data from the National Irrigation Water Quality Program

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ABSTRACT

In October 1985 the U.S. Department of the Interior (DOI), through the National Irrigation Water Quality Program (NIWQP), began a series of field investigations at 26 areas in the Western United States to determine whether irrigation drainage has had harmful effects on fish, wildlife, and humans or has reduced beneficial uses of water. In 1992 NIWQP initiated the Data Synthesis Project to evaluate data collected during the field investigations. Geologic, climatologic, and hydrologic data were evaluated and water, sediment, and biota from the 26 areas were analyzed to identify commonalities and dominant factors that result in irrigation-induced contamination of water and biota.

Data collected for the 26 area investigations have been compiled and merged into a common data base. The structure of the data base is designed to enable assessment of relations between contaminant concentrations in water, sediment, and biota. The data base is available to the scientific community through the World Wide Web at URL <<http://www.usbr.gov/niwqp>>. Analysis of the data base for the Data Synthesis included use of summary statistics, factor analysis, and logistic regression. A Geographic Information System was used to store and analyze spatially oriented digital data such as land use, geology and evaporation rates.

In the U.S. Department of the Interior (DOI) study areas, samples of water, bottom sediment, and biota were collected for trace-element and pesticide analysis. Contaminants most commonly associated with irrigation drainage were identified by comparing concentrations in water with established criteria. For surface water, the criteria used were typically chronic criteria for the protection of freshwater aquatic life. Because ground water can discharge to the surface where wildlife can be exposed to it, the criteria used for ground water were both the maximum contaminant levels (MCL's) for drinking water and the chronic criteria for the protection of freshwater aquatic life.

Data collected by the NIWQP studies indicated that, in surface water, filtered and unfiltered samples had nearly the same concentrations of arsenic, boron, molybdenum, and selenium for concentrations greater than about 10 micrograms per liter. Therefore, in this concentration range, filtered concentrations can be directly compared to biological-effect levels developed for unfiltered samples. In the range of 1 to 10 micrograms per liter there may be a tendency for unfiltered arsenic concentrations to be greater than filtered concentrations. For selenium, however, the data suggest differences from equality in that range result from analytical imprecision and not a general tendency for unfiltered concentrations to be greater than filtered concentrations. This relation may not be true in lentic, nutrient-rich waters because in such settings algae can bioaccumulate large amounts of selenium and other trace elements.

Selenium was the trace element in surface water that most commonly exceeded chronic criteria for the protection of freshwater aquatic life; more than 40 percent of the selenium concentrations in surface-water samples exceeded the U.S. Environmental Protection Agency (USEPA) aquatic-life chronic criterion (5 micrograms per liter). In 12 of the 26 areas at least 25 percent of the surface water-samples had selenium concentrations that either equaled or exceeded the chronic criterion (5 micrograms per liter). More than 28 percent of boron concentrations and almost 17 percent of the molybdenum concentrations exceeded the aquatic life criteria established by the State of California (550 and

19 micrograms per liter, respectively). In ground water, more than 22 percent of the arsenic concentrations and more than 35 percent of the selenium concentrations exceeded the MCL (10 and 50 micrograms per liter, respectively). Few samples of uranium in surface water exceeded a criterion for the protection of aquatic life (300 micrograms per liter), but 44 percent of the uranium concentrations in ground water exceeded the MCL (30 micrograms per liter). Molybdenum, selenium and uranium were the trace elements most commonly found in bottom-sediment samples that exceeded the upper limit of the 95th percentile expected range in soils of the Western United States. Selenium is the only trace element for which ecological sediment guidelines are used in this report. Selenium concentrations commonly exceeded the ecological sediment guideline of two micrograms per gram.

DDT and its degradation products DDD and DDE were the most common pesticide residues found in surface water at concentrations exceeding criteria. However, almost all the samples exceeding the criteria were from a single study area, the Owyhee–Vale Reclamation Project areas in Oregon and Idaho. The organochlorine pesticide chlordane was detected in 30 percent of the bottom-sediment samples, and undegraded DDT was detected in 21 percent. DDT or its degradation products were detected in all 21 study areas where bottom-sediment samples were analyzed for organochlorine pesticides.

A principal-components analysis indicated that elevated selenium concentrations in surface water are not associated with elevated boron, molybdenum, or arsenic concentrations. The occurrence of selenium is associated with sulfate and uranium. The association of boron and molybdenum with chloride suggests that evaporative processes control their concentrations. Arsenic is not associated with any other measured trace element and is associated negatively with selenium.

This report focuses on selenium because it was the trace element most frequently found at concentrations exceeding criteria for the protection of aquatic life. Selenium concentrations in water are dynamic, and, at a given site, the selenium concentration can change by an order of magnitude during a year and from one year to another. In some areas, selenium contamination may not occur during normal or wet periods. However, during a drought, reduced water deliveries may result in selenium contamination by evaporative concentration.

Marine sedimentary rocks, especially those of Late Cretaceous age, are likely to be seleniferous. Irrigation of soils derived from them can contribute large amounts of selenium to drainwater; shallow wells in and near irrigated areas contained hundreds to thousands of micrograms per liter of selenium. The median selenium concentration in surface-water samples from NIWQP sites associated with Upper Cretaceous marine sedimentary rocks is 7 micrograms per liter (range less than 1 to 8,300 micrograms per liter) and from sites not associated with such rocks is 0.4 micrograms per liter (range less than 1 to 390 micrograms per liter).

Irrigation-induced selenium contamination has been observed only in arid or semiarid areas. In those NIWQP study areas having local geologic sources of selenium, typically more than 25 percent of the surface-water samples exceed the chronic criterion for selenium if the evaporation rate is 3.0 times greater than the annual precipitation.

In terminal water bodies, selenium accumulates and is not flushed out. In both terminal and flow-through lakes and ponds, the median selenium concentrations in surface water for samples collected from June through August are nearly the same (1.0 and 0.8 micrograms per liter, respectively). However, the 75th-percentile selenium concentration for terminal water bodies (24 µg/L) is significantly higher than for flow-through systems (4 µg/L).

Selenium concentrations in biota were compared with concentrations that have been demonstrated to have adverse effects on similar species (the effect level) or to have adverse effects on another species if consumed (the dietary effect level). Twenty-five percent of the plant samples had selenium concentrations exceeding the dietary effect level (3 micrograms per gram dry weight) whereas more than 57 percent of the invertebrate samples and 61 percent of the fish samples exceeded the dietary effect level. Of the more than 2,000 bird eggs collected, 44 percent had selenium concentrations exceeding 6 micrograms per gram, a threshold value for reduced hatchability. In 14 areas, selenium concentrations in eggs from some populations of birds exceeded 6 micrograms per gram. Selenium-caused deformities of bird embryos were found in four of the NIWQP study areas; however, most study areas were not systematically surveyed for such deformities.

Eggs were sampled from 34 species of birds belonging to 10 orders. Nearly all the eggs collected come from aquatic species of birds, with American coots, mallards, and American avocets being the three species most frequently collected. Of the 34 species, at least one set of eggs from 16 species had a geometric-mean selenium concentration of at least 12.5 micrograms per gram, a high-risk threshold. All three species of grebes yielded at least one set of high risk eggs, as did four of five species of shorebirds and five of eleven species of waterfowl. Egg-set data were examined to determine if some feeding guilds are more at risk to selenium poisoning than others. Analysis of data for waterbird eggs from the study areas where the 75th percentile selenium concentration in surface water exceeded 5 µg/L suggests that herbivorous birds may bioaccumulate less selenium than insect- and fish-eating birds. For birds from these study areas, selenium concentrations for 39 percent of the egg sets from herbivorous birds fell in the normal range (less than 3 µg/g) while only 7 and 0 percent, respectively, of egg sets from insect- and fish-eating birds fall in the normal range. Although herbivorous birds may bioaccumulate less selenium, it does not appear that any waterbird feeding guilds are particularly well buffered from exposure to selenium contamination.

Predictive tools were developed to aid managers in identifying specific land areas at risk for irrigation-induced selenium contamination. The tools range from identifying broad geographic regions where selenium contamination is likely, to assessing the probability that selenium concentrations in a specific stream or lake exceed the chronic criterion for selenium.

A geographic information system was used to prepare a map that identifies land areas in the Western United States that are susceptible to selenium contamination if irrigated. On the basis of the 75th percentile, selenium concentration in surface water, 12 of the 26 NIWQP study areas were classified as contaminated, two as seleniferous, and 12 as uncontaminated. The map correctly identified both seleniferous areas and 10 of 12 selenium-contaminated areas as susceptible; 10 of 12 uncontaminated areas were correctly identified as not being susceptible. About 160,000 square miles are identified as being susceptible; of that area, about 4,100 square miles have been identified by satellite imagery as actively being irrigated.

Principal-components analysis and pattern-recognition techniques indicate that major-ion chemistry of water samples alone can be used to identify selenium- and nonselenium-producing areas in the Western United States. Water samples composed of simple salts of sulfate typically have concentrations of selenium that exceed 3 µg/g, whereas samples composed of simple salts of chloride or carbonate typically have low selenium concentrations. Weathering of soils that contain reduced-sulfur minerals, such as pyrite, mobilizes sulfur and selenium because selenium commonly substitutes for sulfur in these minerals.

In areas where the bedrock is composed of Upper Cretaceous marine sedimentary rocks, logistic regression of data from the NIWQP sites indicates that if the dissolved-solids concentration equals 1,000 milligrams per liter, the prob-

ability is about 69 percent that the selenium concentration will exceed 5 micrograms per liter, the U.S. Environmental Protection Agency chronic criterion. In areas where the bedrock is not composed of such rocks, the probability is only about 10 percent.

The avian-egg data within the biotic data base were used to make a quantitative toxicological risk assessment. Of the 23 study areas where avian eggs were sampled, 14 areas yielded at least one egg containing 6 µg/g selenium, the threshold for embryotoxicity. However, only 6 of the study areas yielded eggs containing enough selenium to expect selenium-induced teratogenesis of duck embryos. Predicted probabilities of discovering embryo teratogenesis matched field observations in 13 of the 14 study areas reporting results of embryo assessments.

Bird eggs were collected from 161 individual sampling sites and at 79 of those sites selenium concentrations in one or more eggs exceeded 6 µg/g. At the 79 sites where biological effects are expected on the basis of selenium concentrations in the eggs, the median rate was 3.9 percent of the hens losing at least one egg to selenium-induced embryotoxicity. This corresponds to about 1.2 percent selenium-induced egg inviability among otherwise viable eggs. Across all NIWQP study areas, the overall rate of hens projected to lose at least one egg to selenium-induced embryotoxicity is estimated to be 1.9 percent, which corresponds to about 0.3 percent selenium-induced egg inviability among otherwise viable eggs. After accounting for increased mortality of selenium poisoned-hatchlings due to other factors such as weather and predators, it was estimated that that increases of 0.3 and 1.2 percent in inviable eggs would cause approximately a 1.4 and 5.4 percent depression in nesting success.

Regional surveys of nesting success among ducks revealed that duck populations commonly exist near their demographic break-even point. The vulnerable demographic condition of North American duck populations during the mid-1960's to mid-1980's was primarily due to noncontaminant factors, such as poor-quality nesting habitat and dry climatic cycles. Under such conditions, rates of 1.4- to 5.4-percent depression in nesting success caused by exposure to selenium from irrigation projects can be crucial for avian populations already close to their demographic break-even point. Even the worst-case levels of contaminant effects, however, could be tolerated by populations of ducks existing just modestly above demographic break-even points. This suggests the biotic risk to ducks could be addressed by reducing irrigation-induced water pollution but more effectively by restoring high-quality (more predator-safe) nesting habitat.

An analysis at the nesting-site level was made of the relation between selenium content of water and bird eggs. Eggs from 93 bird populations were collected from nesting sites where the water sample collected during April-July contained less than 5 µg/L selenium. The average selenium concentration in egg sets was embryotoxic in 19 of the 93 populations. Of the populations collected at sites where the selenium in the water was less than 1 microgram per liter, only four of 54 populations contained embryotoxic concentrations. Eggs from 65 populations of birds were collected from nesting sites where selenium concentrations in water samples collected during April-July equaled or exceeded 5 µg/L, and 55 of those 65 populations contained embryotoxic concentrations of selenium in the eggs.

An analysis at the study-area level was made of the relation between selenium contamination of water and selenium contamination of the food chain and egg loss due to selenium poisoning. Most food organisms, particularly aquatic invertebrates and fish, contained potentially harmful amounts of selenium in study areas where selenium concentrations in more than 25 percent of the water samples exceed 5 µg/L. The analysis also indicates that some hens are predicted to lose eggs to selenium poisoning in all study areas where selenium concentrations in more than 25 percent of the water samples exceed 5 µg/L. These results suggest that areas where selenium contamination of the food chain and loss of eggs to selenium poisoning is occurring may be identified using the same methods developed to identify areas where selenium contamination of water is likely to occur.

INTRODUCTION

CREATION OF NATIONAL IRRIGATION WATER-QUALITY PROGRAM

In the early 1980's, incidents of mortality, congenital deformities, and reproductive failures in waterfowl were discovered in Kesterson National Wildlife Refuge, western San Joaquin Valley, Calif. The cause of these adverse biological effects was determined to be selenium carried by irrigation drainwater into areas used by wildlife (Ohlendorf, Hoffman, and others, 1986). The U.S. Congress and environmental groups wanted to determine if what happened at Kesterson National Wildlife Refuge was an aberration or if it was symptomatic of a larger problem that might occur elsewhere in the Nation. To answer this specific question and to address general concerns about the quality of irrigation drainage and its potential harmful effects on humans, fish, and wildlife, the U.S. Department of the Interior (DOI) implemented the National Irrigation Water Quality Program (NIWQP) in October 1985. The objective of the NIWQP was to identify the nature and extent of irrigation-induced water-quality problems in the Western United States and to remediate those water-quality problems resulting in risk to humans or to DOI trust responsibilities¹.

SUMMARY OF NATIONAL IRRIGATION WATER-QUALITY PROGRAM

The DOI formed an interbureau group known as the "Task Group on Irrigation Drainage," which included members from the Bureau of Indian Affairs (BIA), Bureau of Reclamation (BOR), U.S. Fish and Wildlife Service (USFWS), and the U.S. Geological Survey (USGS). The purpose of the task group was to prepare a comprehensive plan for reviewing irrigation-drainage concerns for which DOI may have responsibility.

The scope of the management strategy committed the program to identifying and addressing irrigation-induced water-quality and contamination problems in DOI irrigation and drainage facilities, National Wildlife Refuges, and other migratory-bird or endangered-species management areas that may receive drainwater from these DOI facilities, and public and private drinking-water supplies that may be affected by drainwater from these facilities.

A five-phase approach was developed for the identification and subsequent assessment and response to problems that were identified:

¹ The NIWQP generally is not responsible for remediation of water-quality problems caused by anthropogenic chemicals such as pesticides. However, the presence of these chemicals can affect endangered species or migratory birds and thus, to that extent, bear on NIWQP decisions to begin site remediation. For this reason, a substantial amount of data on these anthropogenic chemicals were collected and are presented in this report.

Phase 1: Site Identification—identify sites requiring attention under the scope of the management strategy

Phase 2: Reconnaissance Investigations—determine from existing information and reconnaissance investigations whether irrigation drainage has caused or has the potential to cause harmful effects on human health, fish, or wildlife, or to impair beneficial uses of water

Phase 3: Detailed Studies—conduct intensive studies to determine the extent, magnitude, effects, and causes of contamination problems if reconnaissance investigations or new information indicates a high potential for harmful effects

Phase 4: Planning for Remediation—develop a coordinated plan of action with appropriate Federal, State, and local agencies to address identified problems

Phase 5: Remediation—implement corrective action for those areas and activities in which the DOI has authority and resources once a plan has been developed and authorized.

The DOI has constructed or manages more than 600 irrigation-drainage facilities and national wildlife refuges in 17 Western States. In 1985–86, NIWQP made a comprehensive survey of these DOI projects. To facilitate evaluation of these areas, many smaller areas were eliminated from consideration and other areas were grouped together. As a result, desk evaluations of previously collected water-quality, biological, and geological data and other pertinent information were done for 191 areas in the Western United States (fig. 1), of which 26 were selected for reconnaissance investigations (fig. 2) on the basis of known or strongly suspected irrigation-induced problems identified during phase 1. Field investigations were made by interagency study teams consisting of a USGS scientist as team leader and additional USGS, USFWS, BOR, and BIA professionals.

Reconnaissance investigations (phase 2) were made in 26 areas (table 1; fig. 2) in 14 of the 17 contiguous Western States. Alfalfa is the principal crop in most of the study areas; however, in some areas, cotton or foods such as onions, corn, wheat, and rice are the principal crops. Study-area sizes differ greatly. For example, in the Columbia River Basin in Washington, a total of 575,000 acres was irrigated in 1991 (Embrey and Block, 1995), but from 1968 through 1977, the average was only 4,425 acres in the Vermejo Project area in New Mexico (Bartolino and others, 1996).

Reports describing results of NIWQP investigations for the 26 study areas are listed in table 1. In 9 of the 26 areas, reconnaissance investigations confirmed that irrigation drainage had caused significant harmful effects. Subsequent detailed investigations (phase 3) by NIWQP personnel were undertaken to determine the extent, magnitude, effects, and causes of contamination problems in eight of these areas. In the ninth area, the Tulare Lake Bed area of California (Y in fig. 2 and table 1),

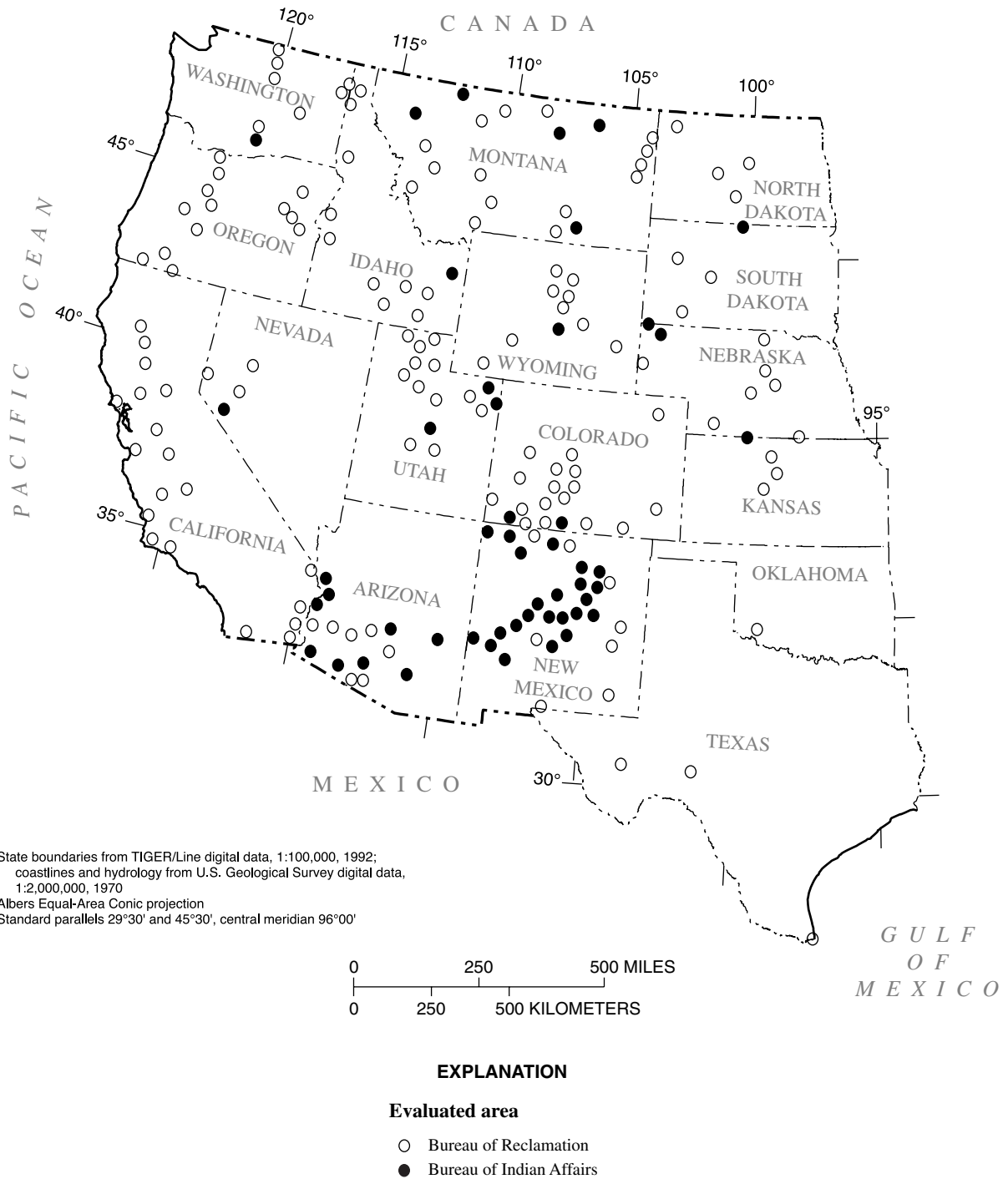


FIGURE 1. Location of 191 areas in the western United States evaluated for irrigation-drainage problems by National Irrigation Water Quality Program task group. Modified after National Research Council (1991).

the equivalent of a detailed investigation was undertaken by a separate Federal/State cooperative research program—the San Joaquin Valley Drainage Program. The program was established in 1984 as a joint Federal–State task force to investigate problems associated with the drainage of irrigated agricultural land in the western and southern parts of the San Joaquin Valley (San Joaquin Valley Drainage Program, 1990); it focused equally on developing options for managing a large volume of agricultural drainage water and on identification of associated toxic hazards. Additional data for some of the sites used during the Tulare Lake Bed area reconnaissance investigation (Schroeder and others, 1988) were presented by Moore and others (1990). Biological data collected for the San Joaquin Valley Drainage Program were used extensively in the current study (see section titled “Avian-Egg Risk Assessment”).

In 1992, after the detailed studies, the remedial part of the NIWQP began. Planning for remediation (phase 4) began in four areas identified by reconnaissance investigations and detailed studies: the Salton Sea area in California (*U* in fig. 2 and table 1), the middle Green River Basin in Utah (*N*); the Stillwater Wildlife Management Area in Nevada (*W*); and the Kendrick Reclamation Project in Wyoming (*H*). Remedial planning subsequently was started in two other areas, the Gunnison River Basin–Grand Valley Project in Colorado (*F*) and the San Juan River area in New Mexico (*V*). A decision on remedial planning is pending for the Sun River area in Montana (*X*). Actual remediation activities are in progress in the middle Green River Basin, the Kendrick Reclamation Project, the Stillwater Wildlife Management Area, and the San Juan River area either by NIWQP participants or by other Federal, State, or local entities in the areas.

The results of the reconnaissance investigation of the Vermejo Project area in New Mexico (*Z*) were not available in time to be included in the analysis of factors common to selenium-contaminated areas, although Vermejo Project area data were used in the comparisons of contaminant concentrations among the study areas.

An additional 13 areas were found to have the potential for irrigation-induced contamination and were selected for field-screening investigations. Although the same general protocols as the reconnaissance investigations were used in these field-screening investigations, fewer samples were collected and the resulting data were not available for use in the data analysis. However, data from some of the areas were used to test conclusions after the data analysis was completed.

APPROACH AND OBJECTIVES OF NATIONAL IRRIGATION WATER QUALITY PROGRAM DATA-SYNTHESIS PROJECT

Early in the planning of NIWQP, the interagency task group realized that a synthesis of the data collected by the reconnaissance and detailed investigations would be an important component of the overall program. A review of NIWQP by the

National Research Council (National Research Council, 1991) supported the need for a systems analysis to explore the linkages and thoroughly address the many dimensions of irrigation-induced water-quality problems. They noted that many of the areas with contamination problems have common characteristics and that DOI should rigorously seek to identify such commonalities (National Research Council, 1991, p. 2)

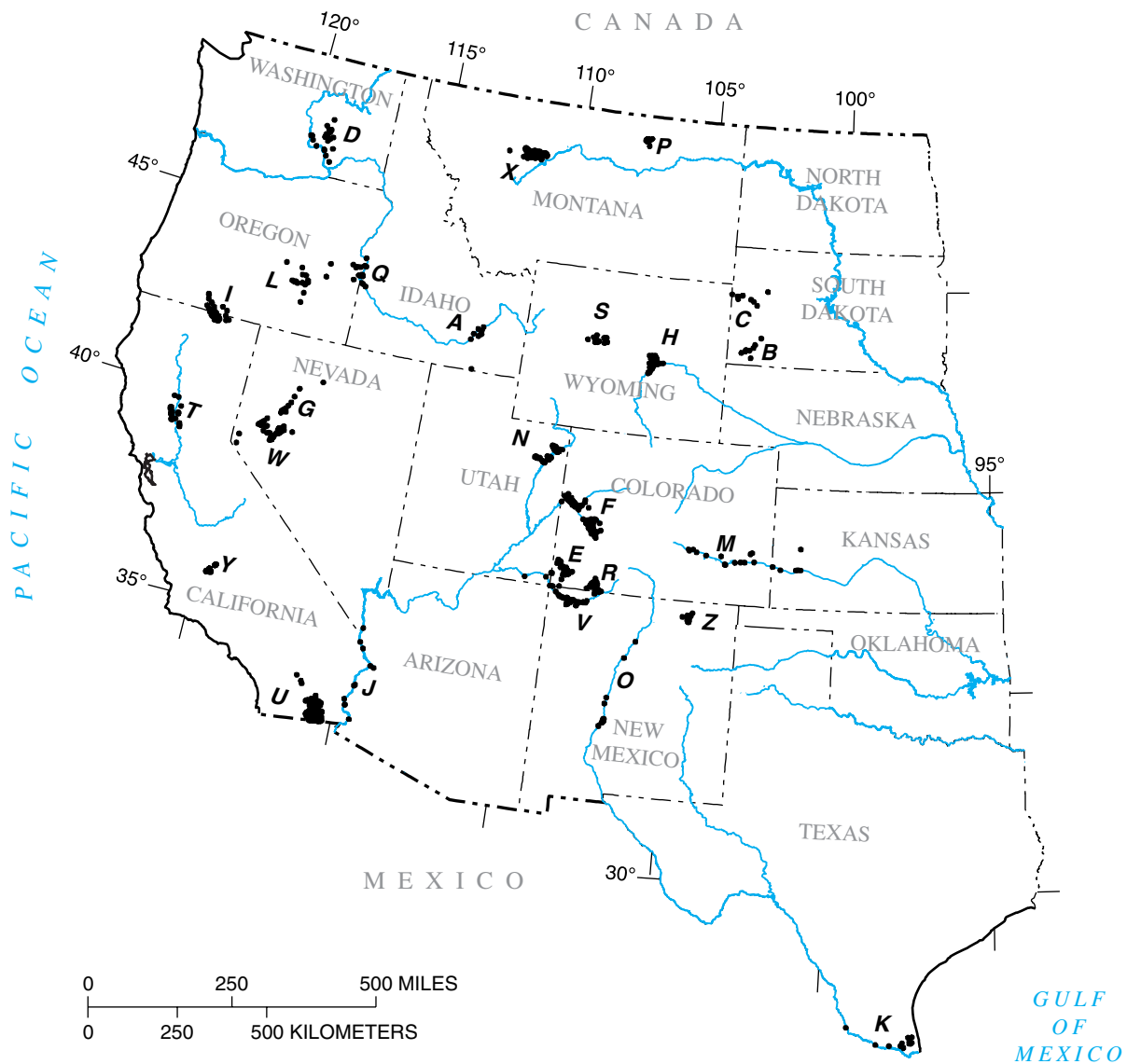
The NIWQP has now completed reconnaissance investigations of 26 areas and field-screening investigations of an additional 13 areas in the 17 Western States. Nationally, only DOI areas have been the focus of investigation, although NIWQP has provided funding for USFWS investigations at several non-DOI areas. The National Research Council (1991, p. 2) noted that the knowledge gained during the NIWQP investigations can be used to forewarn of other problems in the region, whether on public or private land.

The data collected by the NIWQP investigations provide a unique opportunity to identify common characteristics of the sites and the physical, chemical, and biological factors that result in water-quality problems. In April 1992, NIWQP initiated the Data-Synthesis Project, a 5-year effort to evaluate data collected by the completed and ongoing NIWQP investigations.

The data synthesis consisted of an evaluation of data from completed and ongoing NIWQP investigations; no new data were collected for the synthesis. The overall objective of the synthesis was to identify common features of contaminated areas and dominant biologic and physical factors that result in contamination of water and biota in irrigated areas of the Western United States.

Specific objectives of the data-synthesis project were:

- To construct a comprehensive relational data base containing all data collected by the reconnaissance and detailed investigations
- To use the data base to identify the principal contaminants and to make comparisons among the 26 study areas using descriptive statistics
- To use the data base to identify how the physical setting and geochemical and biological processes are related to the magnitude, seasonality, and extent of contamination problems
- To develop tools for predicting biological risk from measurements of contaminant concentrations in water and sediment
- To identify common features of contaminated areas and use this information to develop the capability to predict where irrigation-drainage problems are likely to occur so that potential problem areas, whether or not they are within the purview of the DOI, can be identified



EXPLANATION

- **T** Data-collection site in National Irrigation Water Quality Program study area—Letter is area identifier (table 1), which is used throughout report

FIGURE 2. Location of 26 National Irrigation Water Quality Program study areas (A–Z) selected because of potential irrigation-drainage water-quality problems. Also shown are data-collection sites within study areas. For base credit, see figure 1.

TABLE 1. *Reconnaissance and detailed studies concerning National Irrigation Water Quality Program study areas*

[Symbol: —, detailed study not done]

Study area		References	
Identifier ¹	Name	Reconnaissance studies	Detailed studies
A	American Falls Reservoir, Idaho	Low and Mullins, 1990	—
B	Angostura Reclamation Unit, South Dakota	Greene and others, 1990	—
C	Belle Fourche Reclamation Project, South Dakota	Roddy and others, 1991	—
D	Columbia River Basin, Washington	Embry and Block, 1995	—
E	Dolores–Ute Mountain area, Colorado	Butler and others, 1995	—
F	Gunnison River Basin–Grand Valley Project, Colorado	Butler and others, 1991	Butler and others, 1994, 1996
G	Humboldt River area, Nevada	Seiler and others, 1993	—
H	Kendrick Reclamation Project, Wyoming	Peterson and others, 1988	See, Naftz, and others, 1992; See, Peterson, and Ramirez, 1992.
I	Klamath Basin Refuge Complex, California–Oregon	Sorenson and Schwarzbach, 1991	MacCoy, 1994; Dileanis and others, 1996.
J	Lower Colorado River valley, California–Arizona	Radtke and others, 1988	—
K	Lower Rio Grande valley, Texas	Wells and others, 1988	—
L	Malheur National Wildlife Refuge, Oregon	Rinella and Schuler, 1992	—
M	Middle Arkansas River Basin, Colorado–Kansas	Mueller and others, 1991	—
N	Middle Green River Basin, Utah	Stephens and others, 1988	Peltz and Waddell, 1991; Stephens and others, 1992.
O	Middle Rio Grande, New Mexico	Ong and others, 1992	—
P	Milk River Basin, Montana	Lambing and others, 1988	—
Q	Owyhee–Vale Reclamation Project areas, Oregon–Idaho	Rinella and others, 1994	—
R	Pine River area, Colorado	Butler and others, 1993	—
S	Riverton Reclamation Project, Wyoming	Peterson and others, 1991	—
T	Sacramento Refuge Complex, California	Dileanis and others, 1992	—
U	Salton Sea area, California	Setmire and others, 1990	Schroeder and others, 1993; Setmire and others, 1993.
V	San Juan River area, New Mexico	Blanchard and others, 1993	Thomas and others, 1997
W	Stillwater Wildlife Management Area, Nevada	Hoffman and others, 1990	Rowe and others, 1991; Lico, 1992; Hallock and Hallock, 1993; Hoffman, 1994; Tuttle and Thodal, 1998.
X	Sun River area, Montana	Knapton and others, 1988	Lambing and others, 1994; Nimick and others, 1996.
Y	Tulare Lake Bed area, California	Schroeder and others, 1988	Moore and others, 1990
Z	Vermejo Project area, New Mexico	Bartolino and others, 1996	—

¹ Used in figure 2 to show locations of study areas

PURPOSE AND SCOPE

This report describes the results of the data-synthesis project. Concentrations of contaminants in water, sediment, and biota are compared with criteria and the most important contaminants associated with irrigation drainage are identified. Information on hydrology, climate, geology, geochemistry, and biology are integrated and evaluated as an interdependent system. Some previously published results (Seiler, 1998; Skorupa, 1998; Naftz and Jarman, 1998; Nolan and Clark, 1997) are summarized and the concepts developed in greater detail.

The emphasis in the report is on selenium and the principal determinants used for evaluating whether irrigation drainage is having adverse environmental effects are selenium concentrations in water and bird eggs. The interrelation of geology, climate, and hydrology in determining whether selenium contamination occurs in irrigated areas is explored and methods are developed to predict where selenium contamination will occur. Selenium concentrations in biota are compared with criteria and the relation between selenium concentrations in biota, water, and sediment are explored. A risk assessment for birds evaluates (1) which contaminants are associated with overt embryonic deformities, and (2) the overall demographic significance of irrigation-induced selenium contamination on bird populations in the western United States.

ACKNOWLEDGMENTS

The authors are indebted to colleagues in DOI who participated in NIWQP investigations. They provided detailed information about the study areas, as well as help and encouragement in the building of the data base. We also acknowledge the reviews and helpful suggestions from many people who made the effort to critically examine this extensive report.

The authors want to express their gratitude to Richard Engberg, NIWQP Program Manager, DOI, and Herman Feltz, USGS Bureau Coordinator. They have been unflagging in their support of the authors since the inception of the data synthesis in 1992.

LITERATURE REVIEW

Many reports on selenium have been published; to provide a complete review of all the many aspects of selenium is beyond the scope of this report. This review is limited to describing the discovery of selenium as an important contaminant in the Western United States and emphasizes publications concerning sources of the selenium found in irrigated areas in the Western United States and processes involved in determining selenium concentrations associated with irrigation drainage. Reports that describe the geochemistry, biochemistry, or toxicology of sele-

nium, for example, are not reviewed here. A comprehensive review of publications reporting field measurements of exposure and response to selenium, macrocosm and mesocosm experiments, and selected experimental studies of captive biota was presented elsewhere by the NIWQP (U.S. Department of the Interior, 1998)

HISTORICAL PERSPECTIVE

Since the beginning of irrigated agriculture, water-quality issues have constrained the management of irrigation projects. Salt buildup in the root zone requires the application of more water than plants need so that salts do not accumulate in the soil. The excess water is necessary to maintain the salt balance in the soil.

Except in rare circumstances, deep percolation of the excess water causes rises in the local ground-water table. Managing this excess salty water to keep it out of the root zone has required the construction of drains and facilities for disposing of the water. Until the early 1980's, the primary water-quality concerns for drainwater were salinity, nutrients, and pesticides. After the experience at Kesterson National Wildlife Refuge, the presence of selenium and other trace elements in drainwater was recognized as an important water-quality issue (Ohlendorf, Hoffman, and others, 1986; Presser and Ohlendorf, 1987; Tanji and Valoppi, 1989).

During the early 1930's selenium in pasturage was determined to be the cause of the so-called alkali disease, a disease of cavalry horses in South Dakota first described and reported by Madison (1860). For more than 1,000 years seleniferous pasturage has been known to kill horses; Marco Polo described symptoms of ill horses similar to those of horses in South Dakota (Wright, 1948). Wilcox (1944) attributed the loss of General Custer's cavalry at the Battle of the Little Big Horn to selenium poisoning of horses, which delayed the arrival of his backup troops. Because of frequent illness and death of cattle in the Western United States, investigations were undertaken to determine the cause and extent of the disease.

A series of U.S. Department of Agriculture Technical Bulletins (Byers, 1935, 1936; Byers and others, 1938; Williams and others, 1940, 1941; Lakin and Byers, 1941) describes investigations made during the 1930's and 1940's about the sources, distribution, and effects of selenium. The series provides numerous chemical analyses of soils and plants for many areas in the United States, Mexico, and Canada. Many of the areas investigated by the NIWQP for irrigation-induced water-quality problems were investigated for seleniferous soils and selenium-accumulating plants in that bulletin series. The first report (Byers, 1935) contains an extensive section about selenium in the Belle Fourche Irrigation Area in South Dakota, one of the first areas investigated as part of NIWQP.

Comprehensive summaries of the findings from this era of research began appearing in the mid-1940's and continued into the early-1960's (Moxon and Rhian, 1943; Trelease and Beath, 1949; Rosenfield and Beath, 1957, 1964; Anderson and others, 1961). Many of the important concepts about causes of selenium contamination and areas where it can be expected were known more than 65 years ago. Byers (1935, p. 45) documented the extent of knowledge about selenium sources and selenium-associated problems in the 1930's:

“The source of selenium in soils has been shown to be sulphide minerals occurring in the soil-parent materials. So far as yet known the seleniferous soil-forming material is, for the most part, shales of the Cretaceous period. Soils derived from these shales, or from other seleniferous materials, may retain sufficient selenium to produce toxic vegetation when the mean annual rainfall is insufficient to produce percolation through the soil profile.”

When selenium was identified as the cause of the alkali disease, investigators began to study the effects of selenium on poultry. Even before the 20th century, farmers in western South Dakota and northern Nebraska knew that eggs from hens on their farms did not hatch satisfactorily (Peters, 1904). Franke and others (1936), by injecting selenite into the air cell of eggs before incubation, produced birds having deformed or missing beaks, eyes, and legs. Poley and others (1937) demonstrated that the toxic effects of selenium are not passed on to chicken embryos if selenium is removed from the diet of the mother hen for 6 days prior to egg laying. It is likely investigators from the 1930's would have quickly recognized selenium as the cause of the deformities in birds from Kesterson National Wildlife Refuge.

The fact that irrigation water leaches selenium from soils also was known in the 1930's; at the time, irrigation was considered a remedial method (Byers and others, 1938, p. 71):

“Data are given which show that irrigation is a remedial measure for seleniferous soils and that irrigation drainage waters remove soluble selenium from soils which contain it.”

Nearly 45 years later, in the early 1980's, the harmful effects of drainwater derived from application of irrigation water to seleniferous agricultural soils on aquatic birds and fish were discovered at Kesterson National Wildlife Refuge in San Joaquin Valley, Calif.

Although the ponds at Kesterson National Wildlife Refuge were constructed in 1971 for use in regulating drain flow, two other purposes were served—to dispose of and evaporate agricultural drainwater and to provide wildlife habitat. The inflow was entirely freshwater until 1978 (National Research Council, 1989). During 1974–80, Kesterson Reservoir supported a warm-water fishery typical of the Central Valley in California.

Species found in the reservoir included largemouth and striped bass, bluegill, white catfish, black bullhead, green sunfish, carp, and mosquitofish (Bureau of Reclamation, 1986). By 1981, the water supply was exclusively irrigation drainwater. The delivery of seleniferous drainwater eventually resulted in the collapse of the warm-water fishery and the only fish persisting in the refuge were pollution-tolerant mosquitofish (Skorupa, 1998). Hundreds of adult birds died and nesting birds had complete reproductive failure.

The magnitude of irrigation-related water-quality problems at Kesterson National Wildlife Refuge and elsewhere in the Western United States was presented to the general public in a series of news articles in The Sacramento Bee starting in September 1985. That newspaper reported that dangerous levels of selenium being flushed from BOR project service areas into wildlife refuges in seven states. The House Committee on Interior and Insular Affairs held hearings to allow DOI to comment on the newspaper reports. At the request of the Committee, DOI scientists undertook a preliminary assessment of selenium contamination caused by irrigation drainage from BOR project areas. Their report indicated that evidence of elevated levels of selenium was found at many of the sites, but no evidence could be found to confirm widespread ill effects alleged in the newspaper reports (Deason, 1986).

PREVIOUS NATIONAL IRRIGATION WATER QUALITY PROGRAM EVALUATIONS

Data from seven of the initial NIWQP reconnaissance investigations were evaluated by Sylvester and others (1988), who identified several factors involved in determining the concentration of contaminants associated with irrigation drainage:

- Yearly variations in precipitation and streamflow
- Presence or absence of geologic sources of trace elements
- Arid to semiarid climate
- Presence of topographically closed drainage basins
- Amount and relative contribution of irrigation drainage to wetlands, ponds, and refuges.

Feltz and others (1991) summarized selenium concentrations in water, bottom sediment, and biota for 20 of the study areas. They concluded that elevated concentrations of selenium associated with irrigation drainage can be either localized or widespread within a given study area.

Engberg and Sylvester (1993) analyzed data from 20 of the areas. They recognized the potential for selenium contamination in approximately 12 percent of all irrigated lands in the 17 Western States. They identified possible source material for selenium in each of the 20 areas and concluded that data from these areas supported the earlier conclusions of Sylvester and others (1988).

Presser and others (1994) analyzed published data and some unpublished data for 20 of the study areas. Selenium concentrations in water, bottom sediment, and biota for the 20 areas were summarized. The importance of Cretaceous marine sedimentary rocks in irrigated areas as direct and indirect sources of selenium was discussed. They also discussed how assessments of contamination can be affected by the time of sampling, not only by the season of sampling but also in what particular year samples were collected.

Presser (1994b) described and summarized 11 biogeochemical processes involved in the transport of selenium from rock to waterfowl at Kesterson National Wildlife Refuge. Subsequent data analysis has shown that these processes probably occur in most of the areas investigated by the NIWQP that were contaminated with selenium.

Lemly and others (1993) and Lemly (1993b) summarized published information about the NIWQP investigations. In addition to describing NIWQP investigations, they proposed actions to stop further drainage-related degradation of arid wetlands, including restoration of freshwater inflows to wetlands, and recognition of irrigation drainwater as a class of pollution subject to regulation under the National Pollution Discharge Elimination System permitting process.

The focus of previous analyses of the NIWQP data has been selenium. In this report data from other trace elements and pesticides are examined to evaluate whether this exclusive focus on selenium is warranted. In addition, the ideas and conceptual models related to selenium that have been presented in earlier NIWQP data evaluations are re-evaluated in this report and developed to provide tools for managers who must manage irrigation drainage. Earlier reports have noted the presence of elevated selenium concentrations in biota and biological effects in some NIWQP areas (Lemly, 1995; Hren and Feltz, 1998; Van Derveer and Canton, 1997). In this report biological data for selenium concentrations in birds are placed in their demographic context to answer what the effects of selenium in irrigated areas are on birds at the population level.

METHODS USED

DATA COLLECTION

STUDY-AREA SELECTION

Areas for reconnaissance investigations were selected by the NIWQP Manager for DOI and Bureau Coordinators, who are representatives of the USGS, USFWS, BOR, and BIA. The fundamental criterion for selection was the known occurrence, or high probability of, irrigation-induced contamination by or of a DOI area. Although NIWQP originated as a direct result of the events related to selenium contamination at Kesterson National Wildlife Refuge, the NIWQP has not restricted itself to the investigation of selenium. NIWQP investigations also have documented and addressed irrigation-induced contamination

resulting from increases in salinity and in concentrations of unionized ammonia, pesticides, and toxic trace elements other than selenium (for example, arsenic, boron, molybdenum, and uranium). NIWQP responsibility has been limited in scope to contaminants that are mobilized by the application of irrigation water and that are adversely affecting humans or biota in DOI-managed areas.

SITE SELECTION AND SAMPLING SCHEDULE

Workplans were developed by individual study teams and reviewed by the NIWQP Program Manager and Bureau Coordinators. The Program Manager and Bureau Coordinators provided guidance, but the sampling sites were selected by the individual study teams. All study areas included reference sites, typically on streams or rivers that provided water to the area for irrigation.

Some reconnaissance-study teams primarily selected sites that already had associated data, typically the larger streams in an area. Other reconnaissance-study teams selected sites that they believed were most likely to be contaminated, or they actively searched for contaminated sites. Some study teams concentrated on streams, canals, and drains but did not sample lakes and ponds. Some of the study teams that did sample lakes selected large reservoirs rather than smaller lakes or ponds.

In some areas water and sediment samples were not collected in the same locations as the biological samples. Biological sampling was done opportunistically and therefore was not directed to the same extent as water and sediment sampling. In some areas, water and sediment sampling emphasized streams, canals, and drains and few samples were collected from wildlife-habitat areas (see section titled "Limitations of Data," p. 19).

In some of the initial NIWQP reconnaissance investigations, for example the Lower Colorado River valley (*J*) and Milk River Basin (*P*; fig. 2), almost all water samples were collected during a single sampling round in the middle of the irrigation season, when it was assumed that effects from irrigation would be greatest. Bed-sediment samples were collected after a prolonged period of low or steady flows. Bureau coordinators realized from initial results that seasonal changes in contaminant concentrations could mask contamination. Therefore, in subsequent investigations, samples were collected before the irrigation season began, during the irrigation season, and after the irrigation season ended.

PROTOCOLS FOR DATA COLLECTION AND CHEMICAL ANALYSIS

To enhance comparability of results among the study areas, the investigations were guided by a common protocol for obtaining and analyzing data. Chemical analyses were made by the same laboratories according to consistent analytical protocols throughout the life of the program.

Samples of water, bottom sediment, and biota were collected in each of the study areas. Water samples were analyzed for major constituents except during two of the early reconnaissance investigations. Samples of each medium were analyzed for trace elements, including arsenic, barium, boron, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium, silver, uranium, vanadium, and zinc. Stable isotopes of water were measured during some of the studies, particularly the detailed investigations.

Pesticide analyses were done at the discretion of the study teams on the basis of usage in the study areas. Of the 26 study teams, 24 sampled bottom sediment for organochlorine pesticides and polychlorinated biphenyls, 7 analyzed some bottom-sediment samples for organophosphate pesticides, and 5 analyzed bottom sediment for herbicides. Surface-water samples were analyzed for herbicides in 17 areas and for organochlorine pesticides in 6 areas.

WATER

All NIWQP water samples were collected and analyzed according to standard U.S. Geological Survey methods (U.S. Geological Survey, 1977; Fishman and Friedman, 1989). Water-quality samples were collected at stream sites by using depth-integrating samplers and methods described by Ward and Harr (1990). Where depths were too shallow to use samplers, representative water samples were collected in sample-collection bottles from the centroid of flow or from several verticals across the stream.

Alkalinity, pH, dissolved oxygen, and specific conductance typically were measured in the field. Most trace-element samples were preserved with nitric acid after filtering in the field through a 0.45-micrometer cellulose-nitrate plate filter or 0.45-micrometer polyether-sulfone capsule filter. Samples for dissolved mercury were preserved with nitric acid and potassium dichromate. Samples for nutrient analysis were preserved with mercuric chloride and were chilled on ice and refrigerated until the samples were analyzed.

Water-quality analyses were done at the USGS National Water-Quality Laboratory. Minimum analytical reporting limits for trace elements and pesticides in water are presented in tables 2 and 3. Minimum reporting limits for many of the pesticides analyses were reduced during later investigations and therefore are presented as a range in table 3. Inorganic substances in surface and ground water were analyzed according to methods described by Fishman and Friedman (1989). Most trace elements were measured by using inductively coupled plasma-emission spectroscopy after preconcentration. Arsenic and selenium were analyzed using hydride generation and atomic-absorption spectrometry. Mercury was analyzed using cold-vapor atomic-absorption spectrometry.

TABLE 2. Minimum analytical reporting limits for trace elements in water, bottom sediment, and biota

[Abbreviation and symbol: $\mu\text{g/L}$, micrograms per liter; $\mu\text{g/g}$, micrograms per gram; —, not applicable or not determined]

Constituent	Trace element in water ($\mu\text{g/L}$)	Reporting limit ¹		
		Trace element in bottom sediment		Trace element in tissue ($\mu\text{g/g}$, dry weight)
		$\mu\text{g/g}$, dry weight	Percent	
Aluminum	1	—	0.05	5
Antimony	1	0.1	—	—
Arsenic	1	.1	—	.5
Barium	1	1	—	.5
Beryllium	1	1	—	.1
Boron	10	.4	—	1.5
Cadmium	1	.1	—	.1
Chromium	1	1	—	.5
Copper	1	1	—	.5
Iron	3	—	.05	10
Lead	1	4	—	.5
Manganese	1	4	—	4
Mercury	.1	.2	—	.1
Molybdenum	1	2	—	.5
Nickel	1	2	—	.5
Selenium	1	.1	—	.5
Silver	1	.1	—	—
Uranium	1	.05	—	—
Zinc	1	4	—	20

¹ Minimum concentration of substance that can be identified, measured, or reported with laboratory-determined level of confidence that analyte concentrations are greater than zero. Analyses subject to interference from other substances or properties of sample have higher analytical reporting limit.

Water samples for pesticide analyses were collected by dipping hexane-rinsed and baked borosilicate-glass bottles directly into the stream. These unfiltered samples were chilled on ice for transportation to the laboratory. Organochlorine and organophosphate pesticides in water were extracted by using hexane and were analyzed according to methods described by Wershaw and others (1987). Organophosphate compounds were determined on a gas chromatograph using flame-photometric detectors, and organochlorine compounds were determined on a gas chromatograph using electron-capture detectors. Chlorophenoxy acid herbicides in water were extracted by using either diethyl or methyl *t*-butyl ether from acidified water samples (Wershaw and others, 1987). The extracted herbicides were hydrolyzed to the free acids and then converted to their methyl esters, which were determined by gas chromatography using electron-capture detectors.

TABLE 3. Minimum analytical reporting limits for pesticides in water, bottom sediment, and biota

[Abbreviation and symbol: µg/L, micrograms per liter; µg/g, micrograms per gram; —, not determined]

Constituent	Reporting limit ¹		
	Pesticide in water ² (µg/L)	Pesticide in bottom sediment (µg/g, wet weight)	Pesticide in tissue (µg/g, wet weight)
Organochlorine pesticides			
Aldrin	0.010–0.001	0.1	0.01
Chlordane	.10	1	.01
DDT	.010–.001	.1	.01
DDE	.010–.001	.1	.01
DDD	.010–.001	.1	.01
Dieldrin	.010–.001	.1	.01
Endosulfan	.010–.001	.1	.01
Endrin	.010–.001	.1	.01
Lindane	.010–.001	.1	.01
Methoxychlor	.01	.1	.01
Mirex	.01	.1	.01
Toxaphene	1.0	10	.01
Organophosphate and carbamate pesticides			
Diazinon	0.01	0.1	0.5
Dicamba	.01	—	.01
Malathion	.01	.1	.5
Parathion	.01	.1	.5
Propazine	.10	—	—
Sevin	2.0–.5	—	—
Trithion	.01	.1	—
Chlorophenoxy acid herbicides			
2,4D	0.01	0.1	0.01
2,4,5T	.01	.1	.01
Silvex	.01	.1	—

¹ Minimum concentration of substance that can be identified, measured, or reported with laboratory-determined level of confidence that analyte concentrations are greater than zero. Analyses subject to interference from other substances or properties of sample have higher analytical reporting limit.

² For some pesticides minimum reporting limits were reduced during later investigations, therefore the reporting limit is presented as a range.

SEDIMENT

Bottom-sediment samples for analysis of inorganic constituents were taken from the upper 2 to 4 in. of sediment deposited in streams, marshes, lakes, and drainage ditches. Several samples were collected at each site and thoroughly mixed in a glass container to make a composite sample. Subsamples for inorganic analysis were placed in pint-sized plastic freezer cartons for shipment to the laboratory.

Inorganic analyses of bottom sediment were done by the USGS Environmental Geochemistry Laboratory. Minimum analytical reporting limits for trace elements in bottom sediment are presented in table 2. The analytical methods used were presented by Severson and others (1987). In the laboratory, wet samples were air dried, disaggregated, and run through a 2-mm sieve. Material greater than 2 mm was discarded. Samples were split into two fractions and sieved again. Typically, two size fractions were submitted for analysis—a fine fraction (< 0.062 mm), and a coarse fraction (< 2 mm), which may have included fine material. In analyzing sediment samples, some study teams analyzed only one of the two fractions.

The sediment samples then were digested with hydrochloric acid, hydrofluoric acid, perchloric acid, and aqua regia (a hydrochloric–nitric acid mix). After digestion, the extracts were processed by methods described by Severson and others (1987). Mercury was determined by cold-vapor atomic-absorption spectroscopy, arsenic and selenium by continuous-flow hydride-generation atomic-absorption spectroscopy, uranium and thorium by delayed-neutron-activation analysis, and 40 other elements (including boron after a hot-water extraction) by inductively coupled argon-plasma atomic-emission spectroscopy.

Bottom-sediment samples for pesticide analyses were collected by using stainless-steel equipment. Minimum analytical reporting limits for pesticides in bottom sediment are presented in table 3. In the field, the sediment was composited in a stainless-steel bowl, and then native water from the site where the samples were collected was used to run sediment subsamples through a 2-mm stainless-steel sieve. The samples were stored in pretreated baked glass jars and were chilled on ice for transportation to the laboratory.

Bottom sediment was analyzed for pesticides at the USGS National Water Quality Laboratory. Organochlorine and organophosphate pesticides in sediment were extracted using hexane and were analyzed according to methods described by Wershaw and others (1987). Organophosphate compounds were determined on a gas chromatograph using flame-photometric detectors, and organochlorine compounds were determined on a gas chromatograph using electron-capture detectors. Total organic-carbon content of the sediment also was measured in some samples.

Chlorophenoxy acid herbicides in sediment were extracted by using either diethyl or methyl *t*-butyl ether from an acidified slurry of the sediment sample and water (Wershaw and others, 1987). The extracted herbicides were hydrolyzed to the free acids and then converted to their methyl esters, which were determined by gas chromatography using electron-capture detectors.

BIOTA

Samples were collected, prepared, packaged, stored, and shipped for analysis according to standard procedures outlined by U.S. Fish and Wildlife Service (1986). All handling of biological samples involved sample contact only with forceps, sterilized dissection tools, plastic gloves or bags, aluminum foil, or sterilized plastic or glass jars.

Aquatic vascular plants and algae were collected by hand-picking. Samples of rooted vascular plants, such as cattails, were rinsed extensively with native water to remove sediment. The plant samples were then placed in cleaned jars, weighed, and frozen.

Invertebrates were collected by using a kick-net or by hand-picking. Lake plankton samples were collected by using a plankton tow net. Invertebrate groups were commonly composited to obtain sufficient material for analysis. The invertebrate samples then were placed in cleaned jars, weighed, and frozen.

Fish were collected by using electroshocking equipment and seine or gill nets. Fish were rinsed, weighed, measured for length, and immediately frozen on dry ice until stored in a freezer. Whole-body samples were composited by species into groups of three or more fish. Fillet and egg samples were taken from individual fish and were not composited. Fish samples for analysis of inorganic contaminants were frozen in plastic bags. Fish samples for analysis of organic compounds were wrapped in aluminum foil and placed in plastic bags.

Tissue samples, including muscle, liver, and eggs, were collected from bird species in most study areas. Adult birds were shot using steel pellets and hatchlings were netted. Specimens were refrigerated and tissues removed and frozen within 24 hours. In some instances, to ensure sufficient material for analysis, tissues from two or three individual birds were composited into a single sample.

Nests were located and bird eggs removed. Eggs were opened and the embryos examined for developmental abnormalities. After examination, eggs were placed in cleaned jars, weighed, and frozen. In some instances, small eggs were composited to provide sufficient material for analysis.

Biological tissues were shipped to one of several different laboratories for analysis. These laboratories were contracted by the analytical control facility at the USFWS Patuxent Wildlife Research Center. Trace-element analyses were done by contract laboratories. Although some pesticides were analyzed at the USFWS facility, most were analyzed by contract laboratories. The USFWS facility was responsible for quality assurance and quality control of the biological analyses done by contract laboratories. Minimum analytical reporting limits for trace elements and pesticides in biota are presented in tables 2 and 3.

Analyses for most trace elements in biological tissues were done by using inductively coupled argon-plasma atomic-emission spectrometry after complete digestion of the sample by using nitric and perchloric acids. Analyses for arsenic and selenium in biological tissues were done by using hydride-generation atomic-absorption spectrometry. Analysis for mercury was done by flameless cold-vapor atomic-absorption spectrometry. Plant- and animal-tissue samples for organochlorine pesticide analysis were extracted by using hexane and analyzed by using packed- or capillary-column electron-capture gas chromatography. In most cases, lipid content also was measured in biological material analyzed for organochlorine pesticides.

Typically, 10 percent of the samples collected as part of a NIWQP investigation were field blanks or replicates for quality assurance. Blank samples were used to detect sample contamination introduced during collection, preparation, and shipping. Field replicate samples were collected to detect variability due to sampling method and laboratory variability. Split samples were used to check the precision of analytical results reported by the laboratory.

DATA SYNTHESIS

A data base of chemical, physical, and biological data collected during the 26 NIWQP investigations was created, and the data were analyzed by using a geographic information system (GIS) and statistical and geochemical methods. Information on how to obtain the data base and the methods used by the data-synthesis team in creating the data base and the procedures used in analyzing the data are described in this section.

DATA BASE

AVAILABILITY

The data base has been made available to the scientific community (and public) through the World Wide Web on the NIWQP home page, at URL <<http://www.usbr.gov/niwqp>>. (Additional information about the program can be located by using search engines to find the term "NIWQP" on the Internet.)

For personal-computer-based systems, the data base is available as dBase III files and ASCII (tab-delimited) tables. For personal-computer-based system and UNIX-based workstations that use Ingres or Oracle, SQL scripts and data files are available to create the tables and views.

INTRODUCTION AND STRUCTURE

The data base was designed as a relational data base so that relations among contaminant concentrations in biota, water, and bottom sediment could be explored. In addition to chemical data, the completed data base contains geological, hydrological, climatological, and cultural data that can be used to describe the 26 NIWQP study areas and specific data-collection sites within those areas. These data were collected and merged into a common data base maintained by using the

Ingres relational data-base management system on UNIX workstations. All data-collection sites are georeferenced by latitude and longitude so that the data sets can be included in a GIS.

Seiler and Skorupa's (2001) data dictionary describes the structure (fig. 3) and variables in the data base. Critical linking variables are area, subarea, and site-identification fields. Each of the 26 NIWQP areas was assigned a short identifying name in the area field. If an area had been divided into hydrologically distinct subareas, each of the subareas was assigned a short identifying name in the subarea field. The area table includes information about the geology, climate, land-use, and other physiographic and cultural data.

The data dictionary (Seiler and Skorupa, 2001) is available on-line as a portable document format (pdf) file at URL <<http://pubs.water.usgs.gov/ofr00513>>.

The site table links the analytical chemical data with the area table and contains specific information about each site where data were collected. Data in this table include the type and name of the site; altitude, latitude, and longitude; and a field indicating whether the site is a reference site or a site in or downstream from an irrigated area. Each data-collection site for water and bottom sediment was assigned a unique site-identification number based on the latitude and longitude or the downstream-order number assigned by the USGS.

Different components of the chemical analyses are stored in different tables. For example, for every analysis, field values such as discharge, specific conductance, and temperature are stored in the data base, but only about 1 percent of the analyses have available pesticide data. The different tables are linked by site identification, matrix, date, and time fields; these fields form a unique combination that allows the different tables and components of a chemical analysis to be recombined.

Biological samples commonly were not collected in exactly the same place as the water and sediment samples. So that relations among contaminant concentrations in water, sediment, and biota could be explored, biological sites were assigned the site-identification number of the nearest appropriate site where surface water or sediment had been collected. For instance, fish samples from a stream or pond could be assigned the site-identification number for a stream site several miles upstream or downstream or for a site at the pond outflow. Biological samples were not always assigned a site-identification number. For example, bird samples from a pond where no water samples had been collected were not assigned a site-identification number. Of the 8,217 inorganic samples of biological material in the data base, 3,248 were not linked to a site where water and sediment data were collected (fig. 3.) and 351 of the 1,088 organic samples of biological material were not linked.

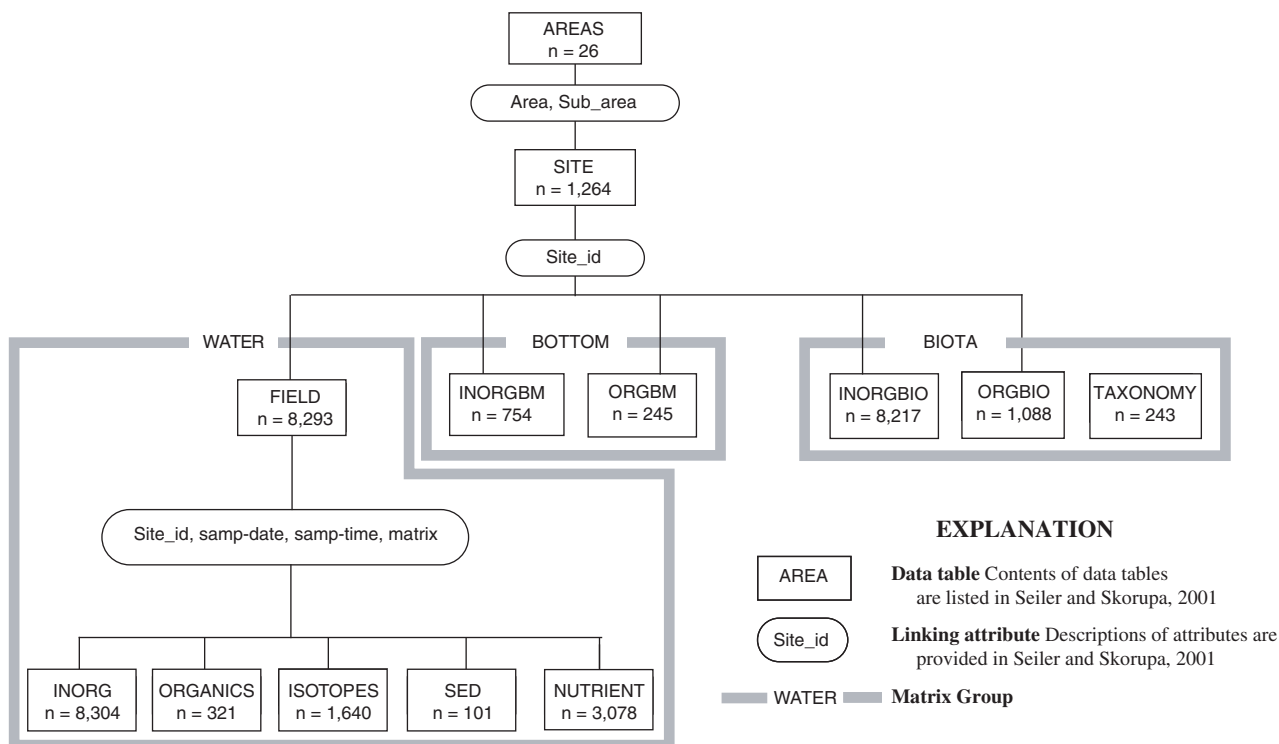


FIGURE 3.—Structure and linking attributes of National Irrigation Water Quality Program (NIWQP) data base. *n*, number of records. Note that 3,248 of the 8,217 samples in the INORGBIO table are not linked to other tables through the site-id variable and 351 samples in the ORGBIO table are not linked.

The following example shows how the structure of the data base allows the relations between different types of data to be explored. Data stored in the INORGBIO table (fig. 3) indicate that the average selenium concentration for 16 American Avocet eggs collected in June 1988 from Rasmus Lee Lake was 72 $\mu\text{g/g}$. The USGS site identification number of the nearest appropriate site where water samples were collected, '424435106370300', is stored with the biological data as the attribute 'siteid'. The attribute 'siteid' links the biological data to physical and chemical data in other tables. Using the value for the siteid attribute from the INORGBIO table to locate samples in the FIELD table indicates that on June 22, 1988 at 1240 a water sample was collected at the site and that the specific conductance of the water was 10,100 microsiemens per centimeter ($\mu\text{S/cm}$) at 25 °C. Data in the INORG table indicate that arsenic, selenium, and uranium concentrations were 2, 120, and 35 $\mu\text{g/L}$, respectively, for that site at that date and time. Data for that siteid in the SITE table indicate the site is in the Kendrick Reclamation Project area (*H*) and that the bedrock at the site has been mapped as Upper Cretaceous marine sedimentary rocks belonging to the Austin and Eagle Ford Groups. Data for the Kendrick Reclamation Project area in the AREA table indicate free water surface evaporation (FWSE) in the area is 42-45 inches per year, that alfalfa is the principal crop, and that the irrigation season typically begins at the beginning of May.

SOURCES OF DATA

All area-specific chemical and biological data collected by the NIWQP were reported in USGS publications (table 1). These publications were the principal sources of data for information describing the study areas and individual sampling sites within the study areas. Information on evaporation rates and geologic units in the areas were obtained by overlaying climatic and geologic maps on maps of the individual data-collection sites. Some area-specific information, such as the typical start and end of the irrigation season and whether specific lakes are terminal or flowthrough, was obtained directly from members of the study teams.

The chemical data collected were stored in several different data bases. Chemical data for all constituents in water and pesticides in sediment were stored in the USGS National Water Information System (NWIS) data base. Inorganic data for sediment were stored in a USGS Geologic Division data base, and data for biological material were stored in personal-computer spreadsheets and data bases in USFWS field offices. Data from these separate data bases were collected and merged into a common data base on UNIX workstations.

Information describing sites where water-quality and most bottom-sediment samples were collected was stored in NWIS. This site information was included automatically during retriev-

als of chemical analyses. For some analyses of bottom sediment, information describing the data-collection sites was not stored in NWIS. Site information for those sites was manually added to the site table.

NWIS is maintained on computers in the USGS Water Resources Division District Offices. Chemical data for water were retrieved from NWIS maintained in the State where the NIWQP investigations were done. For all sites sampled during a NIWQP investigation, chemical data collected during 1986-93 were retrieved by using lists of site-identification numbers obtained from the published reports or from the study-team members.

Chemical analyses of bottom sediment were obtained principally from USGS reports (Severson and others, 1987; Harms and others, 1990; Stewart and others, 1992). Tables of ASCII data were created from these reports, either by scanning the tables and using optical character-recognition software or by using the floppy disk provided with the report. Some unpublished data were provided from the analyzing laboratory as ASCII tables.

Although biological data are stored in USFWS field offices, data from field offices were not entered in the data-synthesis data base because of difficulties in collating data from multiple formats and because of uneven verification. Biological data were entered by creating personal-computer spreadsheets from the original laboratory analytical-results sheets. Some additional data were obtained from the published reports and USFWS study-team members. Data in the spreadsheets then were incorporated into the Ingres data base.

DATA MANIPULATION AND QUALITY ASSURANCE

Data files for water and bottom sediment were manipulated and verified using P-STAT (P-STAT, Inc., 1990) statistical software on the USGS Water Resources Division Nevada District Prime computer. Subsequently the P-STAT files were processed into structured query language (SQL) scripts to create Ingres relational-data-base tables.

Data manipulation involved checking the data against published and draft reports to verify that all analyses were in the data base. Erroneous entries were removed from the NIWQP data base when found. A study-team member was informed of any problems found in the data base. Where data from the quality-assurance samples had been mixed with data from environmental samples, the two types of data were manipulated to separate them. Analyses that were not collected as part of a DOI investigation but were collected at a DOI site were included in the NIWQP data base but were flagged because the data were not verified against published reports.

Personal-computer-based spreadsheets containing biological data were converted to P-STAT files for ordering of columns and adding site-identification numbers and other types of data cleanup or manipulation. These P-STAT files were then converted to an Ingres relational data base.

Quality assurance was done by checking all parameters for 20 percent of all DOI water samples from each area against published data. All discrepancies between published reports and the data base were investigated and resolved, in some instances by calling the study-team leader. In most study areas, less than one percent of the checked values in the NIWQP database differed from published values. For example, when more than 2,000 data values from 93 analyses from the Stillwater Wildlife Management Area (Nevada) were checked, 11 discrepancies were found. In the San Juan River area (New Mexico) only one discrepancy was found in more than 400 individual data values from 11 analyses. The small percentage of errors discovered indicate that the data base accurately reflects the published data.

All discrepancies were checked carefully for evidence of systematic errors. In some cases errors were found and corrected in the programs that manipulated the data from the NWIS database. For example, in one case data manipulation resulted in loss of "<" symbols from one parameter. In another case, most of the land-surface altitudes in the Salton Sea area were wrong because the programs did not handle altitudes less than zero correctly. In other cases, published data were missing from the NIWQP, and NWIS, databases. In those cases the missing data were added to the NIWQP database and the study area team-leader was advised that published data were missing from the NWIS database. Many of the discrepancies found resulted from word-processing and verification errors in published reports; the data in the NIWQP and NWIS databases were correct. For example, the negative sign in δD and $\delta^{18}O$ values in one report had been converted to "<" symbols.

Because relatively few (only about 700) bottom-sediment samples were analyzed, all selenium, arsenic, and molybdenum concentrations in the <0.062-mm fraction were checked against published values. Very few errors in these values were found, only 5 in more than 1,000 values checked differed from published values. In addition, all constituent concentrations were checked against published values for two randomly selected samples from each area. If these checks revealed a disproportionately high number of errors in a study area, then all values for all analyses from that study area were checked.

Because the biological part of the data base was created from the original laboratory reports, those reports were checked against published reports for accuracy of wet-weight to dry-weight conversions, for sampling dates, and in some instances to verify the taxonomic identification of individual samples. Also, after data from each original laboratory report had been entered into the master biotic data base (according to uniform conventions for data rounding and the reporting of values below

detection limits), each datum cell was verified individually for keypad-entry errors by independent members of the data-entry team. Thus, ultimately each datum entry was reviewed for accuracy by no fewer than three members of the data-entry team.

DATA INTERPRETATION

STATISTICAL METHODS

Summary statistics used consisted of resistant measures of central tendency (median) and spread (interquartile range). Because many of the measured contaminant concentrations are less than the reporting limit and because most constituents have multiple reporting limits, robust methods (Helsel and Hirsch, 1992) such as log-normal maximum-likelihood estimation were used to compute estimates of summary statistics.

Box plots were used to compare and contrast the distribution of contaminant concentrations among the different study areas. Box plots show only the individual data points if eight or fewer data points are available. The lower limit of the box plots is the reporting limit; that is, censored data values (concentrations that are less than the reporting limit) are not shown. Whiskers on the boxes are drawn to the 10th and 90th percentiles; observations less than the 10th percentile and greater than the 90th percentile are plotted individually.

For comparing contaminant concentrations among the different study areas, all NIWQP samples except quality-assurance samples were used to calculate summary statistics. Where characterization of contaminant concentrations at an individual site was necessary, the most recent analysis made was selected instead of calculating the median or average concentration for the site. This decision was made because, at many sites, a combination of a limited number of analyses and censored data meant an accurate estimate of the median could not be made even using robust methods.

The software package Pirouette (Infometrix, 1992) was used for pattern-recognition, principal-components analysis (PCA), and classification modeling of data. These methods are used often for multivariate analysis of large data bases (Meglen and Sistko, 1985).

PCA is a mathematical technique for reducing a complex system of correlations into fewer dimensions. Meglen (1991) describes the use of PCA to examine large multivariate data bases. A matrix of correlations is obtained from the original data set and then decomposed using eigen analysis into two matrices—the scores matrix and the loadings matrix. The scores and loading matrices are used to derive the best, mutually independent axes (principal components) that describe the data set. The scores matrix shows relations among the samples, and the loadings matrix contains information about relations among the variables (Meglen, 1991).

Blythe-Still-Casella binomial confidence intervals (Blythe and Still, 1983; Casella, 1987) were calculated using the software package StatXact4 (Cytel Software Corp., 2000), as were all Fisher Exact test statistics.

GEOCHEMICAL METHODS

Geochemical analysis of data was done principally by using the computer program SNORM (Bodine and Jones, 1986). For each analysis, the program calculates the salt norm, which is the quantitative ideal equilibrium assemblage that would crystallize if water evaporated completely at 25°C and at a pressure of 1 bar with atmospheric concentrations of carbon dioxide (Bodine and Jones, 1986). Characterization of water composition by an assemblage of salts provides more information about solute origin and subsequent interaction than major cation–anion predominance graphs provide. Salt-norm data can be useful in evaluating the similarities and differences in water from geochemically different environments.

GEOGRAPHIC INFORMATION SYSTEMS

A GIS was used to store and analyze spatially oriented digital data. GIS data layers (sets of spatially located digital data) showing land use, mean annual precipitation, free-water-surface evaporation, and geology of the United States were obtained or created to use for data analysis. Seiler and others (1999) provided a list of the coverages and details of their creation.

BIOLOGICAL METHODS

Data management and data analysis for risk assessment of selenium concentrations in bird eggs relied primarily on two software packages, Quattro Pro and Statistica. Quattro Pro is a general-purpose spreadsheet program, and Statistica is a comprehensive, modular data-management, statistical-analysis, and graphics program. Statistica conventions and operations are described in a manual by StatSoft (1995). Data analyses for the risk assessment were derived primarily through use of five Statistica modules: (1) Data Management, (2) Basic Statistics, (3) Nonparametric Statistics, (4) Nonlinear Estimation, and (5) Factor Analysis.

Pairwise correlations of concentrations of inorganic constituents in bird eggs are presented in a correlation-matrix format (Sokal and Rohlf, 1995; StatSoft, 1995). Data were log transformed prior to calculation of pairwise product–moment correlation coefficients, and the matrix cells were populated with the probability values (*p*-values) for the corresponding correlation coefficient. Because the correlation matrix is an initial screening of the data for potential associations that might merit further examination, a slightly relaxed *p*-value criterion of *p* < 0.10 was used to identify potentially significant pairwise correlations.

Exploratory factor analysis was done using the Factor Analysis module of the Statistica program. Factor analysis was performed on untransformed chemical data. The principal-components method was used for factors extraction and an upper limit of the top two factors exceeding the Kaiser criterion (eigenvalues > 1) was imposed for factor selection and graphical display of factor loadings. Factor analysis is a technique for simultaneously examining the interrelations or structure of multiple variables. Here, factor analysis is used to provide a graphical display of the relative degree to which different inorganic constituents appeared to be, or not to be, highly correlated with terata of avian embryos. Afifi and Clark (1996) provided a detailed statistical explanation of factor analysis, and the Statistica algorithms and options for completing factor analysis are documented in the manual by StatSoft (1995).

Logistic-regression analysis was used to examine exposure-response or dose-response relations. Logistic regressions were performed using the Nonlinear Estimation module of Statistica. The applicable general logistic model with one independent variable is

$$p = e^{(\beta_0 + \beta_1 X)} / [1 + e^{(\beta_0 + \beta_1 X)}] \quad (1)$$

where *p* is probability of a specific outcome,

$\beta_{0,1}$ are regression coefficients, and

X is the independent variable.

This model is particularly useful for describing the relation between a continuous independent variable (such as the concentration of a chemical in the egg) and a binary or binomial response variable (such as the presence or absence of an adverse effect). As used here, the model estimates the probability of response associated with particular exposures or doses of a chemical. Therefore, logistic regression can be quite useful for risk assessment. Both the regression coefficients (β_0 and β_1) and the precision (standard errors) of the coefficients are calculated by Statistica. In addition, Statistica can be used to plot the logistic-regression curves and to test model significance (by a model chi-square calculation). Documentation for the Statistica logistic-regression algorithms and conventions was presented by StatSoft (1995).

Power analysis was done to assess the power of the NIWQP studies to detect at least one teratogenic (deformed) embryo. Power analysis is based on an equation derived from the laws of binomial probability. Sokal and Rohlf (1995) provided a relevant review of these laws.

DATA SYNTHESIS

NATIONAL IRRIGATION WATER QUALITY PROGRAM DATA BASE

DESCRIPTIVE SUMMARY

A descriptive summary of the contents of the NIWQP data base is provided in tables 4 through 9. The number and types of individual data-collection sites are summarized in table 4. Water and, bottom sediment were collected at 1,264 sites within the 26 NIWQP study areas. Of these sites, 705 of the sites were on rivers, streams, canals, or drains; 211 sites were lakes, reservoirs, and ponds; and 348 sites were wells, springs, and subsurface drains. Of the 348 ground water sites, 315 were wells and 14 were springs. Nineteen subsurface drains were sampled, all from the middle Green River Basin (N).

There are 130 reference sites. Reference sites are upstream from irrigated land within a study area. Of the 130 reference sites, 39 are source-water sites. Source water sites are surface water sites upstream from irrigated lands which represent the water used for irrigation.

Biological samples were collected at 685 sites. At 366 of the sites water and bottom sediment samples were also collected. At 319 sites only biological samples were collected.

Information about the number and types of analyses and analytes from surface-water sites is summarized in table 5. The data base contains results from almost 4,000 surface-water samples collected as part of the NIWQP investigations and more than 3,000 surface-water samples that were collected for other purposes at the same sites. The number and types of analyses and analytes from ground-water sites are summarized in table 6 and from bottom-sediment sites, in table 7. The number and types of biological analyses in the data base are summarized in tables 8 and 9.

Analytes listed in tables 5 through 8 represent classes of chemicals that are in the data base but are not the only analytes in the data base. For example, analyses are available for more than 100 pesticides and organochlorine compounds, although table 5 lists only three pesticides (DDT, parathion, and 2,4-D).

STATISTICAL BIAS

The NIWQP data base is statistically biased. One type of bias results from sampling sites not having been selected randomly. The general project design called for a focus primarily on drains although at least one reference site and at least one receiving stream also were to be sampled. In a few areas, however, many of the sampling sites selected were along main channels of large rivers because they had been used in earlier investigations and therefore had a longer record of sampling for comparison. Preferential selection of main-channel sampling sites increases the number of samples having low contaminant concentrations in

TABLE 4. Water and bottom-sediment data-collection sites in National Irrigation Water Quality Program study areas

Type of data-collection site	Number of sites
Rivers, streams, canals, surface drains	705
Lakes, reservoirs, ponds	211
Wells	315
Springs	14
Subsurface drains	19
Total.....	¹ 1,264

¹ Of these sites, 130 are reference sites, and 39 are source-water sites.

TABLE 5. Description of surface-water analyses in National Irrigation Water Quality Program data base

Description	Number of samples analyzed ¹	
	Filtered sample	Unfiltered sample
Representative Inorganic Analyses		
Major-element chemical analyses	1,661	0
Residue on evaporation at 180 degrees Celsius	1,662	0
Arsenic	1,285	146
Boron	1,783	108
Copper	1,163	88
Molybdenum	1,221	38
Selenium	2,057	545
Uranium	634	247
Zinc	1,288	87
Stable isotopes (deuterium and oxygen-18)	0	221
Representative Nutrient Analyses		
Ammonia	782	0
Nitrite/nitrate	1,408	458
Phosphate	562	0
Representative Pesticides Analyses		
DDT	0	110
Parathion	0	167
2,4-D	0	178

¹ A total of 3,869 surface-water samples were analyzed during National Irrigation Water Quality Program investigations. Analytical results for an additional 3,634 surface-water samples from the same sites but which were not collected as part of a National Irrigation Water Quality Program investigation are in the database but were not included in this summary description.

TABLE 6. Description of ground-water analyses in National Irrigation Water Quality Program data base

Description	Number of samples analyzed ¹
Major-element chemical analyses	441
Residue on evaporation at 180 degrees Celsius	441
Arsenic	348
Boron	483
Copper	149
Molybdenum	344
Selenium	695
Uranium	116
Zinc	192
Stable isotopes (deuterium and oxygen-18)	398
Representative Nutrient Analyses²	
Ammonia	196
Nitrite/nitrate	307
Phosphate	104

¹ A total of 789 ground-water samples were analyzed during National Irrigation Water Quality Program investigations. Analytical results for an additional 125 ground-water samples from the same sites but were not collected as part of a National Irrigation Water Quality Program investigation are in the database but were not included in the summary description.

² All samples were filtered except those for stable isotopes.

TABLE 7. Description of bottom-material analyses in National Irrigation Water Quality Program data base

[Abbreviation and symbol: mm, millimeter; <, less than]

Description	Number of samples analyzed	
	Fine fraction (<0.062 mm)	Coarse fraction (<2 mm)
Representative Inorganic Analyses¹		
Arsenic	345	358
Boron	298	355
Copper	345	358
Molybdenum	345	358
Selenium	346	358
Uranium	326	256
Zinc	345	358
Representative Organic Analyses²		
DDT	0	223
Parathion	0	36
2,4-D	0	16

¹ A total of 707 samples were analyzed for inorganic constituents, 349 in the fine fraction and 358 in the <2mm fraction.

² A total of 245 samples were analyzed for pesticides, all in the <2mm fraction.

the data set. Sites on main channels of large rivers tend to have lower contaminant concentrations than drains or ponds because of lower evaporation rates and greater dilution of added contaminants. This type of sample bias has occurred in the Lower Colorado River valley and San Juan River area reconnaissance investigations. In the Lower Colorado River valley, 8 of the 11 samples were from the main stem of the Colorado River or near it on river diversions. In the San Juan River area, almost 25 percent of the samples within and downstream from irrigated areas were from main-channel river sites (Seiler, 1995).

In some reconnaissance investigations, contaminants were deliberately being sought, and sites were selected because of the likelihood that contaminant concentrations would be high. Preferential selection of such sampling sites increases the number of samples having high contaminant concentrations in the data set.

Another type of bias results from sites not being sampled at the same frequency. During process-oriented investigations, typically the most contaminated sites were sampled more frequently than the least contaminated sites. A bias toward sampling the most contaminated sites increases the number of samples having high contaminant concentrations. This type of sample bias is seen in data from the Kendrick Reclamation Project investigation, in which 20 percent of the 568 surface-water samples were from a single site in a selenium-contaminated lake.

In spite of potential problems caused by bias, the data set was used to determine the degree of contamination in each study area. Areas where sample bias could noticeably raise or lower summary descriptors of contaminant concentrations were identified by examining the data set. During data analysis, the potential effects of sample bias in an area were considered. For example, tools for identifying contaminated areas were not rejected during their construction if their predictions failed to match observations in areas where sample bias occurred.

The data base cannot be used to describe baseline conditions in the Western United States because the 26 study areas were selected due to known, suspected, or potential irrigation-induced contamination. Selenium was not the only contaminant that resulted in study areas having been selected for investigation. Some areas were selected because of previously known salinity, arsenic, or pesticide problems.

LIMITATIONS OF DATA

Data collection in the reconnaissance and detailed investigations was not specifically designed to meet the objectives of the data-synthesis project. The data collected depended on individual project objectives. For the purposes of this data synthesis, the data collected during the reconnaissance and detailed investigations are less than ideal in six principal ways.

TABLE 8. *Description of biological-sample analyses in National Irrigation Water Quality Program data base*

Description	Number of samples analyzed
Representative Inorganic Analyses¹	
Arsenic	7,706
Mercury	7,671
Selenium	8,127
Representative Organic Analyses²	
DDT	853
Arochlor 1254	183

¹ A total of 8,217 samples were analyzed for inorganic constituents.

² A total of 1,088 samples were analyzed for organic constituents.

TABLE 9. *Taxa collected for inorganic analysis in National Irrigation Water Quality Program study areas*

[Symbol: —, none]

Study area		Number of taxa							
Identifier ¹	Name	Plants	Plankton	Aquatic invertebrates	Fish	Amphibians and reptiles	Birds	Mammals	Total
A	American Falls Reservoir, Idaho	3	—	6	28	—	35	—	72
B	Angostura Reclamation Unit, South Dakota	8	—	6	146	—	8	—	168
C	Belle Fourche Reclamation Project, South Dakota	11	—	8	128	—	18	—	165
D	Columbia River Basin, Washington	18	—	9	74	—	53	—	154
E	Dolores–Ute Mountain area, Colorado	54	1	61	198	—	34	1	349
F	Gunnison River Basin–Grand Valley Project, Colorado	48	—	35	608	4	213	1	910
G	Humboldt River area, Nevada	37	—	10	42	—	93	—	182
H	Kendrick Reclamation Project, Wyoming	53	—	45	84	—	484	—	666
I	Klamath Basin Refuge Complex, California–Oregon	15	—	42	42	—	112	—	211
J	Lower Colorado River valley, California–Arizona	28	—	—	31	—	12	—	71
K	Lower Rio Grande valley, Texas	2	—	5	23	7	1	—	38
L	Malheur National Wildlife Refuge, Oregon	5	—	7	11	—	62	—	85
M	Middle Arkansas River Basin, Colorado–Kansas	8	—	7	59	—	110	—	184
N	Middle Green River Basin, Utah	285	—	80	232	1	631	3	1,232
O	Middle Rio Grande, New Mexico	8	—	12	20	—	45	—	85
P	Milk River Basin, Montana	10	5	10	2	—	23	—	50
Q	Owyhee–Vale Reclamation Project areas, Oregon–Idaho	31	—	24	45	—	29	—	129
R	Pine River area, Colorado	40	4	48	184	—	41	7	324
S	Riverton Reclamation Project, Wyoming	16	—	9	73	—	46	—	144
T	Sacramento Refuge Complex, California	8	—	30	27	—	71	—	136
U	Salton Sea area, California	42	—	39	41	8	294	—	424
V	San Juan River area, New Mexico	15	—	15	86	9	63	—	188
W	Stillwater Wildlife Management Area, Nevada	268	—	54	93	—	629	—	1,044
X	Sun River area, Montana	46	—	163	72	6	784	—	1,071
Y	Tulare Lake Bed area, California	9	—	11	33	—	22	—	75
Z	Vermejo Project area, New Mexico	18	—	14	28	—	—	—	60
Total		1,086	10	750	2,410	35	3,913	12	8,217

¹Used in figure 2 to show locations of study areas.

SAMPLING-SITE AGREEMENT

The first limitation of the data is that water and biological samples commonly were not collected in the same locations. For example, plants, insects, fish, and bird tissue, but no water samples may have been collected from a particular pond. This lack of complementary data was particularly problematic for data from the reconnaissance investigations. Typically, during detailed investigations after confirming that contamination was occurring, USGS and USFWS personnel collected additional samples from sites known to be contaminated. To address this limitation and evaluate relations between contaminant concentrations in water and biota, biological sampling sites were assigned the site-identification number of the nearest appropriate site where surface water or sediment were collected.

MATRIX SELECTION

A second limitation of the data results from the data being used in multiple ways. The USGS typically collected 0.45- μm filtered water samples to determine "dissolved" contaminant concentrations for trace elements in water. The USFWS, however, uses total-contaminant concentrations in water because most water-based criteria for assessing potential effects on aquatic life are based on toxicity tests that use whole-water concentrations. The reason for the lack of comparable methods is that the sampling was done for different purposes. Comparison of contaminant concentrations with biological effect levels is only one use of the data. Water-quality data also commonly are used by the USGS in geochemical-speciation models, which require that concentrations are measured using filtered samples.

Comparisons between biological effect levels based on whole-water samples and contaminant concentrations determined for filtered water are problematic. However, for some contaminants, total- and filtered-contaminant concentrations in water are nearly identical, thus allowing for comparison to biological effect levels (see section titled "Relation Between Total- and Filtered-Contaminant Concentrations in Surface Water," p. 44). Also, at least for metals, the U.S. Environmental Protection Agency (USEPA) recommends that dissolved-contaminant concentrations be used to set and measure compliance with water-quality standards and criteria. The agency also determined correction factors that express the percentage of "dissolved" to total-recoverable metal (M.G. Prothro, U.S. Environmental Protection Agency, written commun., 1993).

SPECIES SELECTION

A third limitation of the data is that the taxa collected were not consistent. For example, no birds were collected during the lower Rio Grande valley and Vermejo Project area reconnaissance studies or during the San Juan River area detailed investigation. In some areas, no shorebirds were collected, and in one area, only blackbirds were collected. Although in some areas

specific taxa may not have been present, the inconsistency also can result from other factors. In some areas, the taxa collected depended on the background and specific interests of the field biologist in charge of sample collection.

A fourth limitation is that in some areas samples were not collected from all important feeding guilds. The principal exposure route to higher organisms for most contaminants is through the food they eat rather than the water they drink or live in. Because some feeding guilds are not particularly susceptible to contaminated water, biological problems would be missed if samples were collected only from those feeding guilds. For example, red-winged blackbirds are probably poor indicators of selenium contamination of the wetlands they live in because they consume seeds, spiders, and terrestrial insects. Because of their invertebrate diet and where they forage, however, shorebirds such as black-necked stilts and American avocets are good indicators of selenium contamination of wetlands. Herbivorous birds, such as ducks or American coots, may be good indicators of contamination from trace elements such as arsenic that accumulate more in plant than insect tissue. The data collected by the reconnaissance and detailed investigations would have been more useful for the data synthesis if all reconnaissance and detailed investigations had collected representative fish and birds from specific feeding guilds. If a specific member of a guild was unavailable in an area, substitutions of another species from the same feeding guild could have been made.

TISSUE SELECTION

A fifth limitation of the data is lack of consistency among study areas in the types of tissue that were sampled. Typically, liver tissue was sampled in adult and juvenile birds, but, in one area, a combination of liver and kidney tissue was analyzed. Meaningful comparison of data between study areas is difficult when tissue types do not match because it is not known whether observed differences in contaminant concentrations is due to tissue differences or habitat or exposure differences.

A sixth limitation of the data when assessing the effects of selenium is that few or no bird eggs were collected in some of the study areas. In 21 of the 26 study areas, 10 or more bird eggs were analyzed but in two study areas, no eggs were collected. Egg tissue is useful to collect for two reasons. Survivor bias does not affect eggs because the most contaminated eggs are just as likely to be collected as the least contaminated eggs. In addition, the selenium in the egg is likely to have originated in the area where the egg was collected. With few exceptions, adult birds typically establish residency in an area before laying their eggs; they rest, court, mate, make their nest, and then lay eggs. In the time between arrival of the mating pair and egg laying, selenium accumulated in other areas is depurated fairly quickly from the adult birds. Organochlorine pesticides are not rapidly depurated, however, so the lack of egg data would not be as important if pesticides were being assessed.

IDENTIFICATION OF CONTAMINANTS IN WATER AND SEDIMENT

STANDARDS, CRITERIA, AND GUIDELINES USED

Standards, criteria, and guidelines from multiple sources were used to evaluate contaminant concentrations in water and sediment. The values used for comparison by the data synthesis team and the sources for the values are given in table 10. For surface-water sites, comparisons were made principally with the USEPA freshwater aquatic-life chronic criteria (U.S. Environmental Protection Agency, 1986b, 1987). Because freshwater aquatic-life criteria have not been promulgated by the USEPA for boron, molybdenum, and uranium, the criteria used for those elements were from other sources. Boron and molybdenum were compared to criteria promulgated by the California State Water Resources Control Board (1988) for regulation of agricultural drainage to the San Joaquin River. Uranium concentrations were compared to the proposed Canadian water-quality objective for the protection of aquatic life (Environment Canada, 1983).

For aluminum, the chronic criterion listed in table 10 is valid only within a pH range of 6.5 to 9.0. Aluminum concentrations were not compared to criteria if the pH of the sample was not within that range or was not measured.

For cadmium, chromium(III), copper, lead, and zinc, the acute- and chronic-criteria values listed in table 10 assume that the hardness of the water is 100 mg/L. For silver, the acute-criterion also assumes that the hardness is 100 mg/L. Because, for these trace elements, applicable criteria depend on the water hardness, comparisons to criteria for a sample can be made only if analytical results for calcium and magnesium are available. (Water hardness was calculated from the calcium and magnesium concentrations, and measured trace elements were compared to criteria calculated on the basis of that hardness.)

The chronic criteria for arsenic and chromium depend on their oxidation state, which was not measured as part of NIWQP investigations. Concentrations of these trace elements were compared to applicable criteria by assuming that all the element was in the most toxic oxidation state. Therefore, the percentage of exceedances determined is a maximum. Considering thermodynamics, most of the arsenic in oxygenated surface waters would be in the less toxic oxidation state, arsenic(V), and most chromium would be in the most toxic state, chromium(VI). The percentage of exceedances determined for chromium therefore is assumed to be representative of what would have been determined if the oxidation state had been measured.

The above-listed metals vary substantially in their tendencies to bioaccumulate, however, the USEPA aquatic-life criteria do not account for this. The criteria are produced using a testing protocol that does not include dietary exposure, therefore the criteria listed in table 10 will be overestimates of the toxicity

TABLE 10. Contaminant standards, criteria, and guidelines used by data-synthesis team to evaluate National Irrigation Water Quality Program water and sediment data

[Abbreviations and symbol: µg/L, microgram per liter; µg/g, microgram per gram; —, no standard, criterion, or guideline]

Chemical constituent	Maximum contaminant level ¹ (µg/L)	Acute criterion ² (µg/L)	Chronic criterion ² (µg/L)	Qualitative sediment guideline ³ (µg/g)
Inorganic constituents				
Aluminum	—	⁴ 750	⁴ 87	—
Arsenic	⁵ 10	—	—	22
Arsenic(III)	—	360	180	—
Arsenic(V)	—	⁶ 850	—	—
Boron	⁷ 600	—	⁸ 550	—
Cadmium	5	⁹ 3.9	⁹ 1.1	—
Chromium	100	—	—	200
Chromium(III)	—	⁹ 1,700	⁹ 210	—
Chromium(VI)	—	16	11	—
Copper	1,300	⁹ 18	⁹ 12	90
Lead	15	⁹ 82	⁹ 3.2	55
Molybdenum	⁷ 40	—	⁸ 19	4.
Selenium	50	20	¹⁰ 5/3	¹¹ 1.4/2
Silver	⁷ 100	⁹ 4.1	.12	—
Uranium	¹² 30	—	¹³ 300	5.3
Zinc	⁷ 2,000	⁹ 120	⁹ 110	180
Pesticides				
DDD	—	⁶ 0.6	—	—
DDE	—	⁶ 1,050	—	—
DDT	—	¹⁴ 1.1	¹⁴ 0.001	—
Endrin	2	.18	.0023	—
Lindane	.2	2	.08	—
Malathion	—	—	.1	—
Toxaphene	3	¹⁵ 73	¹⁵ .0002	—

¹ Drinking-water standard for protection of human health. From U.S. Environmental Protection Agency (1996) except as noted.

² Criterion for protection of aquatic life. From U.S. Environmental Protection Agency (1986b) except as noted.

³ Guideline is upper limit of 95 percent expected range in soils from Western United States from Shacklette and Boergen (1984).

⁴ Criterion is pH dependent; value shown is valid for pH = 6.5–9.0.

⁵ In October 2001 the Maximum Contaminant Level was lowered from 50 to 10 micrograms per liter (U.S. Environmental Protection Agency, 2001).

⁶ Data are insufficient to develop criteria; value shown is Lowest Observed-Effect Level.

⁷ Criterion is lifetime health advisory (U.S. Environmental Protection Agency, 1996).

⁸ Chronic criterion from California State Water Resources Control Board (1988).

⁹ Criterion is hardness dependent; value shown is valid for hardness of 100 milligrams per liter CaCO₃.

¹⁰ The value 5 µg/L is from U.S. Environmental Protection Agency 1987 and is the chronic criterion for the protection of freshwater aquatic life (fish and aquatic invertebrates). The value 3 µg/L is a guideline used for the protection of wildlife (semi-aquatic birds and mammals).

¹¹ The value of 1.4 µg/g is the qualitative sediment guideline and the value of 2 µg/g is the ecological sediment guideline (Lemly, 2002).

¹² Criterion from by U.S. Environmental Protection Agency (2000).

¹³ Recommended Canadian water-quality objective for protection of aquatic life (Environment Canada, 1983).

¹⁴ Criterion for total DDT (sum DDD + DDE + DDT). From U.S. Environmental Protection Agency (1980).

¹⁵ Criterion from U.S. Environmental Protection Agency (1986a).

thresholds to the extent that the metals tend to bioaccumulate. The USEPA criteria for selenium are an exception to this generalization. The selenium criteria were based on field data rather than on the standard bioassay protocol. In the case of selenium, the standard protocol produced a chronic criterion of 9.7 $\mu\text{g/L}$ (selenate basis), as opposed to the field-based adopted criterion of 5 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 1987).

For selenium in water, two criteria were used. The first is the USEPA chronic criterion for selenium (5 $\mu\text{g/L}$), a general standard for the protection of freshwater aquatic life (U.S. Environmental Protection Agency, 1987). USEPA's aquatic-life criteria were derived to protect fish and other instream aquatic life but neglect semi-aquatic wildlife (amphibians, reptiles, birds, and mammals), which are more sensitive to the effects of bioaccumulation (Peterson and Nebeker 1992). The second criterion used is 3 $\mu\text{g/L}$. This criterion has been derived independently by several authors for wildlife exposed to contaminated lentic ecosystems. Three $\mu\text{g/L}$ is the low end of a range given by Skorupa and Ohlendorf (1991), who stated that water containing 3 to 20 $\mu\text{g/L}$ total-recoverable selenium is hazardous to some species of birds under some circumstances. Peterson and Nebeker (1992) report that dissolved selenium concentrations in water greater than 2.1 $\mu\text{g/L}$ appear to produce adverse effects in some species of wildlife. Based on bioenergetic modelling, DuBow (1989) concluded that a criterion of 2.8 $\mu\text{g/L}$ for dissolved selenium was required to protect mallard ducks from adverse reproductive effects. Based on a sediment selenium model, Van Derveer and Canton (1997) calculated a 3 $\mu\text{g/L}$ criterion for protection of aquatic life in lentic-aquatic systems rich in organic carbon, such as Kesterson Reservoir, California. Van Derveer and Canton's (1997) result agreed with prior field observations at the Highway 158 arm of Belews Lake, North Carolina, where fish sublethal effects were associated with 3-4 $\mu\text{g/L}$ (U.S. Department of the Interior, 1998).

The criteria used for trace elements and pesticides in ground-water samples are USEPA freshwater aquatic-life chronic criterion and MCL's promulgated for drinking water. For boron, molybdenum, silver, and zinc, drinking-water MCL's have not been promulgated, and concentrations of these elements in ground water were compared to the lifetime health advisory. Although comparisons were made to drinking-water standards, most of the ground-water sites are subsurface drains or observation wells. Few of the NIWQP ground-water sites are sources of drinking water. Although wildlife are not directly exposed to ground water, ground water discharges to surface drains and wildlife may be exposed to it there. For arsenic, the current MCL of 10 $\mu\text{g/L}$ was used. In January 2001 the MCL for arsenic was lowered from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 2001).

Concentrations of pesticides in surface-water samples were compared to acute and chronic criteria for the protection of freshwater aquatic life and to chronic criteria for protection of wildlife. For total DDT (the sum of measured DDD, DDE, and DDT) these criteria range from 9.2 pg/L for full dietary protection of wildlife (U. S. Environmental Protection Agency, 1995) to 1,050 $\mu\text{g/L}$ for protection of aquatic life from brief exposure (U. S. Environmental Protection Agency, 1980). For endrin, lindane, and malathion, U.S. Environmental Protection Agency (1996) criteria were used; for toxaphene, U.S. Environmental Protection Agency (1986a) criteria were applied.

Concentrations of trace metals in bottom sediment were compared to the upper limit of the 95th-percentile expected range of values in soils of the Western United States west of the 96th parallel. About 97.5 percent of randomly collected soil samples in the Western United States should fall below this value which is called the qualitative sediment guideline in this report. The sediment guideline is calculated from data presented in Shacklette and Boerngen (1984, p. 6). Data described by Shacklette and Boerngen (1984) are for soil samples collected at depths of about 8 in., whereas the bottom-sediment samples collected for the NIWQP are from water bodies and were shallower, typically from depths of only 2 to 4 in. Because the horizons sampled are not the same, the soil data of Shacklette and Boerngen (1984) are considered guidelines and are used here for qualitative comparison only.

For selenium, in addition to the qualitative sediment guideline, an ecological sediment guideline is also utilized for comparisons. The ecological sediment guideline is an estimate of the toxicity threshold for fish and wildlife based on field observations of bioaccumulation from sediment to the food chain. The most recent review of such data concluded that a value of 2 $\mu\text{g/g}$ in sediment emerges as the threshold beyond which bioaccumulation in the benthic-invertebrate food chain exceeds the dietary toxicity threshold for fish of 3 $\mu\text{g/g}$ (Lemly, 2002).

SUMMARY STATISTICS AND COMPARISON TO CRITERIA

The distribution of molybdenum concentrations in environmental surface water samples from the NIWQP study areas shown in figure 4 is typical of water-quality data. The histogram shows that the statistical distribution is truncated on the left by the detection limit and is highly skewed to the right by outlier values. Because this distribution is typical of water-quality data, median or 75th-percentile contaminant concentrations (rather than the mean concentration) is used herein to characterize the different study areas. The mean concentration of a contaminant is not a good estimate of the central tendency because the mean is not resistant to the magnitude of a small

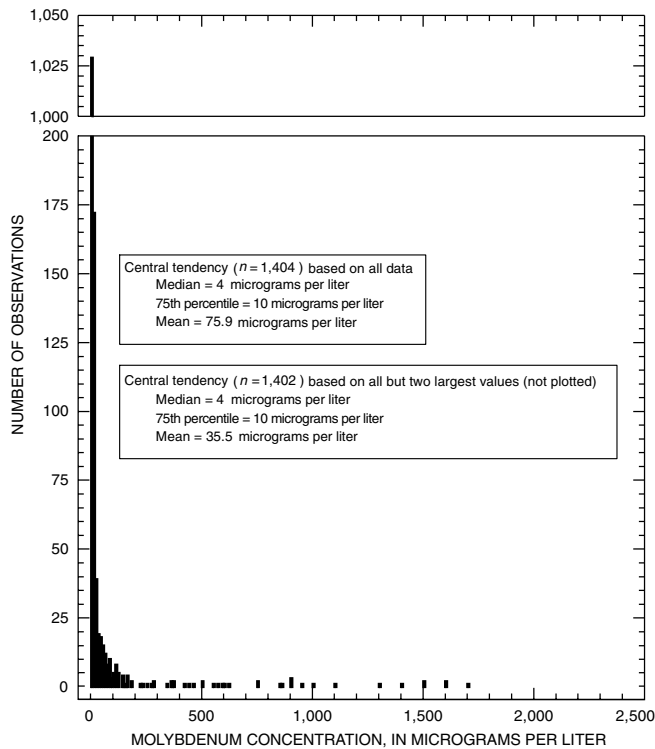


FIGURE 4. Molybdenum concentrations in surface-water samples from National Irrigation Water Quality Program study areas. Two largest molybdenum concentrations (5,000 and 56,000 micrograms per liter) are not shown. Bin interval for histogram is 10 micrograms per liter. Central-tendency summary statistics were calculated by log-probability methods. n , number of observations.

number of points. In the data set, for example, the two greatest concentrations of molybdenum in surface water are 5,000 and 56,000 $\mu\text{g/L}$. With those two samples included, the mean molybdenum concentration is 75.9 $\mu\text{g/L}$; with the two samples excluded the mean molybdenum concentration is 35.5 $\mu\text{g/L}$. The median value (4 $\mu\text{g/L}$) and the 75th-percentile value (10 $\mu\text{g/L}$), in contrast, are the same with or without those two samples.

In this report, statistical summaries of data usually are compared with criteria, rather than comparing individual data points with criteria. Because they are not resistant to effects of outliers, mean values are rarely used in this report to summarize data. Instead, the median or 75th percentile concentration is used to summarize chemical concentrations in water and sediment for comparison with criteria. For biological tissues, the geometric mean is used to summarize chemical concentrations. For data skewed to the right, the geometric mean is usually quite close to the median (Helsel and Hirsch, 1992).

Summary statistics were computed for trace element and pesticide concentrations in surface water, ground water, or bottom sediment (tables 11 through 14). Only samples collected for NIWQP investigations were used. The data set was not manipulated to remove bias. The percentage of samples that had con-

centrations exceeding the detection limit and the percentage that had concentrations exceeding criteria were computed. The results of the mercury analyses were not included in this study because of possible contamination of samples by sampling equipment and containers used in the 1980's (David A. Rickert, U.S. Geological Survey, written commun., 1994).

Summary statistics used in this section include all nonreplicate environmental sample analyses in the NIWQP data base for samples collected at NIWQP sites during DOI investigations. Samples that were collected before or after a DOI investigation are in the data base but were excluded from the statistical analysis. Summary statistics for surface-water and bottom-sediment constituents were based on samples collected at streams, lakes, and surface drains. Summary statistics for ground-water constituents were based on samples collected at wells, springs, and underground drains.

Selenium was the trace element most commonly found in surface water at concentrations exceeding its chronic criterion (table 11); more than 40 percent of the samples exceeded the USEPA chronic criterion. One reason that such a large percentage of the samples exceeded the chronic criterion for selenium is that many of the NIWQP study areas were selected for investigation because of known or suspected selenium contamination.

Additional bias towards selenium as the most important contaminant results because using the entire data set gives extra weight to those sites where more samples were collected. After selenium contaminated sites were identified, more followup samples were collected at contaminated sites than at uncontaminated sites. This type of bias can be removed by using only one sample per site. The most recent sample collected was selected at each of the 802 surface-water sites monitored as part of the NIWQP. At 286 of the 802 sites (36 percent), the most recent sample collected either exceeded or equaled the USEPA chronic criterion for selenium. Thus, selenium remains an important contaminant even after removing bias caused by repeat sampling at contaminated sites.

Boron and molybdenum were the next most commonly found trace elements that exceeded applicable criteria in surface-water samples. More than 28 percent of boron concentrations and almost 17 percent of molybdenum concentrations exceeded the chronic criteria established by California. The types of sample bias found for selenium are not found for boron or molybdenum in the NIWQP data base. Multiple repeat analyses were not made for these elements because of their elevated concentrations, and none of the NIWQP study areas were selected for investigation on the basis of their occurrence.

The chronic criterion for arsenic depends on its oxidation state: Arsenic(III) is much more toxic than arsenic(V). Although arsenic concentration was measured, the amount of the total that was in the form of arsenic(III) was not determined

TABLE 11. Summary statistics for filtered inorganic constituents in water samples from National Irrigation Water Quality Program study areas

[Abbreviations and symbol: µg/L, micrograms per liter; NC, not calculated because values for more than 80 percent of samples are below reporting limit; —, not applicable; <, less than]

Property or constituent	Summary statistics ¹					Exceedance (percent) Relative to:	
	Median ²	Interquartile range ²	Range of observed values	Detects (percent)	Total number of observations	Chronic criterion	MCL ³
Surface Water (streams, lakes, surface drains)							
pH (standard units)	8.3	0.6	3.3 – 11	—	3,620	—	—
Aluminum (µg/L)	9.9	17	<10 – 1,000	54.8	188	⁴ 3.2 (n = 156)	—
Arsenic (µg/L)	2.0	11	<1 – 7,500	80.8	1,285	3.5	—
Boron (µg/L)	220	550	<10 – 260,000	98.2	1,783	28.4	—
Cadmium (µg/L)	NC	NC	<1 – 660	15.7	1,166	⁴ 3.2(n = 1,059)	—
Chromium (µg/L)	.41	1.0	<1 – 15,000	26.9	1,244	⁴ .1(n = 1,134)	—
Copper (µg/L)	2.1	3.4	<1 – 140	73.3	1,163	⁴ 1.0(n = 1,053)	—
Lead (µg/L)	NC	NC	<5 – 74	9.1	1,113	⁴ 2.1(n = 1,003)	—
Molybdenum (µg/L)	4.0	10	<1 – 56,000	82.6	1,221	16.7	—
Selenium (µg/L)	2.0	12	<1 – 8,300	67.2	2,057	40.1	—
Silver (µg/L)	NC	NC	<1 – 5	6.9	332	⁴ .4(n = 223)	—
Uranium (µg/L)	9.0	26	<1 – 470	95.6	634	⁵ 1.6	—
Zinc (µg/L)	6.6	13	<10 – 19,000	66.5	1,288	⁴ 3.1(n = 1,151)	—
Ground Water (wells, springs, subsurface drains)							
pH (standard units)	7.3	0.5	5.0 – 9.1	—	760	—	—
Aluminum (µg/L)	21	31	<10 – 370	73.0	174	7.5	—
Arsenic (µg/L)	2.0	6.0	<1 – 1,400	79.9	348	10.6	22.4
Boron (µg/L)	1,400	1,720	10 – 120,000	100	483	76.6	⁶ 74.5
Cadmium (µg/L)	NC	NC	<1 – 100	16.3	147	⁴ 3.7 (n=134)	1.4
Chromium (µg/L)	.87	1.8	<1 – 50	40.4	193	⁴ 0 (n=180)	0
Copper (µg/L)	4.0	9.0	<1 – 180	84.6	149	⁴ 7.4 (n=136)	0
Lead (µg/L)	NC	NC	<5 – 18	9.5	168	⁴ 1.3 (n=155)	0.6
Molybdenum (µg/L)	17	27	<1 – 28,000	95.6	344	44.2	⁶ 20.6
Selenium (µg/L)	26	80	<1 – 16,000	82.9	694	70.2	35.6
Silver (µg/L)	NC	NC	<1 – 1	15.0	40	⁴ 3.4 (n=29)	⁶ 0
Uranium (µg/L)	20	133	<1 – 1,500	94.0	116	9.5	⁷ 44.0
Zinc (µg/L)	20	34	<10 – 15,000	81.8	192	⁴ 14.4 (n=181)	⁶ 3.1

¹ Summary statistics are for nonreplicate, filtered environmental samples collected as part of a NIWQP investigation.

² The median and interquartile range were computed using adjusted log-normal maximum-likelihood methods (Helsel and Cohn, 1988). The interquartile range describes the spread of the data. It measures the range of the central 50 percent of the data and is defined as the 75th percentile minus the 25th percentile.

³ Relative to maximum contaminant level (U.S. Environmental Protection Agency, 1996) except as noted.

⁴ *n* is the number of observations out of the total number of observations for which ancillary data (such as pH or hardness) needed for comparison with criterion were available.

⁵ Relative to recommended Canadian water-quality objective for protection of aquatic life (Environment Canada, 1983).

⁶ Relative to lifetime health advisory (U.S. Environmental Protection Agency, 1996).

⁷ Relative to maximum contaminant level (U.S. Environmental Protection Agency, 2000).

as part of the NIWQP. Slightly less than 4 percent of the arsenic values exceeded the criteria for arsenic(III). The actual percentage of exceedances might have been much less than this had arsenic species been measured because arsenic(V) would be expected from thermodynamic considerations to be the predominant species in oxygenated surface water.

Median concentrations of most trace elements were greater in ground water than in surface water, and fewer samples had concentrations less than the detection limit (table 11). Trace-element concentrations are typically higher in ground water than surface water because ground water commonly is in close contact for long periods with aquifer material containing trace elements. Another reason for the higher values may be sample bias. Few reference sites were selected for ground water; most ground-water sites were either underground drains or wells in irrigated areas.

In ground-water samples, boron was the trace element that most frequently exceeded the MCL or lifetime health advisory (table 11). The median boron concentration in NIWQP ground-water samples was more than twice the lifetime health advisory. Forty-four percent of the uranium samples exceeded the MCL, more than 35 percent of the selenium samples exceeded the MCL, and 22 percent of the arsenic samples exceeded the MCL (table 11). Although most of the wells NIWQP sampled are not used as sources of drinking water, these results indicate there

may be human-health concerns in some farming areas for households that depend on shallow wells for their drinking water.

Except for molybdenum, selenium and uranium, trace elements in bottom sediment generally do not exceed the qualitative sediment guidelines (table 12). Selenium is the only trace element for which ecological sediment guidelines are used in this report. Selenium concentrations commonly exceeded both the qualitative and ecological sediment guidelines.

For arsenic and molybdenum, most of the samples that exceed the guideline are from one study area—the Stillwater Wildlife Management Area in Nevada (*W*). A high percentage of bottom-sediment samples had molybdenum concentrations less than the detection limit, but molybdenum was almost always detected in ground water. Molybdenum has a high geochemical mobility and thus a tendency to enter into solution in water under normal earth-surface conditions (Hem, 1985).

In surface water and bottom sediment, DDT and degradation products of DDT were the pesticides most commonly found at concentrations exceeding the reporting limit (tables 13 and 14). The only pesticides to exceed criteria in surface water were malathion and DDT (and its degradation products). A single sample of malathion from Lower Rio Grande valley in Texas

TABLE 12. Summary statistics for inorganic constituents in bottom-sediment samples from National Irrigation Water Quality Program study areas

[Abbreviations and symbol: NC, not calculated because values for more than 80 percent of samples are below reporting limit; $\mu\text{g/g}$, micrograms per gram; —, not determined because a soils guideline has not been established for the constituent; <, less than]

Chemical constituent	Summary statistics ¹					Exceedance ³ (percent)
	Median ² ($\mu\text{g/g}$)	Interquartile range ² ($\mu\text{g/g}$)	Range of observed values ($\mu\text{g/g}$)	Detects (percent)	Total number of observations	
Aluminum	62,000	20,000	20,000–98,000	100	345	—
Arsenic	6.5	4.9	<10 – 370	96.8	345	5.4
Boron	1.7	2.5	<.4 – 390	95.0	298	—
Cadmium	NC	NC	<2 – 2	.7	280	—
Chromium	54	27	2 – 270	100	345	2.3
Copper	22	14	5 – 520	100	345	1.2
Lead	17	5	<4 – 470	98.6	345	1.7
Molybdenum	.55	1.4	<2 – 73	20.9	345	13
Selenium	.6	1.5	<.1 – 85	98.3	346	⁴ 22.5
Silver	NC	NC	<1 – <1	0	265	—
Uranium	4.0	3.5	.25 – 56.6	100	326	27.6
Zinc	77	36	23 – 510	100	345	2.3

¹ Summary statistics are for nonreplicate, fine fraction (<0.062 mm) environmental samples collected as part of a NIWQP investigation.

² The median and interquartile range were computed using adjusted log-normal maximum-likelihood methods (Helsel and Cohn, 1988). The interquartile range describes the spread of the data. It measures the range of the central 50 percent of the data and is defined as the 75th percentile minus the 25th percentile.

³ Relative to qualitative sediment guideline (table 10) except as noted.

⁴ Relative to ecological sediment guideline (see text for discussion).

TABLE 13. Summary statistics for selected pesticides in surface-water samples from National Irrigation Water Quality Program study areas

[Abbreviations and symbols: NC, not calculated because values for more than 80 percent of samples are below reporting limit; ng/L, nanograms per liter; —, not determined because applicable criterion has not been established for the constituent; <, less than]

Chemical constituent	Summary statistics ¹					
	Median ² (ng/L)	Interquartile range ² (ng/L)	Range of observed values (ng/L)	Detects (percent)	Total number of observations	Exceedance ³ (percent)
DDD	0.3	0.7	<1 – 10	21	107	—
DDE	NC	NC	<1 – 38	15	107	—
DDT	NC	NC	<1 – 36	15	107	⁴ 21
Endrin	NC	NC	<1 – 20	9.0	108	0
Lindane	NC	NC	<1 – 2	1.8	107	0
Malathion	NC	NC	<10 – 710	4.8	168	.6
Toxaphene	NC	NC	<1,000 – <1,000	0	107	0

¹ Summary statistics are for nonreplicate, environmental surface-water samples collected as part of a NIWQP investigation.

² The median and interquartile range were computed using adjusted log-normal maximum-likelihood methods (Helsel and Cohn, 1988). The interquartile range describes the spread of the data. It measures the range of the central 50 percent of the data and is defined as the 75th percentile minus the 25th percentile.

³ Exceedance relative to chronic criteria (table 10).

⁴ Because exceedance was calculated by using total DDT (sum DDD + DDE + DDT), exceedance may be greater than detects.

TABLE 14. Summary statistics for selected pesticides in bottom-sediment samples from National Irrigation Water Quality Program study areas

[NC, not calculated because values for more than 80 percent of samples are below reporting limit]

Chemical constituent	Summary statistics				
	Median ¹	Interquartile range ¹	Range of observed values	Detects (percent)	Total number of observations
(micrograms per kilogram)					
Organochlorine pesticides					
Aldrin	NC	NC	<0.1 – 1.5	6	219
Chlordane	0.49	0.88	<1 – 30	30	221
DDD	.14	1.1	<.1 – 24	55	221
DDE	.5	1.8	<.1 – 67	81	220
DDT	.007	.07	<.1 – 86	21	219
Endrin	NC	NC	<.1 – 1.0	3	221
Lindane	NC	NC	<.1 – 4.7	1	220
Methoxychlor	NC	NC	<.1 – 45	5	215
Mirex	NC	NC	<.1 – 0.5	.5	221
Toxaphene	NC	NC	<10 – 40	2	221
Organophosphate pesticides					
Malathion	NC	NC	<0.1 – <0.1	0	36
Parathion	NC	NC	<.1 – .1	2	36
Trithion	NC	NC	<.1 – <.1	0	36
Herbicides					
2,4-D	NC	NC	<0.1 – <0.1	0	16
Silvex	NC	NC	<.1 – <.1	0	16
2,4,5-T	NC	NC	<.1 – <.1	0	16

¹ Computed using adjusted log-normal maximum-likelihood methods (Helsel and Cohn, 1988).

exceeded the chronic criterion. Twenty-one percent of total-DDT concentrations in surface water exceeded the chronic criterion, however, most of the samples that exceeded the chronic criterion were from one area: the Owyhee area in Oregon and Idaho.

Degradation products of DDT were detected in 81 percent of the bottom-sediment samples and in about 20 percent of those surface-water samples that were analyzed for the degradation products. Although none of the samples exceeded 1,050 µg/L DDE, the lowest observed-effect level (LOEL) (U.S. Environmental Protection Agency, 1986b), DDE concentrations thousands of times less than the LOEL can adversely affect wildlife because of its bioaccumulation. In addition, DDE and several other organochlorine compounds can modulate the endocrine system and affect reproduction in invertebrates, fish, and wildlife (U.S. Environmental Protection Agency, 1997). Kelce and others (1995) concluded that “the reported increased incidence of developmental male reproductive system abnormalities in wildlife and humans may reflect antiandrogenic activity of the persistent DDT metabolite *p,p'*-DDE * * * ”

NATIONAL IRRIGATION WATER QUALITY PROGRAM STUDY-AREA COMPARISONS

Box plots of contaminant concentrations in surface water, ground water, and bottom sediment were prepared for the 26 study areas. Contaminant concentrations from an area were compared to regulatory and proposed criteria and to concentrations from other areas. Summary statistics used in this section include all nonreplicate sample analyses in the NIWQP data base for samples collected at NIWQP sites during DOI investigations. Data values from samples that were collected before or after a DOI investigation are in the data base but were excluded from the statistical analysis.

DISSOLVED SOLIDS

The dissolved-solids concentrations at source water sites in almost all the areas were typically less than 500 mg/L and most were less than 1,000 mg/L (fig. 5A). Source water sites are surface water sites upstream from irrigated lands which represent the water used for irrigation. For 9 of the 25 study areas analyzed (A, B, D, I, J, Q, R, S, and T), dissolved-solids concentrations in surface-water samples did not exceed 3,000 mg/L, even after irrigation (fig. 5B), and in only 2 of the 25 areas (Y and Z) was the median greater than 3,000 mg/L (fig. 5B). The greatest dissolved-solids concentrations were found in arid areas having terminal lakes or ponds. In 4 of the 26 areas (H, W, Y, and Z), more than 10 percent of the samples had dissolved-solids concentrations exceeding 10,000 mg/L.

ARSENIC

Arsenic concentrations in surface water potentially exceed the chronic criterion in only 3 of the 26 areas, Humboldt River area, Malheur National Wildlife Refuge area, and Stillwater Wildlife Management Area (G, L, and W). Although arsenic concentrations determined as part of the NIWQP cannot be compared directly to the chronic criteria because the oxidation state of the arsenic was not determined, even if all the arsenic

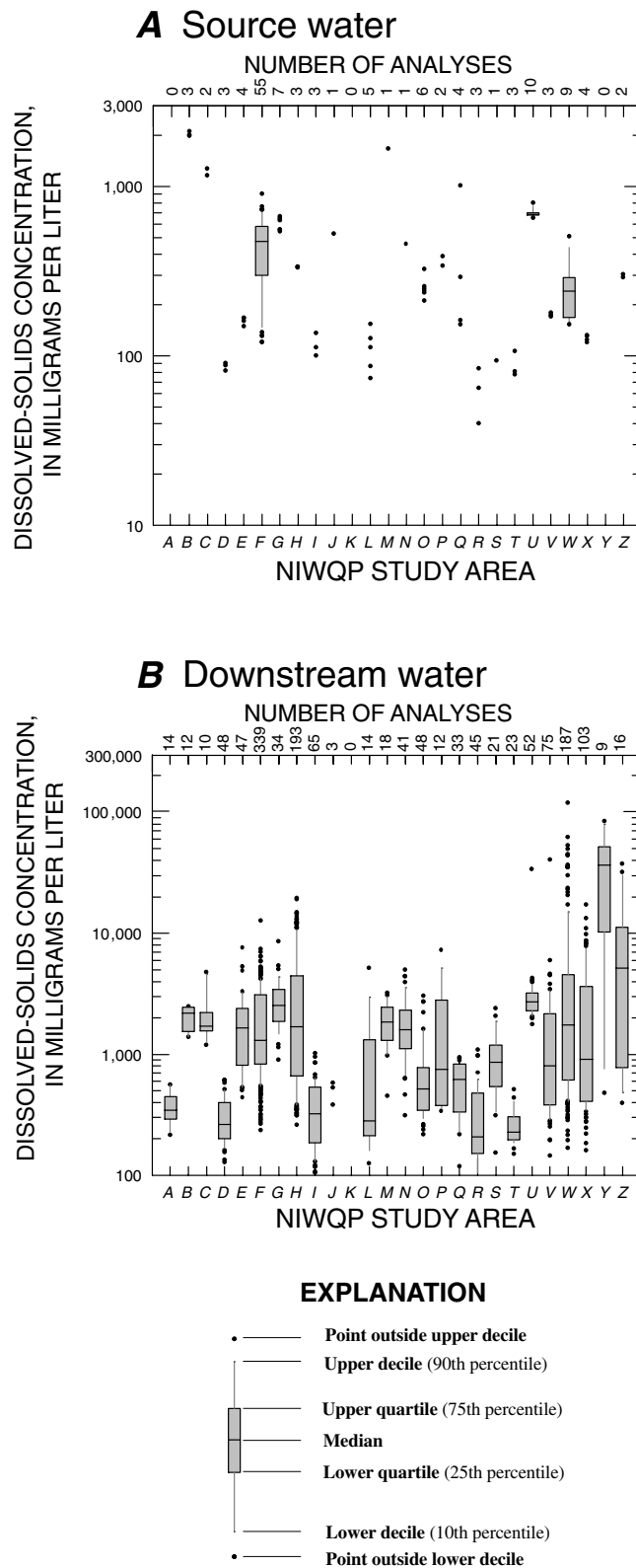


FIGURE 5. Concentrations of total dissolved solids in surface-water samples from source-water sites and from sites in and downstream from irrigated lands in National Irrigation Water Quality Program (NIWQP) study areas. Data points are from non-replicate environmental samples collected as part of a NIWQP investigation.

were in the most toxic oxidation state, only a low percentage of the NIWQP samples would exceed the criterion. The MCL for arsenic was lowered from 50 to 10 µg/L in January 2001 (U.S. Environmental Protection Agency, 2001). The median arsenic concentration exceeded the current 10-µg/L MCL in surface water (fig. 6) in four areas (G, I, Q, and W), and in 7 areas 25

percent or more of the samples exceeded the MCL. All the ground-water samples from two areas (G and W) and one of two ground-water samples from the middle Rio Grande area (O) exceeded the MCL. In three areas with high arsenic concentrations in surface water (I, L, and Q), arsenic concentrations were not determined in ground water.

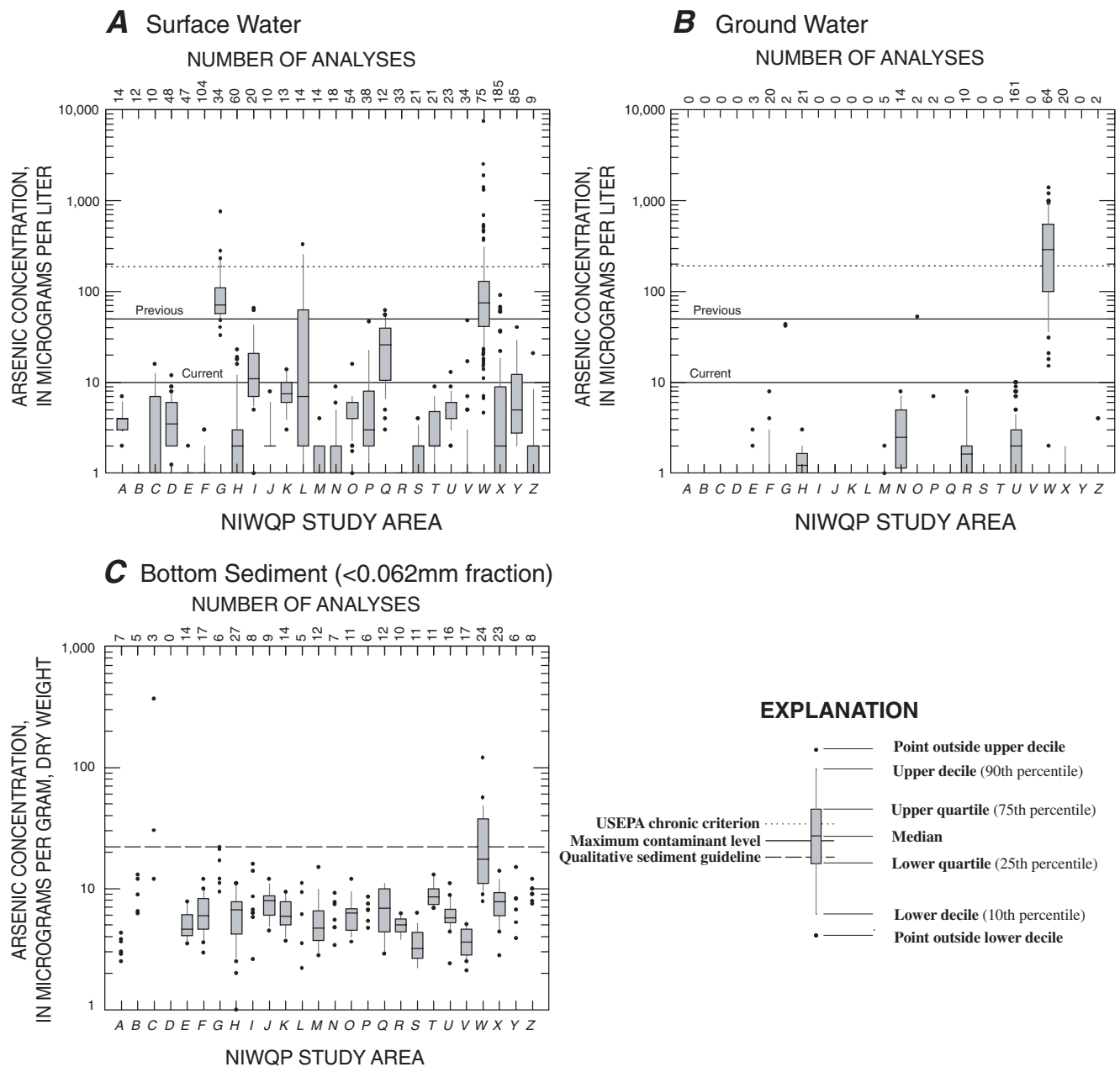


FIGURE 6. Concentrations of arsenic in surface water, ground water, and bottom sediment from sites in and downstream from irrigated lands in National Irrigation Water Quality Program (NIWQP) study areas. USEPA, U.S. Environmental Protection Agency. Data points are from non-replicate environmental samples collected as part of a NIWQP investigation.

The highest arsenic concentrations in surface water typically were found in terminal lakes in areas where irrigated land is associated with rocks and soils of volcanic origin. In the Stillwater Wildlife Management Area (*W*), seepage of impounded irrigation water and natural evaporation has created small, isolated ponds having arsenic concentrations exceeding 30 mg/L (Tuttle and Thodal, 1998).

All of the arsenic concentrations in ground-water samples from the Stillwater Wildlife Management Area exceed the current MCL; however, few, if any, of the wells sampled as part of the NIWQP are used as drinking-water sources. In the Stillwater Wildlife Management Area, 55 percent of the ground-water samples had arsenic concentrations that exceeded 180 µg/L, which could affect wildlife adversely in areas where ground water discharges to surface drains.

The highest concentrations of arsenic in bottom sediment were in the Belle Fourche Reclamation Project (*C*), Humboldt River area (*G*), and Stillwater Wildlife Management Area (*W*). Elevated arsenic concentrations in the Humboldt River area were expected because abandoned arsenic mills and associated tailings are found along the edge of a lake in the Humboldt Wildlife Management Area (Seiler and others, 1993).

BORON

In 6 of the 26 study areas (*G*, *K*, *N*, *U*, *W*, and *Y*), the median boron concentration in surface water exceeded the aquatic-life chronic criterion of 550 µg/L (fig. 7A). Boron is extremely soluble and boron concentrations can have a wide range. In the Stillwater Wildlife Management Area (*W*) and Tulare Lake Bed area (*Y*), boron concentrations ranged from approximately 200 µg/L to more than 100,000 µg/L. Three of the four evaporation ponds sampled as part of the Tulare Lake Bed area reconnaissance investigation had boron concentrations exceeding 100,000 µg/L; the greatest concentration was 140,000 µg/L (Schroeder and others, 1988). Typically, the study areas having the highest boron concentrations have lakes or ponds in terminal sinks where boron is evaporatively concentrated.

In 4 of the 13 areas where ground water was analyzed for boron (*H*, *N*, *U*, and *W*), more than 50 percent of the samples exceeded the lifetime health advisory (fig. 7B). In 4 other areas (*E*, *M*, *P*, and *R*) all boron concentrations were less than the health advisory. Overall, almost 75 percent of the boron concentrations in ground water exceeded the health advisory. Sampling bias is a substantial reason for the high percentage of exceedances. More than 60 percent of the samples were collected from 2 areas (*U* and *W*) where boron concentrations typically exceeded the health advisory.

In bottom sediment, the median concentration was commonly 2 to 8 µg/g (fig. 7C). Concentrations of boron in sediment exceeding 50 µg/g are found in areas where elevated concentrations of boron are found in surface and ground water.

MOLYBDENUM

In 3 of the 26 areas (*G*, *W*, and *Y*), the median molybdenum concentration in surface water exceeded the aquatic-life chronic criterion of 19 µg/L (fig. 8A). The study areas having the highest molybdenum concentrations have lakes or ponds in terminal sinks. Similar to boron, the range of molybdenum concentrations is wide. For example, in the Stillwater Wildlife Management Area (*W*), molybdenum concentrations span a range of more than three orders of magnitude.

In 3 of the 26 areas (*N*, *R*, and *W*), more than 25 percent of the ground-water samples exceeded the lifetime health advisory for molybdenum (fig. 8B). In the Stillwater Wildlife Management Area (*W*), molybdenum in more than 50 percent of the samples exceeded the advisory. Only a few percent of bottom-sediment samples exceeded the qualitative sediment guideline for molybdenum (fig. 8C) and more than half were from the Stillwater Wildlife Management Area.

SELENIUM

SURFACE WATER

Selenium concentrations in the source water used for irrigation in the NIWQP areas typically are less than the reporting limit of 1 µg/L. Source-water sites are upstream of irrigated land, and hence are unaffected by irrigation in the study area. In 23 of the 26 areas, samples were taken of the source water used for irrigation and in only 7 of these areas (*B*, *C*, *F*, *H*, *J*, *M*, and *U*) did a sample of source water contain selenium concentrations exceeding 1 µg/L (fig. 9A). Commonly, where the source water did contain measurable amounts of selenium, concentrations ranged from 1 to 3 µg/L. However, in 2 of the 7 areas (*F* and *M*), even some source-water samples contained selenium concentrations exceeding 5 µg/L. Selenium sources available to the water used for irrigation can include irrigation drainwater from areas upstream or drainage from seleniferous rocks in the watershed. Selenium concentrations in source water exceeding 5 µg/L are very unusual, and according to Hamilton's (1999) historical analysis of selenium in the Colorado River Basin, are more likely linked to both land-use practices and native geology than to native geology alone.

The importance of irrigation in determining selenium concentrations was examined by comparing selenium concentrations at reference sites and at sites effected by irrigation. Selenium concentrations were measured at 802 individual sites—693 sites in and downstream from irrigated land and 109 reference sites. The most recent non-replicate selenium value measured at each site was selected to represent the selenium concentration at the site. For the reference sites, the median concentration was <1 µg/L and the 75th percentile was 2 µg/L. For the sites in and downstream from irrigated land, the median concentration was 2 µg/L and the 75th percentile was 15 µg/L.

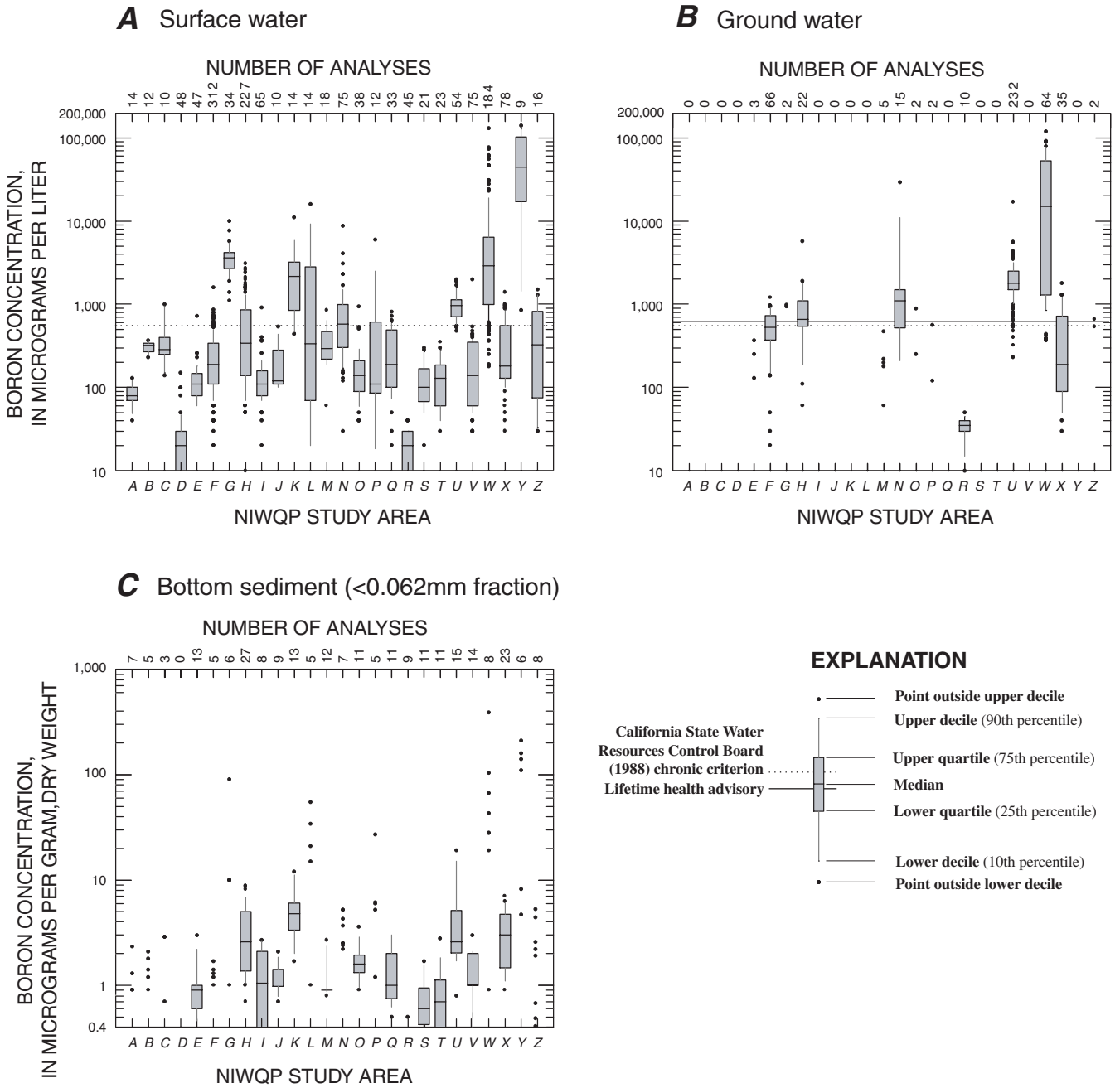


FIGURE 7. Concentrations of boron in surface water, ground water, and bottom sediment from sites in and downstream from irrigated areas in National Irrigation Water Quality Program (NIWQP) study areas. Chronic criterion is from California State Water Resources Control Board (1988). Data points are from non-replicate environmental samples collected as part of a NIWQP investigation.

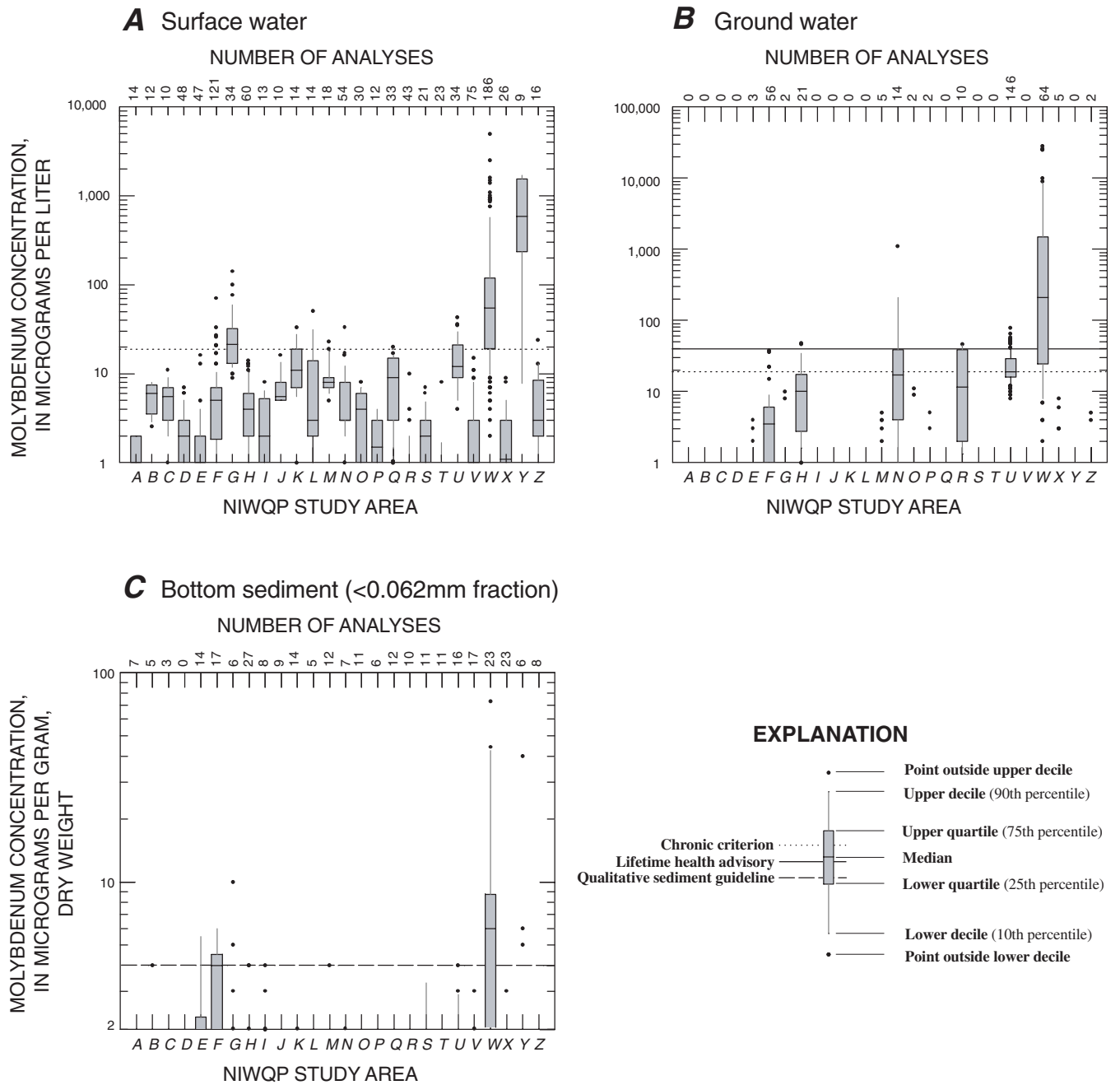
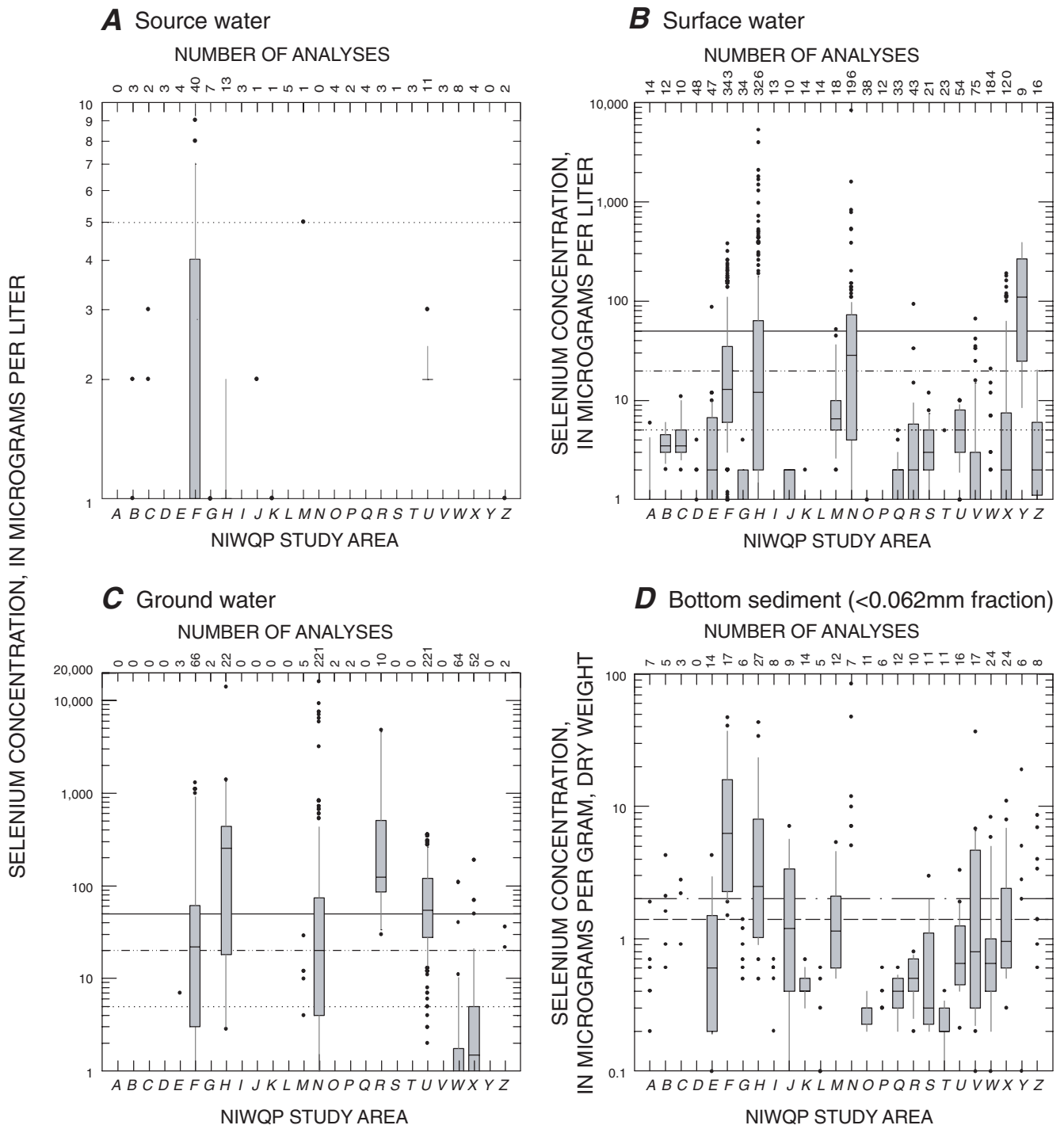


FIGURE 8. Concentrations of molybdenum in surface water, ground water, and bottom sediment from sites in and downstream from irrigated lands in National Irrigation Water Quality Program (NIWQP) study areas. Some NIWQP areas either show no plotted data because data were below reporting limit or were not plotted because no analyses of the given type were done. USEPA, U.S. Environmental Protection Agency. Data points are from non-replicate environmental samples collected as part of a NIWQP investigation.



EXPLANATION

- Point outside upper decile
 - Upper decile (90th percentile)
 - Upper quartile (75th percentile)
 - Median
 - Lower quartile (25th percentile)
 - Lower decile (10th percentile)
 - Point outside lower decile
-
- USEPA acute criterion
 - USEPA chronic criterion
 - Maximum contaminant level
 - Qualitative sediment guideline
 - Ecological sediment guideline

FIGURE 9. Concentrations of selenium in source water used for irrigation and in surface water, ground water, and bottom sediment from sites in and downstream from irrigated areas in National Irrigation Water Quality Program (NIWQP) study areas. USEPA, U.S. Environmental Protection Agency. Data points are from non-replicate environmental samples collected as part of a NIWQP investigation.

In 12 of the 26 areas, the median selenium concentration in surface water of the streams, canals, drains, ponds, and lakes in and downstream from irrigated land was less than the reporting limit (1 µg/L) (fig. 9B). In 3 of these 12 areas (*I*, *L*, and *P*), selenium was not detected in any surface-water samples.

In 12 of the 26 areas at least 25 percent of the surface water samples had selenium concentrations that either equaled or exceeded the U.S. Environmental Protection Agency aquatic-life chronic criterion (5 µg/L). In 6 areas (*F*, *H*, *M*, *N*, *U*, and *Y*), 50 percent or more of the surface-water samples exceeded the chronic criterion. In 6 other areas (*C*, *E*, *R*, *S*, *X*, and *Z*), between 25 and 50 percent of the samples equaled or exceeded the chronic criterion.

Typically, the range of selenium concentrations in contaminated areas spans several orders of magnitude. In the Kendrick Reclamation Project (*H*) and in the middle Green River Basin (*N*), selenium concentrations in surface water ranged from less than 1 µg/L to more than 5,000 µg/L.

GROUND WATER

Wells were sampled for selenium in only 13 of the 26 areas (fig. 9C). In 7 of those 13 areas (*F*, *H*, *N*, *R*, *U*, *W*, and *X*), selenium concentrations in some samples exceeded the MCL and in 3 of those 7 areas (*H*, *R*, and *U*), selenium concentrations exceeded the MCL in more than 50 percent of the samples. Because selenium in ground water ultimately discharges to the surface where wildlife may be exposed to it, selenium concentrations in ground water were also compared with criteria for the protection of aquatic life. In more than 70 percent of the well-water samples, selenium concentrations exceeded the chronic criterion. Samples from subsurface drains were collected in only one area, the middle Green River area (*N*). The median selenium concentration in the subsurface-drain samples was 25 µg/L (range 4 to 75 µg/L).

In the Kendrick Reclamation Project (*H*) and in the Middle Green River Basin (*N*), some well waters contained selenium concentrations exceeding 10,000 µg/L. Two of the wells in the middle Green River Basin were at one time used as sources of drinking water; selenium in one of them ranged from 83 to 90 µg/L. Although their data were not included in the NIWQP data base, See, Peterson, and Ramirez (1992) reported that selenium concentrations in 49 domestic wells (sampled by the Natrona County Department of Health) in the vicinity of the Kendrick Reclamation Project ranged from less than 5 to 1,700 µg/L.

BOTTOM SEDIMENT

In 15 of the 25 areas where fine fraction (<0.062 mm) bottom-sediment samples were collected (fig. 9D), at least some of the samples exceeded the ecological sediment guideline value of 2 mg/kg for selenium (Lemly, 2002). In four areas (*F*, *H*, *N*, and *Z*) selenium concentrations in more than 50 percent of the bottom sediment samples exceed the ecological sediment guideline.

URANIUM

Leaching of soil and rock by irrigation water can produce concentrations of dissolved uranium that may threaten nearby drinking water supplies (Zielinski and others, 1995). Because the USEPA has not promulgated any criterion for uranium for the protection of freshwater aquatic life, the criterion used was the proposed Canadian Water-Quality Objective of 300 µg/L and the MCL of 30 µg/L. These values for uranium are based on its potential chronic toxicity (kidney damage) in mammals, not on its radioactivity. Haseltine and Sileo (1983) indicated that metallic uranium in the diet did not cause kidney damage or weight loss in American black ducks (*Anas rubripes*); their study was the only one found on the effects of uranium on wild-life.

Few surface-water samples exceeded the Canadian Water-Quality Objective for uranium for the protection of aquatic life (fig. 10A). Ground water in only 10 of the 26 areas was sampled for uranium. Individual uranium concentrations exceeding the MCL were measured in 4 of those 10 areas (*H*, *M*, *U*, and *W*; fig. 10B) and the median uranium concentration exceeded the MCL in 2 areas (*U* and *W*). Although uranium commonly exceeds the MCL in some areas, uranium alone would not restrict use of the water. All samples that exceeded the criterion for uranium also exceeded the National Secondary Drinking Water standard for total dissolved solids (fig. 11).

In the fine (< 0.062-mm) fraction, uranium in more than 25 percent of the bottom-sediment samples exceeded the qualitative sediment guideline (5.3 µg/g). In 15 of the 25 study areas where bottom sediment was sampled, at least one bottom-sediment sample exceeded the guideline for uranium (fig. 10C); in 5 of the 25 study areas (*F*, *G*, *N*, *V*, and *W*), the median uranium concentration exceeded the guideline.

PESTICIDES

Pesticides were sampled in surface water at the discretion of the study teams and were sampled in only 7 of the 26 areas (*D*, *J*, *K*, *N*, *P*, *Q*, and *U*). DDT's degradation products, DDE and DDD, were detected more frequently than undegraded DDT, which was found in surface water only in the one area (*Q*). Although 22 of the 107 samples (21 percent) analyzed for total DDT (sum of DDD + DDE + DDT) exceeded the chronic criterion, 18 of those 22 samples were from the Owyhee-Vale Reclamation Project areas (*Q*; fig. 12A). Five additional samples for the Salton Sea area (*U*), four of which exceeded the chronic criterion, are shown in figure 12 but were not included in the calculation of the percent exceedances in table 13. The samples from the Salton Sea area were collected from NIWQP sites and analyzed by USGS personnel during the reconnaissance investigation, but were not analyzed as part of the NIWQP investigations.

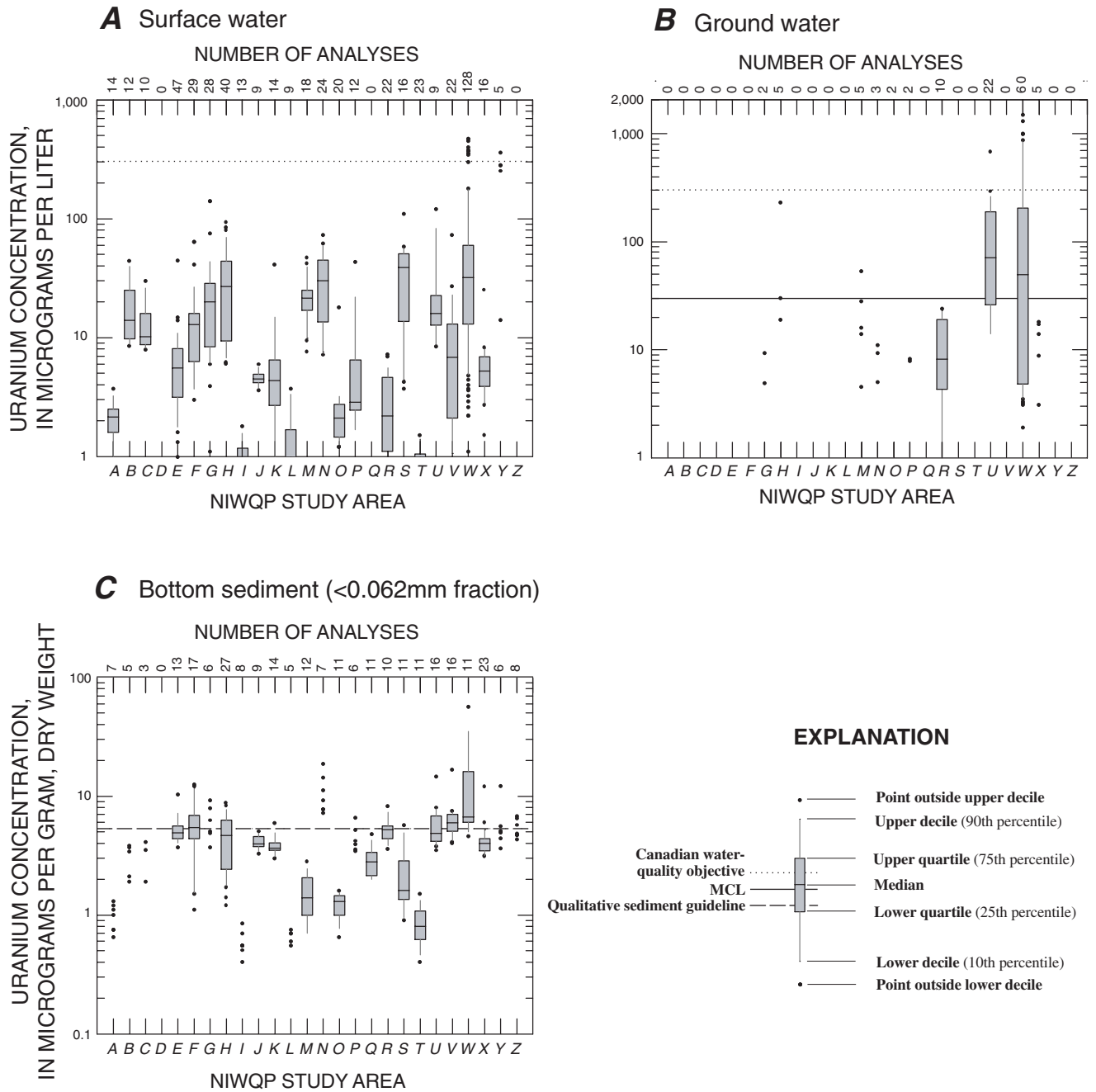


FIGURE 10. Concentrations of uranium in surface water, ground water, and bottom sediment from sites in and downstream from irrigated areas in National Irrigation Water Quality Program (NIWQP) study areas. MCL, maximum contaminant level; USEPA, U.S. Environmental Protection Agency. Data points are from non-replicate environmental samples collected as part of a NIWQP investigation.

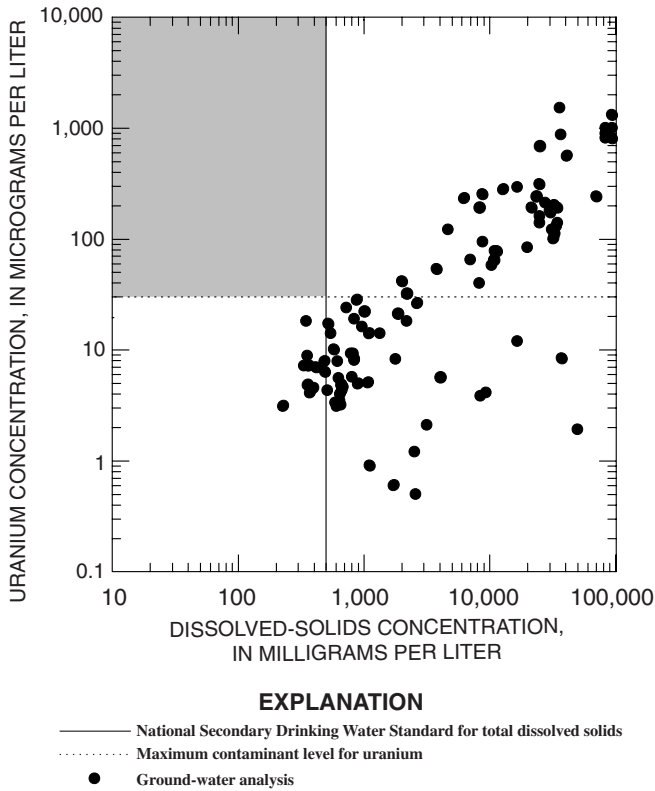


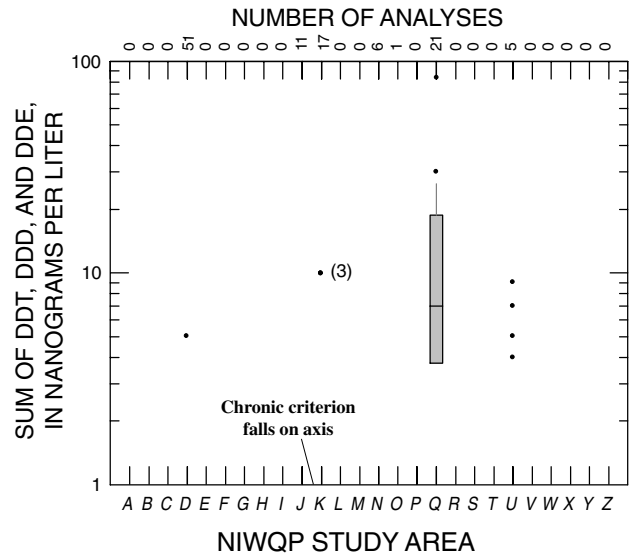
FIGURE 11. Relation between uranium and total dissolved-solids concentrations in ground water in National Irrigation Water Quality Program (NIWQP) study areas. Shaded area shows where uranium samples would exceed maximum contaminant level (MCL) without exceeding standard for dissolved solids. Data points are from non-replicate environmental samples collected as part of a NIWQP investigation.

Erosion of agricultural soils is the probable source of DDT now found in surface water. DDT or its degradation products were detected in bottom-sediment samples in all 21 areas in which they were sampled (fig. 12B). In 7 of these 21 areas (D, J, K, Q, T, U, and Y) total DDT concentrations exceeding 10 µg/kg were measured in the bottom sediment, and in 2 areas (Q and U) the median concentration exceeded 10 µg/kg.

CONTAMINANT ASSOCIATIONS

What contaminants are associated in surface water? What are the relations between concentrations in water and bottom sediment? What are the relations between filtered- and total-contaminant concentrations in water? Answers to these questions can provide information about sources of contaminants and the processes that affect their concentrations. Relations between selenium concentrations in biota, water, and sediment are discussed in the section titled "Relation Between Selenium in Water, Sediment, and Biota," p. 107.

A Surface water



B Bottom sediment

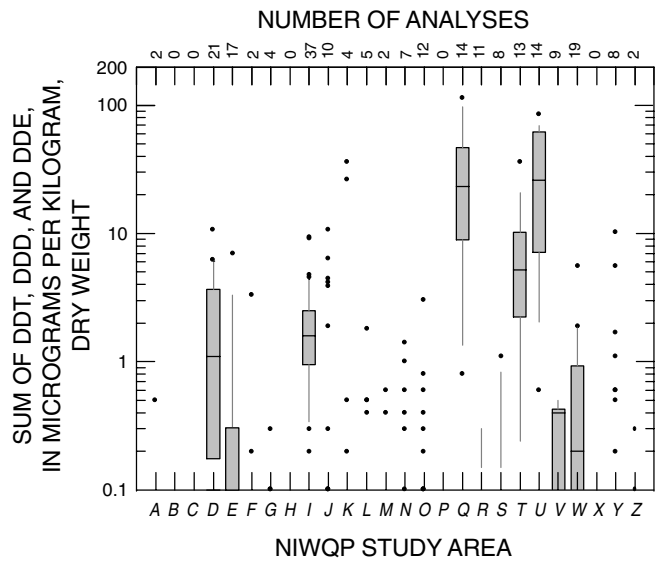


FIGURE 12. Concentrations of total DDT (DDT plus metabolites) in surface water and bottom sediment in National Irrigation Water Quality Program (NIWQP) study areas. USEPA, U.S. Environmental Protection Agency. Data points are from non-replicate environmental samples collected as part of a NIWQP investigation.

RELATION BETWEEN MAJOR-ION AND TRACE-ELEMENT CONCENTRATIONS IN SURFACE WATER

A resources manager needs to know whether the existence of selenium problems in an area indicates that some other element, such as uranium or boron, also is likely to be a problem there. To examine contaminant associations in surface water, principal-components analysis (PCA) was applied to median concentrations of trace elements (arsenic, boron, molybdenum, selenium, and uranium), major constituents (calcium, magnesium, sodium, chloride, and sulfate), and alkalinity for each of the NIWQP study areas. Data from only 21 of the 26 NIWQP areas were used in the principal-components analysis because data on uranium in surface water were not collected in 3 areas (*D*, *Q*, and *Z*; fig. 10A) and major-constituent data were not collected in 2 areas (*K* and *P*).

Median concentrations for the PCA were determined for constituent concentrations in environmental, non-replicate surface-water samples from sites within and downstream from irrigated areas. In calculating medians, trace-element data from an analysis were included even if the analytical suite was incomplete and major constituents were not determined. The number of analyses used to calculate median concentrations of the trace elements arsenic, boron, molybdenum, and selenium is shown in figures 6 through 10. To reduce the effects that scale and extreme values in the data set have on the statistical analysis, all median concentrations were ranked, and the rank replaced the actual values. For example, the highest median concentrations for selenium (110 $\mu\text{g/L}$; fig. 9) and chloride (9,600 mg/L) were assigned values of 21 and the lowest median concentrations were assigned values of 1.

Two principal components best explain the data set. The first two principal components account for 95 percent of the total variance. The loadings for the first two principal components were plotted to evaluate the occurrence of distinct clusters (fig. 13A). The principal-components loadings form two distinct groups of major constituents and trace elements and show arsenic as an outlier.

The principal-components analysis shows that selenium is associated with calcium, magnesium, sodium, sulfate, and uranium (fig. 13A). Presser (1994a, p. 144) noted that in fluids issuing from rocks in the mountains along the west side of the San Joaquin Valley, Calif., only sodium sulfate and magnesium sulfate waters contained selenium concentrations greater than 3 $\mu\text{g/L}$. The association of selenium and sulfate likely is the result of weathering of marine shales containing selenium-bearing reduced-sulfur minerals (Presser, 1994a; Naftz, 1996a). Pyrite is considered to be a main source of sulfur in shales (Presser and Swain, 1990), and much of the selenium in the Earth's crust occurs in sulfide minerals (Berrow and Ure, 1989). The processes of acid generation during the weathering of pyrite and subsequent neutralization and cation exchange with clay minerals may explain the association of calcium, magnesium, and sodium with selenium.

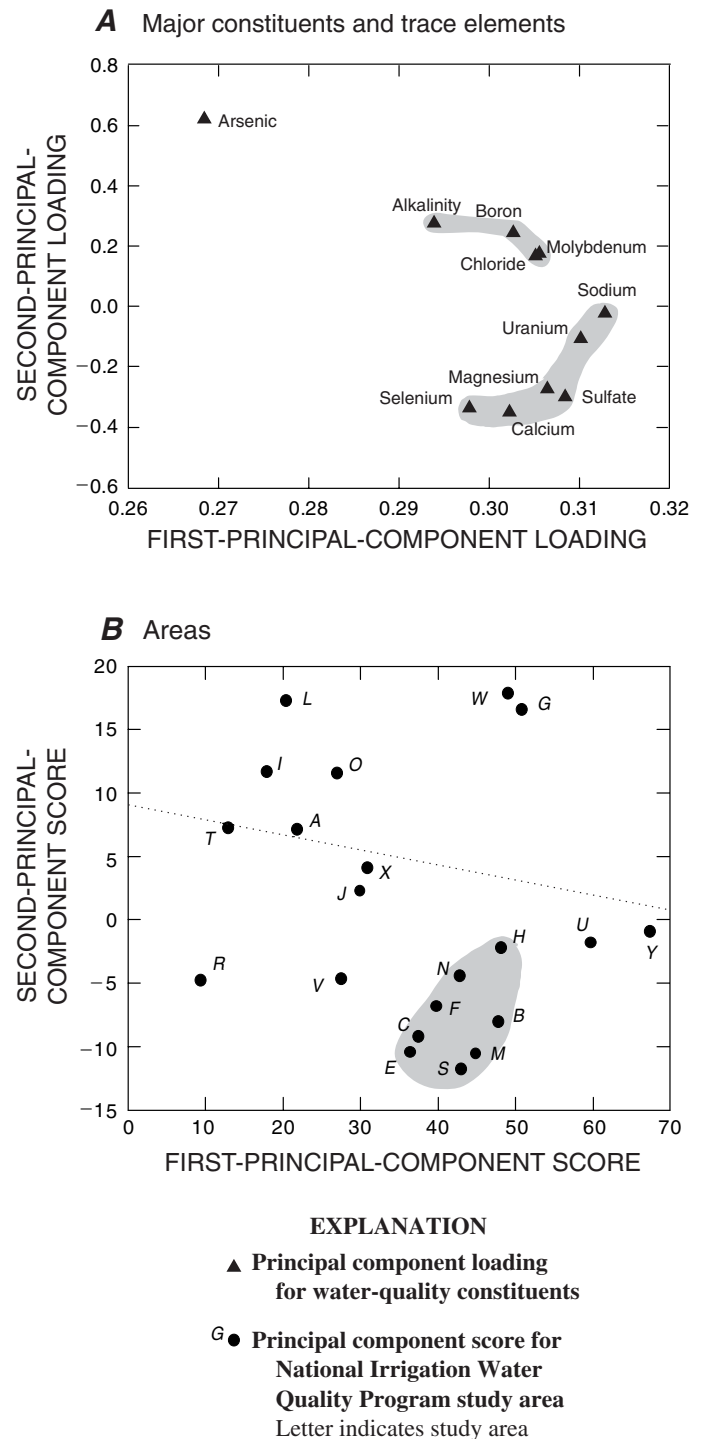


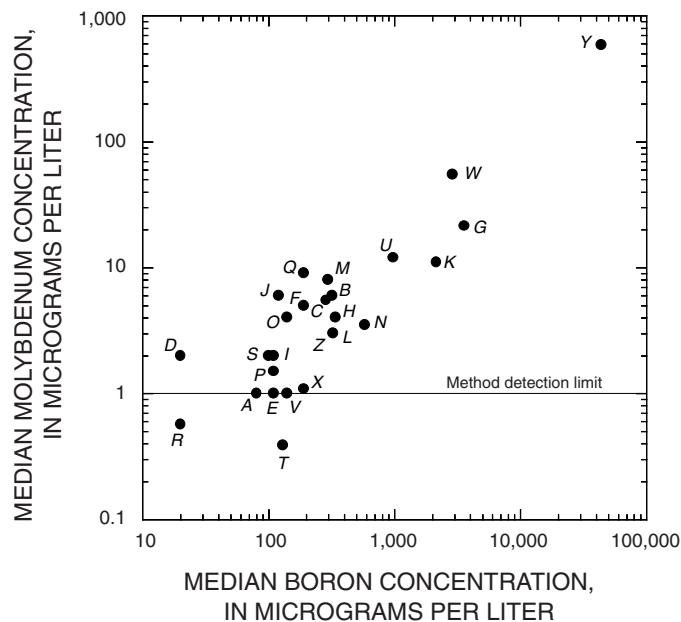
FIGURE 13. Principal-components analysis results. Letters (A–Z) identify National Irrigation Water Quality Program study areas (fig. 2). **A**, major-constituents and trace-element loadings; shaded areas show occurrence of 2 clusters with arsenic as an outlier. **B**, study-area scores; dividing line separates areas associated with Upper Cretaceous marine sedimentary rocks from those not so associated. Shaded area shows study areas having irrigated land that lies on Upper Cretaceous marine sedimentary rocks. Data from five areas (*D*, *K*, *P*, *Q*, and *Z*) not used because uranium or major-ion data were not collected.

The importance of geology in explaining the NIWQP data is indicated by a grouping of geologically related study areas on a plot of principal-components scores (fig. 13B). All study areas below the dividing line are either directly or indirectly associated with Upper Cretaceous marine sedimentary rocks (Seiler, 1995); the eight areas in the cluster (B, C, E, F, H, M, N, and S) have irrigated land that lies on Upper Cretaceous marine sedimentary rocks.

Sulfate and selenium are closely associated on the principal-components loadings plot (fig. 13A). This association is a result of the similar chemical and physical properties of sulfur and selenium. The close association of sulfate and selenium may have caused previous investigators to attribute cases of livestock poisoning to selenium when it was actually due to sulfate. O'Toole and others (1996) concluded that many field cases of "blind staggers" in livestock that previously had been attributed to selenium were caused by malignant catarrhal fever, or (polioencephalomalacia), a disease that is closely associated with excess dietary sulfate in water, feed, and some weeds.

Selenium and uranium appear to be associated (fig. 13A). Such an association is probably because of their similar redox chemistry. Both are insoluble under reducing conditions and soluble under oxidizing conditions (Drever, 1988), and both commonly occur in sediment rich in organic material. Elevated selenium concentrations are common in sedimentary rocks associated with uranium roll-front deposits in the Western United States (Levinson, 1980). Naftz and Rice (1989) observed that *in situ* mining techniques to extract uranium can increase selenium concentrations in ground water. In Wyoming uranium mines, the injection of an alkaline, oxidizing lixiviant to mobilize uranium mobilizes selenium in the ore deposit as well. Similarly, percolation of alkaline, oxygen-containing irrigation water through soil could mobilize uranium and selenium. Application of irrigation water can result in elevated uranium concentrations without selenium concentrations being elevated if the soils are uraniumiferous but not seleniumiferous. This occurs at Stillwater Wildlife Management Area (W), which has among the lowest selenium but highest uranium concentrations of the 26 study areas (figs. 9 and 10).

Boron and molybdenum are associated with each other (figs. 13A and 14), and both are associated with chloride (fig. 13A). Their association with chloride suggests that evaporative processes control their concentrations. Boron and chloride are conservative and increase together in all 26 areas. However, the association of molybdenum and chloride is complex. In some areas, molybdenum is positively associated with chloride and in other areas it is negatively associated (fig. 15).

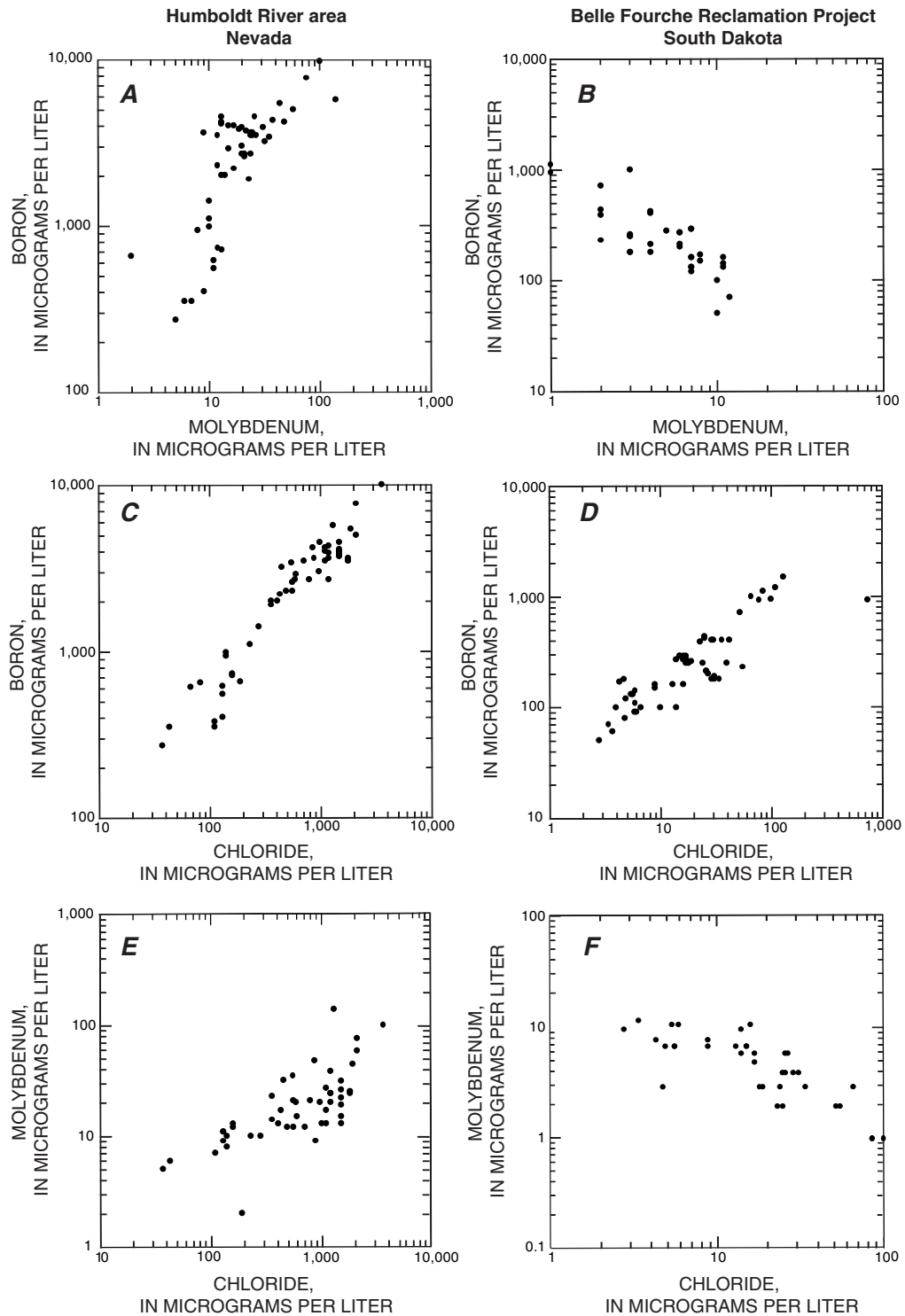


EXPLANATION

● Data point for National Irrigation Water Quality Program study area—Letter indicates study area

FIGURE 14. Relation between median molybdenum and boron concentrations in surface water from National Irrigation Water Quality Program (NIWQP) study areas. Letter identifies study area (fig. 2).

Arsenic is not associated with any of the other measured trace elements (fig. 13A) and is negatively associated with selenium. The negative association may result in part from differing adsorption chemistry of the two elements. Masscheleyn and others (1991) reported that, under highly oxidizing conditions, arsenic solubility is low and selenium solubility is high, probably because arsenic(V) is strongly adsorbed to iron oxy-hydroxides whereas selenium(VI) adsorption is minimal. Another potential reason for the negative association is differing geologic sources. Where arsenic concentrations are high in water, geologic source materials tend to be relatively high in volcanic glass or are iron-oxide-bearing igneous rocks (Welch and others, 1988); in contrast, igneous rocks tend to have low concentrations of selenium (Berrow and Ure, 1989). The four areas having the highest median arsenic concentrations (G, I, Q, and W) all lie on, or are adjacent to, Tertiary volcanic rocks and are not associated with Upper Cretaceous marine rocks.



EXPLANATION

- Surface-water analysis

FIGURE 15. Relations between boron and molybdenum, boron and chloride, and molybdenum and chloride concentrations in surface-water samples from two National Irrigation Water Quality Program (NIWQP) study areas, Humboldt River area (NIWQP area G; Nevada) and Belle Fourche Reclamation Project (NIWQP area C; South Dakota). Data points are from non-replicate environmental samples collected as part of a NIWQP investigation.

RELATION BETWEEN CONTAMINANT CONCENTRATIONS IN SURFACE WATER AND BOTTOM SEDIMENT

Comparisons were made among arsenic, boron, molybdenum, selenium, and uranium concentrations in surface water and bottom sediment. Comparisons were made at both the study-area level and the data-collection-site level. For comparisons at the study-area level (fig. 16), median concentrations of the constituents in surface water and in the fine (< 0.062-mm) fraction of bottom sediment at sites in and downstream from irrigated lands were determined. Median concentrations less than the reporting limit were estimated by adjusted log-normal maximum-likelihood methods (Helsel and Cohn, 1988). In some instances, too few values were greater than the reporting limit, such as for molybdenum in bottom sediment, to make an estimate of the median concentration. In such instances, data from the study area were not plotted.

For comparisons at the level of individual sites (fig. 17), the most recent analysis made was selected to represent surface-water and bottom-sediment contaminant concentrations at the site. For surface water, typically three or four surface-water analyses were made at a data-collection site. Typically, samples for bottom-sediment analysis were collected only once at a data-collection site during a NIWQP investigation. Because of the small number of samples at most sites, robust methods could not be used to characterize the central tendency at the site level, especially where the data included censored values. Censored values were not plotted in figure 17.

Linear regression of median concentrations of contaminants in NIWQP study areas indicates a significant relation ($p < 0.05$) between boron, selenium, and uranium concentrations in surface water and bottom sediment after log transformation. The p -value is a significance level, or probability, and has a range of 0 to 1. A p -value of 0.05 means a 5-percent likelihood that concentrations in water and bottom sediment are not related or that the observed relation is simply due to chance. Statistical tradition uses a value of 0.05 for the significance level, but other values may be used depending on the objectives of the investigators (Helsel and Hirsch, 1992). The arsenic, boron, molybdenum, selenium, and uranium concentrations in surface water at individual sites also are significantly related to the concentrations in bottom sediment ($p < 0.05$) at the site after log transformation (fig. 17).

Two reasons are possible for the relation between boron concentrations in surface water and bottom sediment (figs. 16 and 17). Boron is an essential nutrient for higher plants (Vymazal, 1995). In sediment high in organic matter, decomposing plant matter may contribute large amounts of boron to the sediment. Reported boron concentrations in aquatic and wetland plants were tabulated by Vymazal (1995). Concentrations from 1 to 50 $\mu\text{g/g}$ were reported most commonly, but concentrations exceeding 2,500 $\mu\text{g/g}$ have been reported for a species of duckweed from Michigan (Glandon and McNabb, 1978).

The relation between boron concentrations in surface water and bottom sediment also may be an artifact of analytical procedures. Some of the boron attributed to the bottom sediment actually originates as boron dissolved in the water associated with the bottom sediment and remains behind as the sample is dried. Because percentage moisture was not measured as part of the analysis, the actual amount of boron attributable to residual water cannot be estimated. However, it is likely to be substantial for some samples. From simple mathematics, if the moisture content of the sample is 50 percent, then the amount of boron contributed to a gram of sediment by the water would be 0.1 percent of the boron concentration in the water. In some samples, residual boron from the water could contribute from ten to more than a hundred micrograms to the bottom sediment. Although a similar effect at elevated concentrations can be expected for other trace elements, this effect is most likely to be important for boron because it commonly attains concentrations in water greater than 1,000 $\mu\text{g/L}$ (figs. 7A, B).

Because selenium bioaccumulates and is incorporated into living tissue, many investigators have observed a relation between bottom-sediment selenium concentration and organic-carbon content (Weres and others, 1989; Presser and others, 1994; Van Derveer and Canton, 1997). Van Derveer and Canton (1997), using data from Colorado streams and four NIWQP study areas (B, C, H, and W), reported a highly significant relation between selenium concentration in bottom sediment and the product of selenium in water and the total organic-carbon content of bottom sediment. Although a similar strong relation for selenium holds for data from all NIWQP sites (fig. 18), no such relation holds for arsenic, molybdenum, and uranium. For boron, the relation shown in figure 18 may be an artifact of the analytical process.

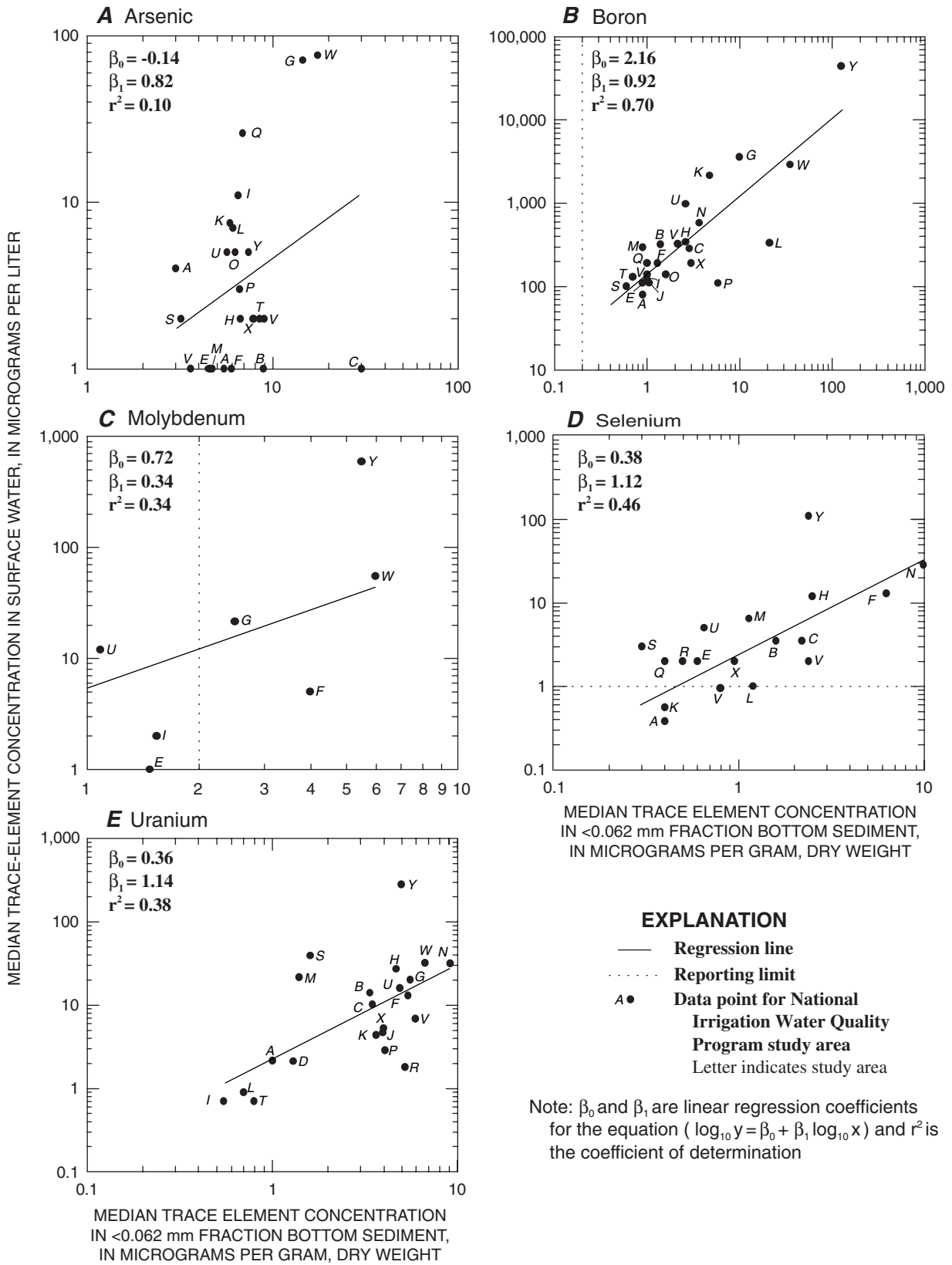


FIGURE 16. Relation between median concentrations of selected trace elements in surface water and in <0.062-millimeter-fraction bottom sediment in National Irrigation Water Quality Program study areas. Derivation of below-reporting-limit values is explained in text.

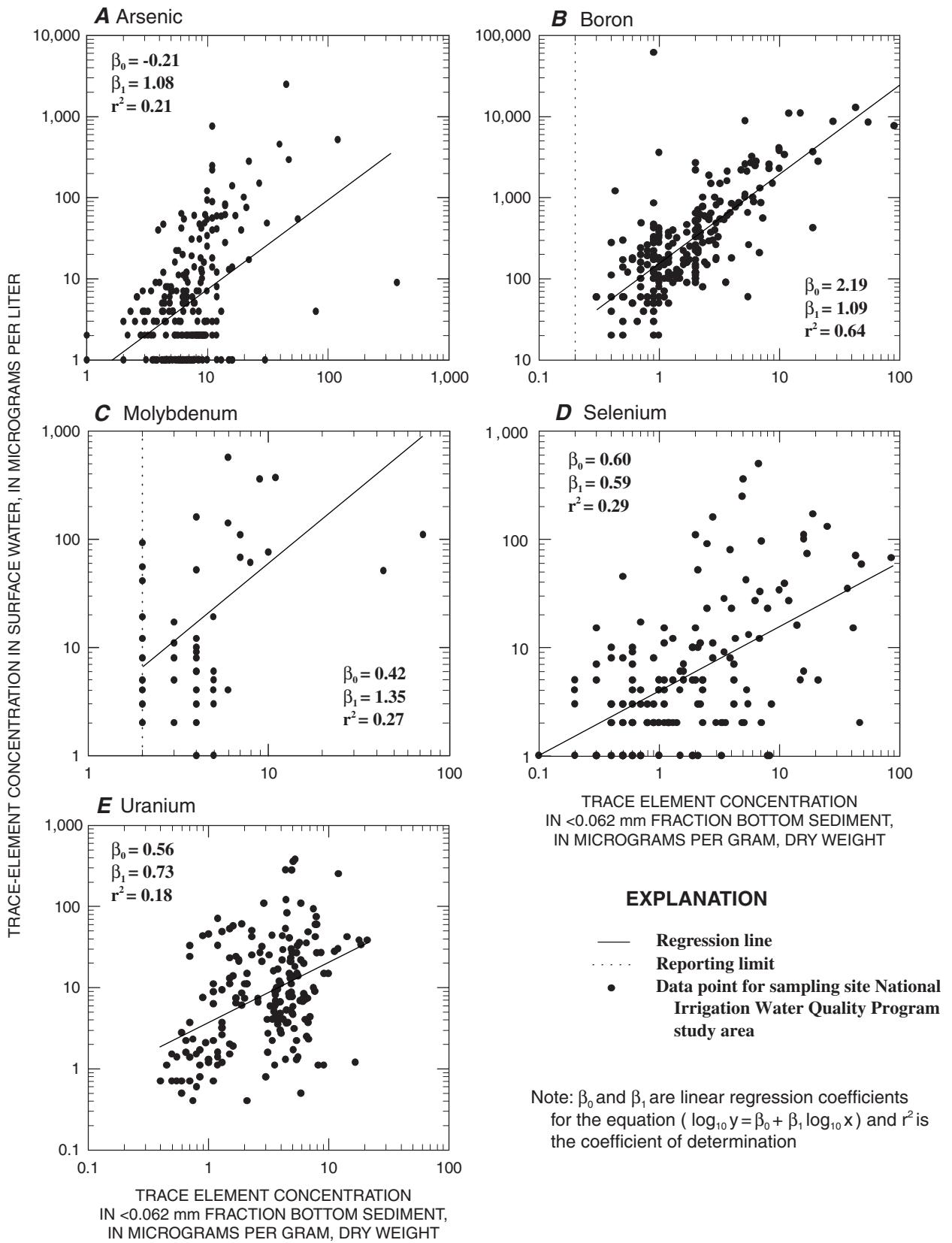


FIGURE 17. Relation between concentrations of selected trace elements in surface water and in <0.062-millimeter-fraction bottom sediment at individual data-collection sites. Data points are from non-replicate environmental samples collected as part of a NIWQP investigation.

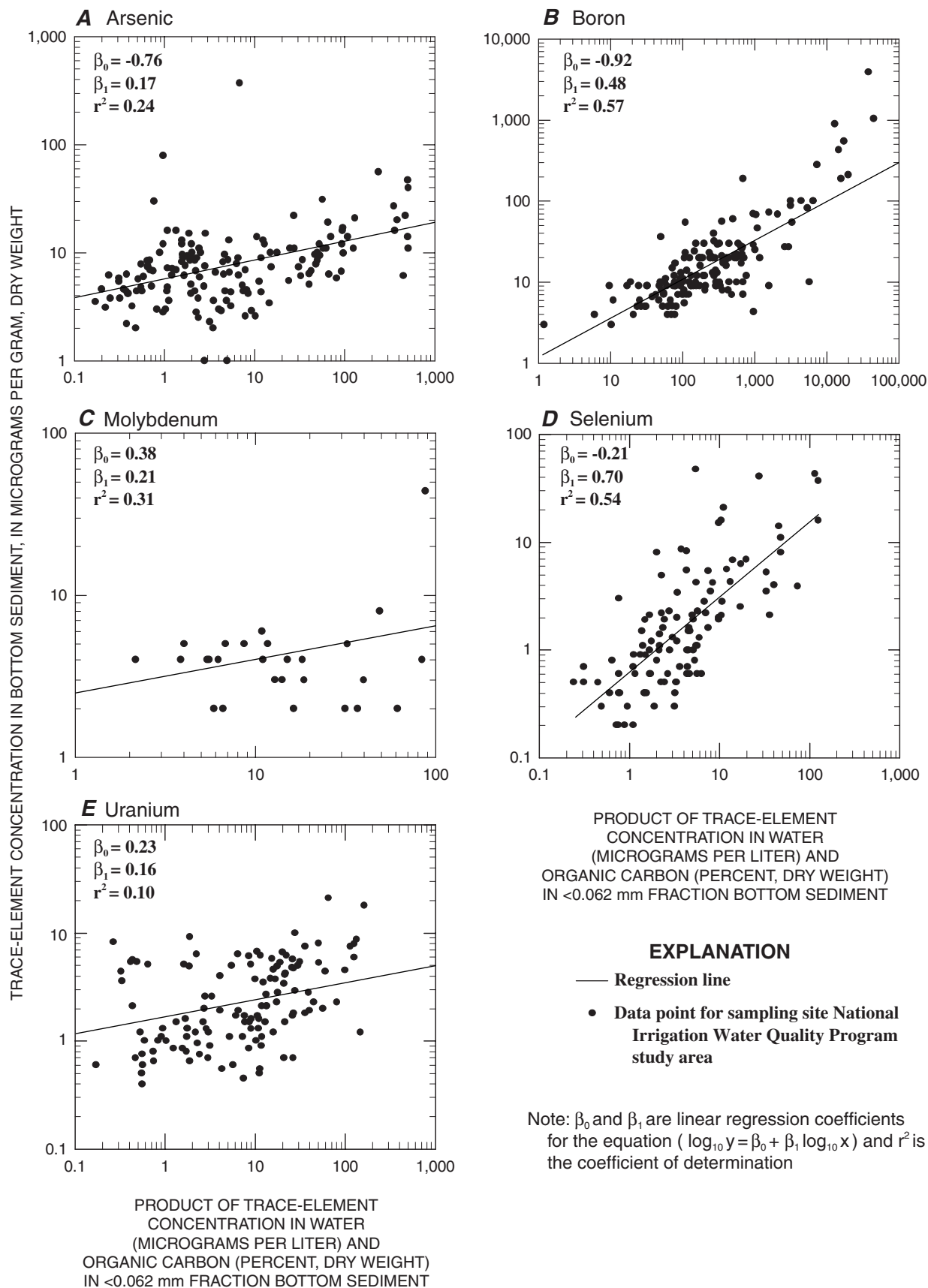


FIGURE 18. Relation between trace-element concentrations in bottom sediment and product of percentage organic carbon in <0.062-millimeter-fraction bottom sediment and trace-element concentrations in surface water. Data points are from non-replicate environmental samples collected as part of a NIWQP investigation.

RELATION BETWEEN TOTAL- AND FILTERED-CONTAMINANT CONCENTRATIONS IN SURFACE WATER

The USFWS typically measures total-contaminant concentrations in unfiltered water samples when developing relations between biological effect and environmental-contaminant concentrations; however, the USGS typically measures contaminant concentrations for trace elements in filtered-water samples. Determining the relation between contaminant concentrations in filtered and unfiltered water is necessary so that comparisons can be made between biological-effect levels determined by the USFWS and contaminant concentrations measured by the USGS.

Some study teams measured both total- and filtered-water trace-element concentrations in surface-water samples they collected. Comparison of the two types of concentrations in surface water for arsenic, boron, molybdenum, and selenium indicates that they were nearly the same (fig. 19). Filtered-water aluminum concentrations, however, are typically much less than total concentrations. These results indicate that for concentrations greater than about 10 µg/L, arsenic, boron, molybdenum, and selenium concentrations in filtered samples may be directly compared to biological-effect levels developed by using unfiltered samples.

For arsenic, the relation likely does not apply in the range of 1 to 10 µg/L. Of 153 samples in which filtered arsenic concentrations were in the range of 1 to 10 µg/L, filtered concentrations equaled unfiltered concentrations in 87 samples. In 18 samples filtered concentrations were greater than unfiltered concentrations and in 48 samples unfiltered concentrations were greater than filtered concentrations. This suggests that, in this range, there may be a tendency for unfiltered concentrations to be greater than filtered concentrations.

For selenium, the relation likely applies in the range of 1 to 10 µg/L. Of 216 samples in which filtered selenium concentrations were in the range 1 to 10 µg/L, filtered concentrations equaled unfiltered concentrations in 136 samples. In 40 samples, filtered concentrations were greater than unfiltered concentrations, and in 40 other samples unfiltered concentrations were greater than filtered concentrations. This suggests differences from equality result from analytical imprecision and not a general tendency for unfiltered concentrations to be greater than filtered concentrations.

The relation between trace-element concentrations in total and filtered samples is expected given typical suspended-sediment concentrations in the water and trace-element concentrations in sediment. The median aluminum concentration in the fine (< 0.062-mm) fraction of bottom-sediment samples collected by the NIWQP was 6.2 percent (table 12). Assuming that this fine fraction is representative of suspended sediment, a suspended-sediment concentration of only 10 mg/L would contribute 620 µg of aluminum to a liter of water. However, the median selenium concentration in the fine fraction of bottom-sediment

samples collected by the NIWQP is 0.6 µg/g (table 12). If this fraction is representative of suspended sediment, 2,000 mg/L suspended sediment would contribute only 1.2 µg of selenium to a liter of water.

For those elements that bioaccumulate, total concentrations could be higher than filtered-water concentrations in lentic, nutrient-rich waters with large algal populations. Fujii (1988) reported total selenium concentrations in five evaporation ponds in the Tulare Lake Bed area that averaged 1.7 times greater than corresponding filtered concentrations. Algae are important because they can accumulate large amounts of selenium in their tissues. Bennet and others (1986) demonstrated that in the laboratory the single-celled freshwater algae *Chlorella pyrenoidosa* could accumulate selenium to concentrations of 2,600 to 3,100 µg/g dry weight. One mg/L of algae containing this much selenium would add 2.6 to 3.1 µg/L of particulate selenium to the water. Settings where algae have the potential to substantially affect the relation between filtered- and total-selenium concentrations should be apparent because water containing 1 mg/L of algae probably would be discolored. Chlorophyll a constitutes 1-2 percent of the dry weight of planktonic algae (Franson, 1995), hence, water containing 1 mg/L of algae would contain 10-20 µg/L of chlorophyll a. Water containing 10-15 µg/L of chlorophyll a can be discolored and water containing 20-30 µg/L of chlorophyll a will be deeply discolored (Raschke, 1993).

CONCEPTUAL MODEL OF SELENIUM CONTAMINATION IN IRRIGATED AREAS

The emphasis of the rest of this report is on selenium for two reasons. First, discussion in the section titled "Summary Statistics and Comparison to Criteria" (p. 23), indicated that in the NIWQP data set selenium is the contaminant associated with irrigation drainage that most often exceeds the chronic criterion for the protection of aquatic life. More than 40 percent of the surface water samples collected during NIWQP investigations exceeded the criterion. Second, wildlife are extremely sensitive to selenium. Thresholds for dietary toxicity in vertebrate animals are only slightly greater than nutritionally optimal levels, therefore, relatively small perturbations in the dietary exposure of vertebrate animals are potentially harmful.

This section of the report presents a conceptual model of why soils in irrigated areas of the Western United States are seleniferous; how irrigation mobilizes selenium, how the climate and hydrology of an area interact to determine whether selenium contamination of water occurs, and how selenium enters the food chain. The conceptual model includes a brief description of selenium biogeochemistry and describes processes of: (1) selenium enrichment in marine rocks principally through biological processes; (2) selenium enrichment in soil and ground water in irrigated areas and its subsequent transport to areas supporting fish and wildlife; (3) selenium enrichment in water and sediment through hydrologic processes in wildlife habitat; and (4) selenium incorporation into the food chain and, ultimately, exposure of wildlife to it.

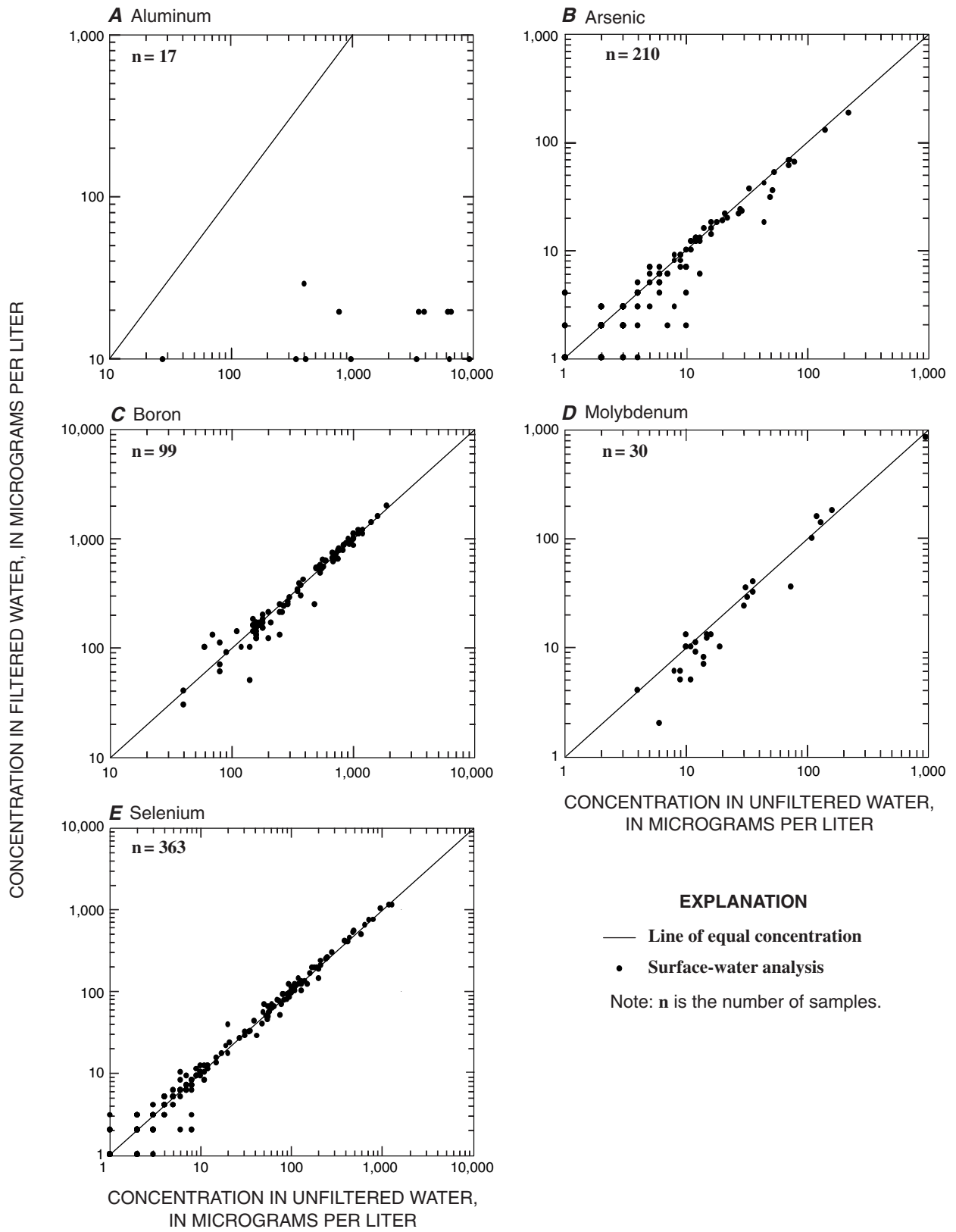


FIGURE 19. Relation between concentrations of aluminum, arsenic, boron, molybdenum, and selenium in filtered and in unfiltered surface water. Data points are from non-replicate environmental samples collected as part of a NIWQP investigation.

SELENIUM BIOGEOCHEMISTRY

Selenium biogeochemistry is reviewed in numerous articles and is summarized here. Selenium is a member of the sulfur family (Group VIA of the periodic table), and as such selenium and sulfur have similar chemical properties. Selenium has three common oxidation states: Se^{+6} (SeO_4^{-2} , selenate), Se^{+4} (SeO_3^{-2} , selenite), and Se^{-2} (selenide). Less common in nature is elemental selenium (Se^0).

Selenium geochemistry is very dependent on the pH and redox conditions of the environment. In wetlands the forms of selenium found in the water column and underlying sediment are commonly different because the water contains dissolved oxygen whereas sediments, particularly wetland sediments, are often anoxic. In water, the oxyanions of selenium, selenate and selenite, are most common. Selenate is the most soluble because selenite has a strong affinity for clays and iron oxyhydroxides and readily forms stable, insoluble complexes. In water selenides would be rather rare except possibly in organic compounds. In anoxic wetland sediments, selenides and elemental selenium are most common. Anaerobic bacteria in sediments are capable of reducing selenate to elemental selenium. Selenides are found in both metallic and organic forms. Selenide substitutes for sulfur in many metallic sulfide minerals such as pyrite (FeS_2). Much of the selenium in the crust of the earth is found in these sulfide minerals.

Selenates are readily taken up by organisms and biotransformed into organic forms such as seleno-amino acids and dimethylselenide. The essential requirement for selenium in animals is attributed to enzymes containing selenium, in particular glutathione peroxidase. Although some algae have an essential growth requirement for selenium, no essential organoselenium compounds have been reported for either algae or higher plants (Vyzamal, 1995).

ENRICHMENT OF SELENIUM IN ROCKS

Selenium is found in many geologic units. The distribution of selenium in rocks of the United States and the world have been reviewed by Rosenfeld and Beath (1964) and Berrow and Ure (1989). The average selenium content of the crust of the Earth is about 0.05 mg/kg (Fortescue, 1992). Igneous rocks tend to have low contents of selenium whereas relatively large contents are found in all sedimentary rocks (Berrow and Ure, 1989).

In the interior of the Western United States, selenium commonly is associated with fine-grained marine sedimentary rocks of Late Cretaceous age (Anderson and others, 1961; Howard, 1977). Lakin and Byers (1941, p. 2) concluded that

*“All areas of soils derived from material of Cretaceous age are then open to suspicion of the presence of harmful quantities of selenium * * *”*

Trelease and Beath (1949, p. 95) noted that about 80 percent of all plant specimens containing more than 50 mg/kg selenium had been collected from Cretaceous units. In the Diablo Range along the west side of San Joaquin Valley, Calif., Tidball and others (1991, p. 109) noted that marine rocks of Late Cretaceous to Oligocene age are variously seleniferous, whereas nonmarine rocks of Pliocene and younger age tend to be non-seleniferous.

Understanding general mechanisms by which selenium is incorporated into rocks is important because irrigation of soils derived from those rocks can contribute selenium to areas supporting fish and wildlife. Until relatively recently, the emphasis has been on physical processes as mechanisms for selenium enrichment of marine rocks of Cretaceous age. More recently, however, biological processes occurring in marine environments have been proposed as the principal driving mechanism behind selenium enrichment in marine rocks of all ages.

One source of selenium in ancient marine deposits is the direct deposition of particulate matter derived either from erosion of seleniferous deposits on the continental mass or from fallout of seleniferous atmospheric dusts and particles. Several authors have proposed that Cretaceous oceans were enriched in selenium originating from contemporaneous volcanic activity. Selenium is present in volcanic gases because volatile selenium escapes along with volatile sulfur from cooling rocks and from volcanoes (Berrow and Ure, 1989). The presence of selenium in volcanic gases led Byers and others (1936, p. 823) to conclude that selenium in Cretaceous marine rocks was primarily from rainout of volcanic gases. Soils and sediment near volcanic activity are relatively rich in selenium because selenium is likely to be present in the atmosphere in a particulate form and is subject to removal by rain relatively close to its point of origin (Berrow and Ure, 1989). Toward the close of the Late Cretaceous, in what is now the Western United States, violent volcanic activity continued while a large inland sea and the Rocky Mountains formed (Trelease and Beath, 1949). Berrow and Ure (1989, p. 219) stated that much of the selenium in Cretaceous sedimentary rocks must have been derived from volcanic dusts and gases emitted into the atmosphere because igneous rocks tend to have low concentrations of selenium. Rosenfeld and Beath (1964, p. 12) concluded that erosion of seleniferous volcanic rocks and rainout of volcanic dust and gases were the explanation for the distribution of selenium in different geological units.

These physical explanations for selenium enrichment in Cretaceous rocks are incomplete because they do not consider biological processes. In fact, biological processes causing deposition of selenium in marine sediments likely are of greater importance than physical processes. Presser (1994a) suggested the bioaccumulation of selenium in ancient seas and later deposition and diagenesis of the seleniferous organic matter is a primary mechanism of selenium enrichment in ancient sedimentary deposits. Planktonic organic matter carries minor

elements to the sea floor directly and also drives redox reactions that determine the suite of elements which precipitate from bottom water (Piper, 1994). Piper (1994, p. 110) concluded that the biologic cycle is the single dominating influence on the minor-element composition of virtually all sedimentary rocks having high contents of marine phases such as organic matter, apatite, silica, calcite, and dolomite.

Any marine deposit laid down in a shallow, productive environment may be seleniferous. Selenium bioaccumulates in marine phytoplankton to concentrations several thousand times greater than that in the seawater. Selenium concentrations in present-day seawater average about 0.09 $\mu\text{g/L}$ (Hem, 1985) and in marine phytoplankton are 3 mg/g (Brumsack, 1986). Because selenium stimulates the growth of some marine phytoplankton and is a required mineral nutrient for some algae (Vymazal, 1995), bioaccumulation and deposition of seleniferous organic matter would have occurred even if selenium concentrations in ancient oceans were not enriched by volcanic activity. Sindeeva (1964, p. 291) noted that selenium was present in sizeable amounts in recently deposited sea-bottom sediments in the Bering Sea, the Arctic Ocean, the Caribbean, the northern part of the Atlantic Ocean, and the Gulf of California. The Phosphoria Formation in the Northwestern United States is a marine sedimentary deposit of Permian age that contains high concentrations of selenium throughout the deposit (Piper and others, 2000).

Tertiary continental sedimentary deposits derived by the reworking of Upper Cretaceous marine sedimentary rocks exposed by mountain uplifts and subsequently eroded also may be seleniferous. Trelease and Beath (1949, p. 96) commented that it is not surprising many Tertiary rocks are seleniferous because they represent rock debris derived from erosion of Cretaceous and older rocks during uplifting associated with the development of the Rocky Mountains. Whether continental sedimentary deposits are seleniferous depends on several factors: whether the parent rock was seleniferous, whether reduced selenium in the rock was exposed to the strongly oxidizing conditions required to mobilize the selenium, and whether the rock was leached enough to remove any selenium.

ENRICHMENT OF SELENIUM IN SOILS AND GROUND WATER IN IRRIGATED AREAS

Application of irrigation water to seleniferous soils can mobilize selenium and create hydraulic gradients that cause the discharge of seleniferous ground water into drains and other surface-water bodies. Because drainage from agricultural areas can be a principal source of selenium to areas supporting fish and wildlife, an understanding of the processes by which seleniferous rocks cause soils and ground water in agricultural areas to become seleniferous is important. General mechanisms by which soils and ground water in irrigated areas become enriched in selenium are described below.

In the simplest mechanism, selenium in soil originates in a seleniferous soil-parent rock beneath the soils. Soils are seleniferous because selenium-containing minerals remain in the soil following pedochemical weathering of the parent rock. Ground water becomes seleniferous because water percolating through the soil and rock reacts with the selenium-containing minerals and dissolves selenium. In areas where a seleniferous soil-parent rock is beneath the soils, application of irrigation water accelerates the weathering processes and mobilizes more selenium than would occur naturally. Areas having soils that may become seleniferous by this natural weathering process can be identified by geologic maps showing the bedrock distribution of seleniferous sedimentary rocks and deposits.

A second mechanism involves transport of selenium from upland areas in the mountains surrounding irrigated areas. Presser (1994a, b) describes how seleniferous sedimentary deposits tens of miles upland from irrigated land can contribute selenium to land downslope through processes of active weathering, alluvial-fan building, and local drainage. Ground water moving through seleniferous rocks and deposits can discharge to streams, and dissolved selenium can be carried in surface water to downgradient areas. Evaporation of ground water in seleniferous rocks or deposits can wick selenium salts to the surface, and subsequently surface water can strip selenium from the surface exposures. Erosion of seleniferous rocks or deposits upland can carry insoluble selenium to downgradient areas by mass wasting and subsequent transport of suspended sediment in surface water. Areas having soils that may become seleniferous by this process can be identified by geologic and topographic maps because they are adjacent to and downslope from seleniferous sediments and deposits.

The third mechanism involves soils and ground water in an area becoming seleniferous by selenium being transported into the area by surface water. Unlike the second mechanism, the geologic source of the selenium can be hundreds of miles upstream from the contaminated area. Areas having soils that may become seleniferous by this process can be identified by geologic and watershed maps because they will be downstream from seleniferous sediments and deposits.

Application of oxygenated water to irrigated areas weathers reduced selenium in the soil. In addition, application of nitrate fertilizers has been shown to enhance the oxidation of selenium (Wright, 1999) and inhibit reduction of selenium oxyanions (Benson, 1998). Oxyanions of selenium accumulate in the root zone through evapotranspiration of the applied water. To prevent salt buildup from harming the crops, excess water must be applied to fields to flush the salts from the root zone. This excess water carries selenium from the root zone to the water table and results in enrichment of selenium in the ground water. Drains installed in irrigated areas to lower the water table and prevent waterlogging of the soil carry seleniferous ground water to surface water bodies and, ultimately, to wildlife areas.

Climate strongly influences the selenium content of the ground water in irrigated areas. In humid areas, leaching of the soils by rainfall during geologic time before irrigation began would have removed much of the soluble selenium produced by weathering. In arid areas, any soluble selenium produced by weathering would remain in the soil profile because rainfall is insufficient to leach the soils. Trelease and Beath (1949, p. 56) noted that soils supporting seleniferous vegetation have been found only in areas where the mean annual rainfall is less than 20 in., and so is insufficient to leach soil of soluble selenium compounds.

Evapotranspiration consumes water and, hence, selenium salts released by weathering processes become concentrated in the soil water and ground water. Typically, drying of the soil causes a moisture gradient between the soil surface and the water table. As a result, water evaporates directly from the water table. Evaporation also increases ground-water loss by its effects on the transpiration rate of plants. Because roots restrict which minerals enter the plant, removal of water from the sub-surface by plants can enrich contaminant concentrations in the remaining water.

ENRICHMENT OF SELENIUM IN WATER IN FISH AND WILDLIFE HABITAT

Wildlife may be exposed to selenium in ground water from irrigated areas when it discharges to seeps or surface drains. Wildlife congregate near the seeps or lakes or ponds receiving irrigation drainage. Whether selenium concentrations in areas supporting fish and wildlife become elevated above those in the water entering the area depends on the climate and hydrology of the area.

Climate is important in two ways. First, areas having higher amounts of precipitation have greater, diffuse inflows of fresh-water, which dilute contaminants. Second, high rates of evaporation leads to evaporative enrichment of contaminant concentrations in surface and ground water. Direct evaporation from a water body causes contaminant concentrations to increase by removing water and leaving the contaminant in the remaining water. Walker Lake, a terminal lake in western Nevada, provides an example of the amount of water that can be lost through evaporation and its effect on concentration: During 1987–94, nearly all surface-water inflow to the lake was diverted for agricultural use. During the same period, evaporative losses caused a water-level decline of almost 26 ft and a dissolved-solids concentration increase of about 4,000 mg/L (Thomas, 1995).

The presence of terminal lakes or ponds is an important factor in determining whether selenium enrichment of the water occurs in an area. Selenium concentrations increase in lakes and ponds through evaporative enrichment, however, in terminal lakes or ponds, selenium is not flushed out during normal spring runoff. Elevated concentrations in the water eventually may result because the selenium from several seasons remains, although biological processes may transfer selenium in the water column to the sediment.

The occurrence of elevated concentrations of selenium in terminal ponds is biologically significant. In general, ponds are more attractive nesting and foraging habitat to waterbirds than drains because drains and canals typically have steeper sides than ponds. Also, the flow velocity in canals is usually too swift to allow for nesting. Even in selenium-contaminated ponds, lush growths of emergent vegetation can develop and create attractive nesting areas. Hartshorn (1985) observed that Kesterson Reservoir looked surprisingly alive and that some of the shallow ponds were choked with cattails.

INCORPORATION OF SELENIUM INTO THE FOOD CHAIN AND WILDLIFE EXPOSURE TO IT

Aquatic cycling of selenium in wetlands and its incorporation into food chains is described in detail by Lemly and Smith (1987) and those concepts are summarized here. Microorganisms, algae, and higher plants take up selenate directly from the water into the cell interior where it is reduced and incorporated in organoselenium compounds. Death and decay of the organisms carries the reduced selenium compounds into the sediments, as does the fecal matter from consumers of the microorganisms and plants. Selenium is also removed from the water column through reduction of selenate to selenite and subsequent settling following adsorption onto clays and particulates. Tanji (1989) observed that evaporation increased chloride concentrations twofold in a series of ponds in the San Joaquin Valley but selenium concentrations remained nearly constant, indicating that up to 50 percent of the selenium in the water column was removed to the sediments.

Once in the sediments, selenium is effectively mobilized in most aquatic systems into food chains. Selenium is directly taken up by rooted plants and bottom-dwelling invertebrates and detrital-feeding fish and wildlife. Selenium also is released from sediments back into the water column following oxidation resulting from plant roots, microorganisms and the burrowing activity of benthic invertebrates.

Wildlife in wetlands receiving seleniferous water receive potentially toxic doses of selenium when they consume food organisms that have sequestered large amounts of selenium in their tissues. Waterborne selenium, *per se*, is not very toxic to wildlife, rather toxic exposure principally occurs through the food chain (U.S. Department of the Interior, 1998). Most of the combined waterborne and dietary uptake of selenium occurs at the primary producer and primary consumer (phytoplankton and zooplankton) levels (Lemly, 1996c). Because of bioconcentration, tissues of food organisms contain selenium in concentrations tens to thousands of times greater than the concentrations in their food or water. Selenium can accumulate in tissues of food-chain organisms to levels that are toxic to predators such as fish and birds without effects on the growth, reproduction, or survival of the food-chain organisms (Lemly, 1996c).

IMPLICATIONS OF THE CONCEPTUAL MODEL

An important implication of the conceptual model is that it suggests irrigated areas with potential selenium problems may be identifiable *a priori* on the basis of selenium chemistry, and the area's geology, climate, and hydrology. Basic knowledge of selenium chemistry, and its similarity to sulfur, may be useful in identifying water types and levels of salinity where selenium concentrations in water reach harmful levels. The association of selenium with marine rocks suggests geologic maps may be useful in identifying irrigated areas where soils may be seleniferous. If selenium is present in an ecosystem, knowledge of the climate and hydrology may allow predictions to be made on whether evaporative processes will be sufficient to concentrate selenium in water to harmful levels.

Another important implication of the conceptual model is that some feeding guilds may be more at risk than others. Because of bioaccumulation, selenium concentrations often increase between trophic levels. Plants, being at a lower trophic level, likely will contain less selenium than aquatic invertebrates and fish which consume plant matter and/or detritus. As a result, top-level consumers, such as insectivorous and piscivorous birds and fish, usually will be exposed to more selenium through their diets than birds and fish consuming plant matter and/or detritus. Hence, within an area receiving irrigation drain water from seleniferous soils, predatory birds and fish may be at more risk than foraging birds and fish.

Ideas developed in the conceptual model were tested in the following sections to determine whether they were consistent with data collected from the NIWQP study areas. Physical and biological processes involving selenium in NIWQP study areas were analyzed, and to the extent possible, results from the analysis were used to develop tools for use by managers. Because of the types of data collected during NIWQP investigations, analysis of the data emphasizes water and birds rather than sediment, food-chain organisms, and fish. Biological data were analyzed, however, to determine if certain food-chain organisms and feeding guilds are buffered from the effects of selenium contamination in wetlands.

The remainder of the report also addresses issues not raised in the conceptual model. A risk assessment addresses whether other contaminants associated with irrigation drainage could be the cause of observed deformities of bird embryos, and what the effects of selenium are at the population level. The final section of the report addresses the relation between selenium levels in water, sediment and biota and the relation between selenium levels in water and predicted numbers of hens losing eggs to selenium poisoning.

PHYSICAL AND CHEMICAL PROCESSES INVOLVING SELENIUM IN NIWQP AREAS

SELENIUM CONCENTRATIONS

A single selenium concentration was assigned to each study area to compare with criteria and to represent that area's degree of selenium contamination. The 75th percentile of the selenium concentrations from surface-water sites in and downstream from irrigated land (table 15) was selected as this value. The 75th-percentile selenium concentration is the value that is exceeded by 25 percent of the samples from an area. The median concentration was not used because many of the investigations were done only at a reconnaissance level; an area would have to be extremely contaminated before 50 percent of the samples would exceed criterion. Additionally, the 75th percentile can accommodate more nondetects than the median. If 25 percent of the samples had detectable concentrations of selenium, then the 75th percentile is known exactly. The 75th percentile is conservative in that aquatic birds, for instance, probably are exposed to selenium-contaminated water in an area where 25 percent of the samples from that area exceed criteria.

Areas were classified as contaminated or seleniferous if the 75th percentile exceeded water-quality criteria. Of the 26 areas, 12 were ranked as contaminated (*C, E, F, H, M, N, R, S, U, X, Y, and Z*; table 15) because selenium concentrations in 25 percent or more of the surface-water samples exceeded the chronic criterion for the protection of freshwater aquatic life (5 µg/L; U.S. Environmental Protection Agency, 1987). Of the remaining 14 areas, 2 were classified as seleniferous (*B and V*) because selenium concentrations in 25 percent or more of the surface-water samples exceeded the guideline for protection of wildlife, 3 µg/L (table 10). Even though normal background concentrations of selenium in uncontaminated freshwater ecosystems are less than 1 µg/L (U.S. Department of Interior, 1998), for this report areas were classified as uncontaminated if the 75th percentile was less than 3 µg/L.

SOURCES OF SELENIUM

DISTRIBUTION OF SELENIFEROUS ROCKS IN THE WESTERN UNITED STATES

The King and Beikman (1974) 1:2,500,000-scale geologic map of the United States was used as the source of geological information about NIWQP study areas in the Western United States because the geologic units are consistent at a national scale. King and Beikman (1974) mapped Quaternary deposits in the Western United States only if they are thick and extensive; instead of mapping surficial glacial deposits, they showed the limits of glaciation. Thus, older bedrock may be covered by younger glacial deposits not shown on their map.

TABLE 15. Classification of National Irrigation Water Quality Program study areas by selenium content of surface water in and downstream from irrigated areas

[Area classification: C, contaminated (75th percentile of selenium concentrations equals or exceeds 5 micrograms per liter); S, seleniferous (75th percentile of selenium concentration equals or exceeds 3 but is less than 5 micrograms per liter); UC, uncontaminated (75th percentile of selenium concentrations is less than 3 micrograms per liter). Abbreviation and symbol: µg/L, microgram per liter; <, less than]

Identifier ³	Study area Name	Selenium concentration ¹ (µg/L)			Number of observations	Area classification	Area ranking ²
		Median	75th percentile	Range			
A	American Falls Reservoir, Idaho	<1	1.0	<1–6	14	UC	18.5
B	Angostura Reclamation Unit, South Dakota	3.5	4.5	<1–6	12	S	13
C	Belle Fourche Reclamation Project, South Dakota	3.5	5.0	2–11	10	C	11.5
D	Columbia River Basin, Washington	<1	<1	<1–4	48	UC	23
E	Dolores–Ute Mountain area, Colorado	2.0	7.0	<1–88	47	C	8
F	Gunnison River Basin–Grand Valley Project, Colorado	13	35	<1–380	343	C	4
G	Humboldt River area, Nevada	<1	2.0	<1–4	34	UC	16
H	Kendrick Reclamation Project, Wyoming	12	64	<1–5,300	236	C	3
I	Klamath Basin Refuge Complex, California–Oregon	<1	<1	<1–<1	13	UC	23
J	Lower Colorado River valley, California–Arizona	1.0	2.0	<1–2	13	UC	16
K	Lower Rio Grande valley, Texas	<1	1.0	<1–2	14	UC	18.5
L	Malheur National Wildlife Refuge, Oregon	<1	<1	<1–<1	14	UC	23
M	Middle Arkansas River Basin, Colorado–Kansas	6.5	10	2–52	18	C	5
N	Middle Green River Basin, Utah	29	73	<1–8,300	196	C	2
O	Middle Rio Grande, New Mexico	<1	<1	<1–1	38	UC	23
P	Milk River Basin, Montana	<1	<1	<1–<1	12	UC	23
Q	Owyhee–Vale Reclamation Project areas, Oregon–Idaho	2.0	2.0	<1–5	33	UC	16
R	Pine River area, Colorado	2.0	6.0	<1–94	43	C	9.5
S	Riverton Reclamation Project, Wyoming	3.0	5.0	<1–12	21	C	11.5
T	Sacramento Refuge Complex, California	<1	<1	<1–5	23	UC	23
U	Salton Sea area, California	5.0	8.0	1–10	54	C	6
V	San Juan River area, New Mexico	<1	3.0	<1–67	75	S	14
W	Stillwater Wildlife Management Area, Nevada	<1	<1	<1–21	184	UC	23
X	Sun River area, Montana	2.0	7.5	<1–190	120	C	7
Y	Tulare Lake Bed area, California	110	⁴ 265	<1–390	9	C	1
Z	Vermejo Project area, New Mexico	2.0	6.0	<1–23	16	C	9.5

¹ Analyses of non-replicate, filtered surface-water samples collected during a NIWQP investigation from study area in and downstream from irrigated lands.

² Ranking of study area from most to least contaminated on the basis of 75th percentile selenium concentration.

³ Used in figure 2 to show locations of study areas.

⁴ This value was based on a limited number of samples from one pond system. A better regional value for the Tulare Lake Bed area is provided by Moore and others (1990), who report an acreage-weighted geometric-mean selenium concentration of 49 µg/L for 7,224 acres of evaporation ponds in the area.