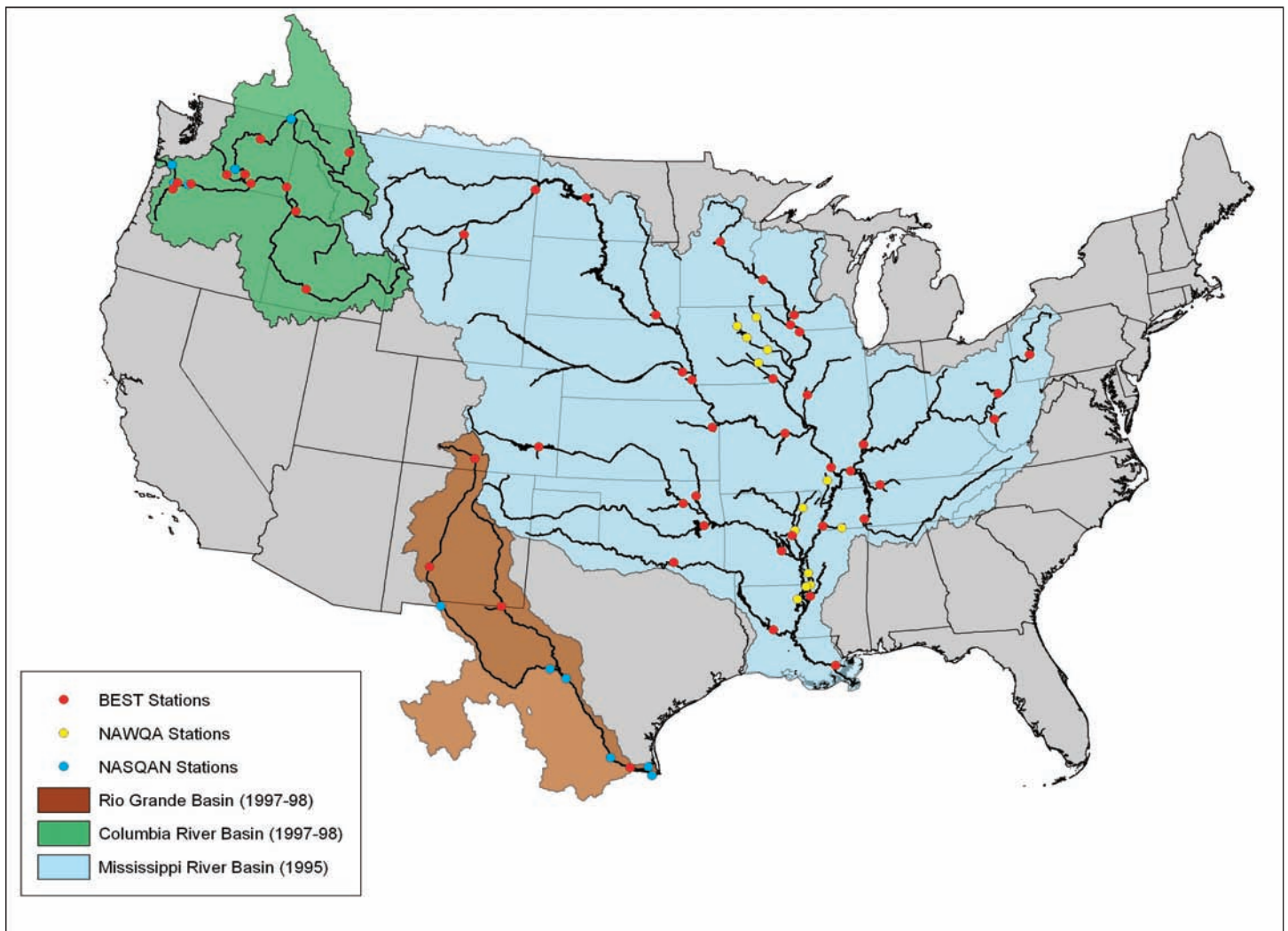


# Development of an Approach for Integrating Components of the U.S. Geological Survey Biomonitoring of Environmental Status and Trends (BEST) and National Stream Quantity Accounting Network (NASQAN) Programs for Large U.S. Rivers



Scientific Investigations Report 2005—5083

**Cover:** Map of the conterminous United States showing waterways, river basins and BEST stations sampled in 1995 and 1997-98. BEST, Biomonitoring of Environmental Status and Trends program; NASQAN, National Stream Quantity Accounting Network; NAWQA, National Water-Quality Assessment program.

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By Nancy J. Bauch, Christopher J. Schmitt, and Charles G. Crawford

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## Conversion Factors

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in)
millimeter (mm)	0.03937	inch (in)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
square kilometer (km <sup>2</sup> )	0.3861	square mile (mi)
cubic kilometer (km <sup>3</sup> )	0.2399	cubic mile (mi <sup>3</sup> )
Volume		
milliliter (mL)	0.03381	fluid ounce (fl. oz)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
cubic meter (cm <sup>3</sup> )	0.0002642	million gallons (Mgal)
Mass		
kilogram (kg)	2.205	pound, avoirdupois (lb)
Concentration		
microgram per gram (µg/g)	=	part per million (ppm; 10 <sup>6</sup> )
nanogram per gram (ng/g)	=	part per billion (ppb; 10 <sup>9</sup> )
picogram per gram (pg/g)	=	part per trillion (ppt; 10 <sup>12</sup> )
milligram per millimeter (mg/mL)	=	part per thousand (ppt; 10 <sup>3</sup> )
milligram per liter (mg/L)	=	part per million (ppm; 10 <sup>6</sup> )
microgram per liter (µg/L)	=	part per billion (ppb; 10 <sup>9</sup> )

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

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

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

$$^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8$$





# Development of an Approach for Integrating Components of the U.S. Geological Survey Biomonitoring of Environmental Status and Trends (BEST) and National Stream Quantity Accounting Network (NASQAN) Programs for Large U.S. Rivers

By Nancy J. Bauch<sup>1</sup>, Christopher J. Schmitt<sup>2</sup>, and Charles G. Crawford<sup>3</sup>

## Abstract

A national-scale framework for monitoring environmental contaminants in fish and effects of contaminant exposure on fish in large U.S. rivers has been proposed by the Biomonitoring of Environmental Status and Trends (BEST) Program of the U.S. Geological Survey (USGS). The framework shares many features and objectives with the USGS National Stream Quantity Accounting Network (NASQAN) Program, which monitors water quality in large U.S. river basins—those with drainage areas of 250,000 to 1,200,000 square miles at their most downstream stations. Because the two programs appear to be complementary, this study was initiated in 2001 to investigate alternative techniques for summarizing and integrating the water-quality data with the fish-contaminant and fish-health data, and to provide recommendations to the BEST program for future integrated studies.

Test data sets from BEST and NASQAN stations in the Columbia River and Rio Grande basins (CRB and RGB, respectively) with fish data for 1997-98 and water-quality data for water years 1995-98 were compiled. Water-quality data for field properties, trace elements, and water-soluble

pesticides were summarized as time-weighted concentrations, concentrations in the most recent water sample prior to fish collection, frequency-of-detection, and total toxicity estimates, and were compared to guidelines for the protection of freshwater aquatic life. Individual and total concentrations of contaminants in fish, mean values of fish-health observation indicators, and median values of fish-health measurement indicators were computed by station, species, and gender. Most analyses of fish data were restricted to common carp (*Cyprinus carpio*), the most widely distributed species. Where appropriate, fish data were further summarized by age and gonadal stage. The ratio of the stable isotopes <sup>15</sup>N and <sup>14</sup>N ( $\delta^{15}$ N) of particulate organic matter in water and fish were summarized as means and ranges. Relations between water-quality and fish data were investigated with Kendall's tau correlation coefficient and the Kruskal-Wallis test to illustrate the types of analyses that could be performed on such data sets.

Only a small number of stations in each basin met minimum sample criteria, and the resulting test data sets contained too few observations for in-depth analysis. The analyses and results are reported to illustrate how data from the two programs might be combined and how results of the integrated data can be interpreted. Examples include documentation of statistically significant positive correlations ( $p \leq 0.05$ ) between the following NASQAN and BEST variables (respectively): atrazine with external lesions; atrazine and zinc with external anomalies; arsenic, copper, and total trace elements (sum of arsenic, chromium, copper, and zinc concentrations) with ethoxyresorufin *O*-deethylase activity; specific conductance, copper, and total trace elements with percent of tissue occupied by macrophage aggregates; total trace elements

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with splenosomatic index and condition factor; copper with condition factor; and arsenic, copper, total trace elements, and zinc with health-assessment index. Other significant correlations between NASQAN and BEST variables included trophic position ( $\delta^{15}\text{N}$  of fish minus  $\delta^{15}\text{N}$  of particulate organic matter in water) with total organochlorine pesticides and total PCBs in fish. In-depth analyses using these techniques could be conducted using larger data sets.

Recommendations to the BEST Program pertain to the quantity of water-quality and fish data, additional water-quality parameters to measure, summarization and integration techniques, the use of guidelines for the protection of freshwater aquatic life, substitution methods for censored data, use of water and fish trace-element and  $\delta^{15}\text{N}$  data, and additional data (suspended- and streambed-sediment) parameters that could be included in future integrated studies. Data sets combined and summarized in the manner described here would represent a comprehensive assessment of fish exposure to contaminants and the effects of exposure on the fish.

## Introduction

The U.S. Geological Survey (USGS) Biomonitoring of Environmental Status and Trends (BEST) Program has initiated testing of a national-scale framework for monitoring environmental contaminants and their effects in U.S. rivers. In this framework, fish are collected periodically from selected sites on large rivers (nominally those with drainage areas greater than 20,000 square miles at their most downstream stations) and analyzed for a suite of accumulative environmental contaminants (such as hydrophobic organic chemicals, metals, and metalloids) and for biological indicators of exposure to contaminants and their effects. The BEST program conducted studies in the Mississippi River Basin (MRB), Columbia River Basin (CRB), and Rio Grande Basin (RGB) to evaluate this proposed suite of chemical and biological methods (Schmitt and others 1999a, 2004; Schmitt, 2002; Hinck and others 2004), and similar investigations are underway in other basins. The 1995 MRB study (Schmitt, 2002) included stations in two USGS National Water-Quality Assessment (NAWQA) Program study units lying within the basin. The CRB and RGB studies, initiated in 1997 (Schmitt and others, 2004; Hinck and others, 2004), included stations from the USGS National Stream Quantity Accounting Network (NASQAN) Program, two of which were also NAWQA stations.

The NASQAN program monitors water quality in five large (250,000 to 1,200,000 square miles) U.S. river systems—the Colorado, Columbia, Mississippi, Rio Grande, and Yukon—by regularly measuring the concentrations of dissolved and suspended substances. NASQAN analytes include hydrophyllic contaminants (such as water-soluble pesticides, major ions, and selected trace elements) as well as nutrients,

carbon, and other parameters. Because quantifying mass flux is an important NASQAN objective, continuous discharge measurements are also obtained.

The proposed national-scale component of the BEST program shares many features and objectives with NASQAN, and the programs appear to be complementary. The BEST program studies in the CRB and RGB therefore incorporated NASQAN stations as sampling locations to evaluate the compatibility of the two programs. The study reported here was initiated in 2001 to investigate techniques for summarizing and integrating fish-contaminant data from the BEST program for 1997-98 and water-quality data from the NASQAN program for water years (WYs) 1995-98. (Note: A water year is the time period from October 1 of the year preceding the designated water year through September 30 of the designated water year; for example, WY 1995 is October 1, 1994 through September 30, 1995.) Test data sets containing selected BEST and NASQAN data for the CRB and RGB were used as examples for summarizing and integrating monitoring data for large river basins in the U.S. and to provide recommendations to the BEST and NASQAN programs to enhance the existing complementary relationships between the two programs. As such, the study illustrates opportunities for information sharing among USGS programs.

## Background

The 1995 and 1997-98 BEST studies in the MRB (Schmitt, 2002), CRB (Hinck and others, 2004), and RGB (Schmitt and others, 2004) evolved from the fish component of the National Contaminant Biomonitoring Program (NCBP) (Schmitt and others, 1999c). The NCBP originated as part of the National Pesticide Monitoring Program (NPMP), a multi-agency effort in which the U.S. Fish and Wildlife Service (USFWS) participated by periodically collecting and analyzing avian wildlife, starlings, and freshwater fish (Johnson and others, 1967; Bunck and others, 1987; Schmitt and Bunck, 1995). Fish collection stations were located at key points in major U.S. rivers and in the open waters of the Great Lakes, with the objective of characterizing geographic trends in the concentrations of toxins that accumulate in fish and, thereby, threaten both fish and fish-eating wildlife. The fish component of the NCBP was revised several times during its 20-year history; prior to its last implementation during 1986-87, 115 stations were sampled every other year (Schmitt and Bunck, 1995; Schmitt and others, 1999c). From each station, a total of three composite samples of two species (a piscivore and a benthivore) was collected and analyzed for whole-body concentrations of organochlorine chemicals (pesticides and industrial chemicals), heavy metals, and metalloids.

## BEST Program

Bio-accumulative contaminants in large rivers are still perceived to be important. Nevertheless, by the mid-1980s it was apparent that contaminant threats represented by contemporary-use pesticides (that is, herbicides and short-lived insecticides) and other chemicals not amenable to monitoring through chemical analysis of animal carcasses were not being addressed by the NCBP. Consequently, planning was initiated for an expanded program that would include biological components and which would be targeted towards habitats, lands, and species of greater concern to the USFWS. This expanded program—the BEST program—was initiated in 1992 and was transferred to the USGS in 1996 after several years of development and pilot studies (BEST, 1996; Schmitt, 2002).

The BEST program documents spatial and temporal trends in the exposure of organisms and ecosystems to contaminants and the effects of exposure on selected organisms (BEST, 1996). This is accomplished through the application of chemical and biological methods spanning several levels of biological organization (such as cellular, organ, organism) and through the incorporation of information from other programs and sources. Similar weight-of-evidence approaches underlie other environmental monitoring programs (for example, Hirsch and others, 1988). The suite of BEST program methods includes chemical analysis of persistent accumulative contaminants in fish and biological indicators (biomarkers) of chemical exposure and the effects of such exposure (BEST, 1996; Schmitt and Dethloff, 2000). Some biomarkers integrate the cumulative effects of multiple contaminants and other environmental stressors (Adams, 1990).

## NASQAN Program

The NASQAN program also spans multiple decades and was designed to provide general information on status and trends of contaminants in large watersheds. NASQAN originally sought to account for the quantity and quality of water moving within the U.S., document temporal and geographic trends in water quality, and provide a database against which to evaluate future changes in water quality and quantity. First implemented in 1970, by 1978 NASQAN was sampling more than 500 fixed (long-term) stations. NASQAN stations were situated at the lowermost points in hydrologic accounting units, typically at the terminus or confluence of major waterways. As such, some stations were originally located at or near NCBP sites (Smith and others, 1988). At each station, discharge was measured and water samples were collected monthly and analyzed for a suite of water-quality constituents including suspended sediments, nutrients, total and fecal coliform bacteria, and major and trace elements.

The NASQAN program was reviewed by the USGS several times. In general, findings relative to temporal and geographic trends were deemed interesting and informative; however, like the NCBP, the program itself was perceived as somewhat deficient because of its inability to assess causation with respect to observed water-quality changes and a lack of focus on specific contemporary water-quality issues. Additional technical problems identified through internal and external reviews included the questionable suitability of monthly sampling for estimating mass flux of chemical constituents; the tenuous connection between conditions at the lowest points in sub-basins, where samples were collected, to upstream conditions; and a lack of analytical quality control for some analytes, most notably trace metals (Windom and others, 1991; Hooper and others, 1996). A major re-design of the program was consequently initiated in 1993 and completed in 1995. The redesigned program, initially called NASQAN II (henceforth known as NASQAN), was phased into operation in the mid-1990s (Hooper and others, 1996).

For the first five years (1996-2001) after the major redesign, NASQAN focused on the four largest river systems of the conterminous states—the Colorado, Columbia, Mississippi, and Rio Grande (Hooper and others, 1996; U.S. Geological Survey, 1997, 2003). The program sought to estimate the mass flux or loads of materials from and through these large river systems. Specifically, NASQAN was designed to characterize large (20,000 to 70,000 square miles) sub-basins of the four river systems, determine regional source areas for dissolved and suspended water constituents, and assess the effects of human activities on the concentrations and amounts of these materials (U.S. Geological Survey, 1997). Other intended uses of NASQAN data included documenting long-term trends in constituent fluxes and concentrations; calculating constituent loads to receiving waters; providing a framework for more detailed assessments of water-quality conditions and their causes; and, together with information from the NAWQA program (Hirsch and others, 1988), evaluating the influences of land use practices and water quality in lower-order basins on conditions in large rivers using water-quality models (Hooper and others, 1996; U.S. Geological Survey, 1997).

To achieve these objectives, NASQAN stations located at the downstream limits of sub-basins within the four main basins [current (2005) total  $n = 27$ ] are sampled at varying, flow-dependent intervals, with the sampling frequency determined independently for each station. Typically, stations are sampled 6-15 times annually with the most intensive sampling conducted during high-flow periods, when variability is characteristically greatest. NASQAN water samples are analyzed for about 100 dissolved and 30 suspended constituents. These include carbon (dissolved and suspended organic carbon, dissolved inorganic carbon), major ions (calcium, chloride, sulfate, and others), nutrients (total and dissolved forms of nitrogen and phosphorus), hydrophyllic pesticides (insecticides and herbicides, such as carbofuran and atrazine, respectively), field properties (discharge, water temperature, dissolved oxygen, pH, specific conductivity), suspended sedi-

## 4 Approach for Integrating BEST and NASQAN

ment, and suspended and dissolved trace elements (arsenic, lead, zinc, and others). Discharge is monitored continuously at all sites.

The NASQAN program began a special five-year phase of study in 2001. Resources were redirected to an intensive sampling program in the Yukon River basin, and sampling in the Colorado and Columbia River basins was significantly decreased to only one and two stations, respectively. Sampling in the MRB and RGB remained unchanged from that of 1996-2001 (U.S. Geological Survey, 2003).

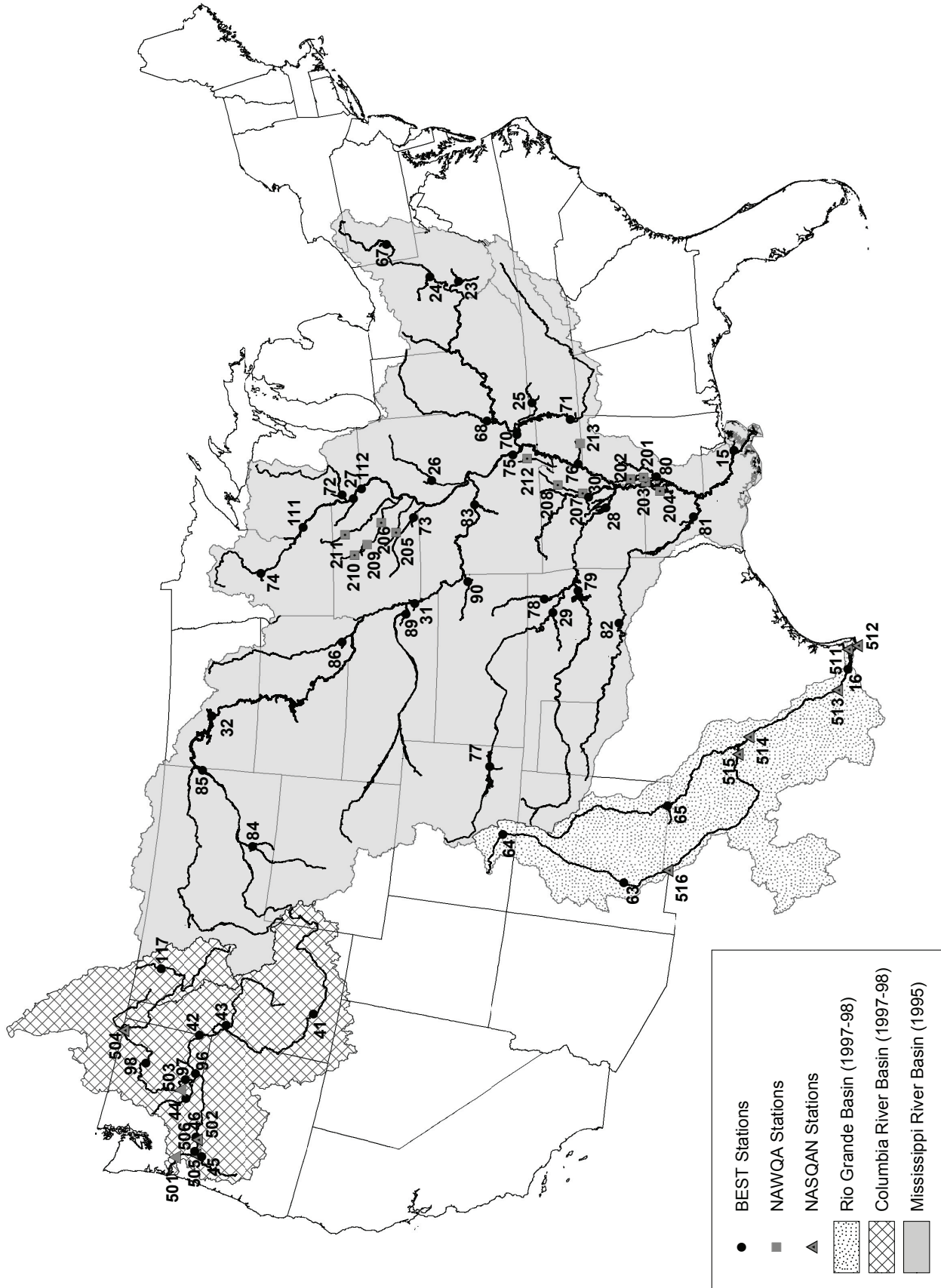
### BEST Program Implementation Projects

The BEST program conducted studies designed to test its aquatic ecosystem methods in large rivers. The studies were implemented cooperatively with other USGS water-monitoring programs. Historic NCBP fish-collection stations in the MRB ( $n = 33$ ) were sampled in late 1995 (Schmitt and others, 1995), and NCBP sites in the CRB ( $n = 10$ ) and RGB ( $n = 5$ ) were sampled in 1997-98 (Hinck and others, 2004; Schmitt and others, 2004; fig. 1). These studies were designed to provide contemporary information on the distribution and abundance of bioaccumulable contaminants and to test the feasibility of incorporating biological indicators into a large-scale monitoring program. More specifically, the objectives of the projects were to: (1) field-test, evaluate, and optimize the suite of aquatic indicators selected for use in the BEST program; (2) document and characterize the geographic distribution of chemical contaminants and their effects on fish and wildlife at selected sites in the large rivers of the MRB, CRB, and RGB; (3) compare the findings for bioaccumulable contaminants with those of previous NCBP fish collections; and (4) evaluate and demonstrate the technical and logistic feasibility of implementing the BEST program through partnerships with USGS science centers, cooperative research units, universities, and other monitoring programs and U.S. Department of the Interior agencies. To achieve the latter objective, the MRB study (Schmitt, 2002) included sites on smaller rivers and streams in the Eastern Iowa Basins ( $n = 5$ ) and Mississippi Embayment ( $n = 8$ ) study units of the NAWQA Program. The 1997-98 projects included five NASQAN sites in each of the CRB (Hinck and others, 2004) and RGB (Schmitt and others, 2004); two in the CRB were concurrent NAWQA stations.

The specific methods incorporated into the BEST studies included analyses of composite samples of whole fish for organochlorine chemical residues (pesticides and industrial chemicals) and elemental contaminants (metals and metalloids) following a sampling protocol derived from the NCBP (Schmitt and others, 1999c); toxicity testing of fish carcass extracts with the H4IIE rat hepatoma cell bioassay (Tillitt and others, 1991); and additional indicators of fish health and condition (table 1). These biological response (fish-health assessment) indicators (tables 1 and 2) were chosen to repre-

sent chemical responses spanning a wide range of biological organization and chemical specificity (Schmitt and Dethloff, 2000). These range from biochemical responses to individual contaminants or groups of structurally similar contaminants to general indicators of fish health that respond to many contaminants, individually and in combination, as well as to other environmental factors (Adams, 1990). Other programs, including NAWQA, include indicators of even higher-level effects, such as the taxonomic composition of the algal, benthic macroinvertebrate, and fish communities. Further information on the biological methods and the rationale for their inclusion is provided elsewhere (BEST, 1996; Schmitt and others, 1999b; Schmitt and Dethloff, 2000; Schmitt, 2002).

Chemical residue and elemental contaminant concentrations in fish reflect concentrations in water and diet to varying degrees. For hydrophobic organic chemicals, it is generally accepted that concentrations in fish are at (or at least tending toward) equilibrium or steady-state with respect to the water (Hamelink and others, 1971). From the earliest days of the NPMP (predecessor of the NCBP), it was tacitly assumed that fish collected from nodal points in major drainages integrate broad expanses of space and time with respect to accumulative contaminants. The dynamics of uptake and elimination are highly variable, however, and the expanse of space and time over which the measurements integrate is consequently also variable. In addition, it is presumed that observed differences in the concentrations of accumulative contaminants in fish (among locations, time periods, or both) reflect differing exposure concentrations, durations, or both. In fact, such differences may at least partly reflect population and ecosystem factors such as longevity and trophic dynamics, the latter including productivity, food chain length, and so on (Kiriluk and others, 1995; Cabana and Rasmussen, 1996; Kendall, 1998). From the environmental manager's perspective, it is important to differentiate between increases or decreases in the concentrations of toxins that are attributable to changing environmental fluxes, which can at least potentially be regulated, from those caused by changing ecological conditions, which are much more difficult (if not impossible) to control. For this reason, the ratio of the stable isotopes  $^{15}\text{N}:$  $^{14}\text{N}$  ( $\delta^{15}\text{N}$ ) in organisms, which can be used as an indicator of trophic position (Cabana and Rasmussen, 1996; Kendall, 1998), was incorporated into the 1995 and 1997-98 BEST projects as a corollary variable. Similar measurements have been made on samples of various media collected under the auspices of the NASQAN and NAWQA programs (Kendall and others, 1999). By accounting for trophic differences, it may be possible to more precisely determine temporal and geographic trends in environmental contaminant concentrations.



**Figure 1.** Map of the conterminous United States showing the waterways, river basins, and BEST stations sampled in 1995 and 1997-98. BEST, Biomonitoring of Environmental Status and Trends program; NASQAN, National Stream Quality Accounting Network; NAWQA, National Water-Quality Assessment program. See Tables 3 and 5 for station descriptions and sampling dates of stations used in this study.

## 6 Approach for Integrating BEST and NASQAN

**Table 1.** Methods incorporated into the 1995 and 1997 BEST large rivers projects.

Method	Description	Tissue(s) examined	Sensitivity	Primary reference(s)
Histopathology	Microscopic examination for the presence of lesions; can provide early indication of chemical exposure	Liver, gill, gonads, spleen, and kidney	Overall organism health and contaminants	Hinton and others (1992); Hinton (1993); Goodbred and others (1997)
Ethoxyresorufin <i>O</i> -deethylase (EROD) activity	Enzyme induction by planar hydrocarbons	Liver	PCBs; chlorinated dioxins and furans; PAHs	Pohl and Fouts (1980); Kennedy and Jones (1994); Whyte and others (2000)
Lysozyme activity	A disease resistance factor that can be suppressed in the presence of contaminants	Blood plasma	Overall organism health	Blazer and others (1994)
Macrophage aggregate analysis	Macrophages are important in the immune system, serving as a first line of defense for the organism and as an antigen processing cell	Spleen	Multiple contaminants including PAHs and metals	Blazer and others (1994); Blazer and others (1997)
H4IIE bioassay	A screening tool to determine the presence of certain classes of planar halogenated compounds	Whole fish (composite samples)	PCBs; chlorinated dioxins and furans	Tillitt and others (1991); Whyte and others (2004)
Vitellogenin	A precursor of egg yolk, normally synthesized in the liver of female fish	Blood plasma	Endocrine-modulating substances	Denslow and others (1999)
Steroid hormones (estradiol and testosterone)	Determine reproductive health and status	Blood plasma	Endocrine-modulating substances	Guillette and others (1994); Goodbred and others (1997)
Chemical analyses	Organochlorine chemical residues and elemental contaminants	Whole fish (composite samples)	Specific analytes	Schmitt and others (1999c)
Somatic indices	The relative mass of some organs is often indicative of chemical exposure	Gonads, spleen, liver	Overall organism health	Grady and others (1992)
Necropsy-based fish health assessment	Visual assessment of external/internal anomalies (for example, lesions, parasites, tumors), which may indicate contaminant-related stress	All	Overall organism health	Goede (1988, 1996); Adams and others (1993); Adams (1990)

### Potential Complementarity of BEST and NASQAN Programs

The large rivers monitoring component of the BEST program and the water monitoring conducted by the NASQAN program appear to complement each other. BEST yields information on the concentrations of persistent hydrophobic organic chemicals, mercury, selenium, and other accumulative contaminants and on the cumulative effects of exposure

to these and other substances. NASQAN yields information on concentrations of water-soluble contaminants to which the fish have been exposed, thereby providing a possible explanation for observed biological findings and observations. The BEST program identified the analysis of hydrophylic contaminants in water as a desirable complement to its suite of organism-based methods for monitoring in aquatic habitats (BEST, 1996). Within sub-basins of the NASQAN basins, the NAWQA program also produces information on contaminants in water, sediment, and biota, as well as on land use and land

**Table 2.** Fish health-assessment indicators and stable isotope, trace element, organochlorine pesticide, and PCB parameter list for fish collected at BEST stations in the Columbia River and Rio Grande basins, 1997-98.

[BHC, benzene hexachloride; %, percent;  $\delta^{15}\text{N}$ , ratio of  $^{15}\text{N}$  to  $^{14}\text{N}$ ; EROD, ethoxyresorufin-*O*-deethylase; g, gram; mm, millimeter; PCBs, polychlorinated biphenyls; TCDD, 2,7,3,8-tetrachlorodibenzo-*p*-dioxin. Fish health-assessment indicators were determined for individual fish.  $\delta^{15}\text{N}$ , trace elements, organochlorine pesticides, and PCBs were determined for composite fish samples. See table 1 for specific tissues that were examined]

Fish health assessment indicators <sup>1</sup>		Stable isotopes and trace elements	Organochlorine chemical residues
Field observations	Field or laboratory measurements	Stable isotope:	
Bile color	Atresia (%)	$\delta^{15}\text{N}$	alpha-BHC
Body surface	EROD activity	<b>Trace elements:</b>	beta-BHC
External lesions	Condition factor	Aluminum	delta-BHC
Left and right eye condition	Gonadosomatic index	Arsenic	gamma-BHC
Aggregated fin condition	Gonad stage (histopathology)	Barium	<i>cis</i> -Chlordane
Gallbladder (bile) fullness	Gonad weight (to 0.01 g)	Boron	<i>trans</i> -Chlordane
Left and right gill condition	Health-assessment index	Beryllium	<i>cis</i> -Nonachlor
Gonad (gender, condition)	Hepatosomatic index	Cadmium	<i>trans</i> -Nonachlor
Gonadal stage (visual)	Length (mm)	Chromium	Oxychlordane
Kidney condition	Liver weight (to 0.1 g)	Copper	Endrin
Liver condition	Macrophage aggregates	Iron	Heptachlor epoxide
Extent of mesenteric fat	Tissue occupied by macrophage aggregates (%)	Lead	Mirex
Opercle condition	Spleen weight (to 0.002 g)	Mercury	Toxaphene
Pseudobranch condition	Splenosomatic index	Magnesium	<i>o,p'</i> -DDD
Spine sample collection	Vitellogenin	Manganese	<i>o,p'</i> -DDE
Spleen condition	Weight (g)	Molybdenum	<i>o,p'</i> -DDT
	Intersex	Nickel	<i>p,p'</i> -DDD
		Selenium	<i>p,p'</i> -DDE
		Strontium	<i>p,p'</i> -DDT
		Vanadium	Hexachlorobenzene
		Zinc	Total PCBs
		Percent moisture	TCDD-equivalents
			Percent lipid

<sup>1</sup>See Schmitt and Dethloff (2000) for description of fish health-assessment indicators.

cover; and the relations among these variables. Thus, the NASQAN and NAWQA programs provide valuable contemporaneous information for the analysis and interpretation of the biological information beyond the chemical analyses acquired by BEST, and BEST provides information on the cumulative effects of exposure in fish to selected chemicals and other stressors measured by NASQAN and NAWQA.

## Integration of BEST and NASQAN Data

The objective of this study was to evaluate alternative techniques for summarizing and integrating data from the BEST and NASQAN programs that monitor contaminants and their effects on fish in large rivers. Interfacing the informa-

tion generated by water programs, NASQAN in particular, with that of the BEST program presents some challenges. Although the programs share similar overall goals related to contaminant monitoring (including the documentation of spatial and temporal trends), their specific objectives are quite different. Each program also has particular data issues (such as censoring and sampling frequency) that could affect data integration. This latter factor and others will be discussed in the evaluation of alternatives for manipulating, summarizing, and packaging the data generated by the programs to better complement each other.

## Problem Statement

The condensation, summarization, and reporting of water-quality measurements made at different spatial and temporal scales has been addressed from several perspectives and are well represented in the literature (for example, Hirsch and others, 1982; Helsel and Hirsch, 1992; Olsen and others, 1999). There are spatial as well as temporal aggregation problems to be resolved. Spatially, the problem may be stated simply as, "To what extent do the measurements made on fish and water represent the same point, segment, or reach of the river being considered?" This question is largely beyond the scope of the present investigation. Although we may refer in passing to station locations and the degree to which BEST/NCBP, NASQAN, and (perhaps) NAWQA stations coincide, we assumed for this investigation that the measurements based on fish and water were collected from the same "place" or site—however this was or will be defined. It is important to note that the topic of fixed station versus probability-based sampling is the focus of substantial debate among water-quality monitoring entities (for example, Olsen and others, 1999). This study therefore focused on the "what" and "when" components of the question—temporal issues and the overlap or complementarity of the programs and their respective endpoints.

Censoring is common and problematic for water constituents. Censored data comprise measured values below the minimum reporting level (MRL) that are reported as less-than (<) concentrations for an analyte or an analyte that is undetected; they are also known as non-detects. The percentage of non-detects is often high for constituents such as trace elements and seasonally applied pesticides. In addition, the distributional properties of water-quality variables often make them difficult to analyze by traditional parametric statistical methods. Consequently, water data are often reported and tested non-parametrically; for a given time period, the median, quartiles, minimum, and maximum are computed and compared, along with incidence (percentage of samples above the reporting level). Where sufficient uncensored observations are present, log-transformed values may be analyzed by parametric methods and reported as geometric means and standard

errors (for example, Goodbred and others, 1997). A number of alternatives are available for dealing with censored data, ranging from very simplistic (replacement of censored values with zeros or other constants; adding constants; replacement with 50% of the censoring level) to complex and computer-intensive (probability-based computation of replacement values and others).

The NASQAN data present an additional challenge. Because of the program's specific objective related to the estimation of mass flux, the measurements are weighted towards the seasons with greatest concentration and flux variability, normally the high-flow seasons. However, the concentrations of hydrophobic chemicals and elemental contaminants in fish are concentration-dependent, not flux-dependent; and the biological response variables measured by the BEST program are generally dose-dependent. In the context of water quality, dose is defined in terms of concentration and duration of exposure. Consequently, the NASQAN data also must be aggregated in a manner that removes temporal bias before they can be combined with the BEST data. Goodbred and others (1997) used time-weighted annual geometric means to describe hydrophyllic pesticide concentrations for comparison with reproductive biomarkers in fish. They noted that the pattern of temporal and geographic variation differs among chemicals, but that seasonal patterns tend to repeat annually at a site; and that time-weighted annual means were therefore good indicators of central tendency. Goodbred and others (1997) also noted that the most relevant measure of exposure of fish to dissolved constituents is difficult to determine, which suggests that a less proscribed approach may be more appropriate.

Pollutant concentrations in water and tissue are reported differently, at least by some investigators. Liquid-phase concentrations of water constituents are typically reported in units of mass per volume, such as micrograms per liter ( $\mu\text{g/L}$ ). Concentrations of suspended constituents may be reported this way or in units of mass [mass/mass, dry weight basis; for example, micrograms per gram ( $\mu\text{g/g}$ )]. Tissue concentrations of inorganic contaminants (metals, metalloids) are generally measured from dried samples and reported in units of mass/mass; however, they may be reported as either dry weight or wet weight concentrations, the latter after adjusting for moisture content (reported as percent). Organic chemical residue concentrations are measured in a lipid extract (mass/lipid mass) and back calculated to wet-weight concentrations (mass/mass) based on gravimetrically determined lipid content (percent).

Statistically, the data describing contaminant concentrations in fish and other organisms share some problems with water data but also are plagued by some of their own. Chemical residue and elemental contaminant data for fish are generally less temporally dynamic than water concentrations and biomarkers, and samples are typically collected and analyzed less frequently. Owing to the expense of analysis and high inter-individual variation, composite samples are commonly analyzed by many programs (including BEST and NAWQA).



The number of composite samples usually is small compared to the sample sizes characteristic of water-monitoring programs. As is true for water data, concentrations of elemental and organic contaminants in fish are often distributed non-normally, and censored values are common. Also like water data, the extremes, central tendencies, variability, and incidence are typically analyzed and reported. Both parametric and non-parametric statistical procedures are used regularly.

The biological response (fish-health assessment) indicators used in the BEST program (table 2) vary greatly in response times and persistence (Adams, 1990). Among the BEST indicators, some (ovotestes in adult male fish, for example) indicate exposure to chemicals at specific points in the early development of individual organisms (Tyler and others, 1998), and may therefore reflect previous conditions that might or might not be reflected by contemporaneous water data. Other indicators (such as reproductive hormones) are ephemeral and extremely sensitive to environmental stimuli, and therefore can reflect both the conditions (chemical and other) to which the organism was exposed at or shortly before the time of capture (Tyler and others, 1998). However, the biological endpoints may also reflect the effects of longer-lived chemicals stored within the organisms, chemicals transferred maternally, the manifestation of early developmental effects, or combinations of these causal agents. Other biological indicators are intermediate, cumulative, or both. For example, liver cancer, as manifested by grossly visible and histopathologically diagnosed tumors, may represent both a historic event (a mutation caused by exposure to a genotoxin, the so-called initiation phase of chemical carcinogenesis) followed by subsequent promotion of the initial mutation. The promoting agent might or might not be the same as the initiator, depending on the chemical or chemicals involved. Consequently, and as noted by Goodbred and others (1997), the most appropriate summary statistics for one variable or group of variables in either the fish or the water data set may not be relevant for other variables without some formidable (and untestable) assumptions.

## Purpose and Approach

The objectives of this report are to (1) describe alternative techniques for summarizing and integrating data from the BEST and NASQAN programs; (2) illustrate, through the use of test data sets, results of the summarization and integration techniques; and (3) provide recommendations to the BEST program for future studies. Because the focus of this study and report is on describing and illustrating techniques for summarizing and integrating NASQAN and BEST data using test data sets, results are presented for illustration purposes only and are not in-depth analyses. The analyses show how data from two monitoring programs can be integrated and how the results can be interpreted.

Given the difficulties identified in the foregoing section, this study was conducted iteratively following three steps. First, the pertinent literature was examined, and techniques used in similar situations were summarized. Because the issue has been addressed by the NAWQA program to some extent (for example, Goodbred and others, 1997) scientists familiar with NASQAN and(or) NAWQA were consulted. Next, test data sets based on BEST and NASQAN studies in the CRB and RGB were assembled for comparisons of alternative summarization and integration techniques. The data sets included biological variables based on individual fish (biomarkers, age, and others) and composite samples (concentrations of organochlorine and elemental contaminants, and  $\delta^{15}\text{N}$ ) from the BEST program, and concentrations of pertinent measured parameters in water from the NASQAN program for stations in the two basins for the period of record preceding the date of fish collection at each station. Because only selected trace elements and  $\delta^{15}\text{N}$  are common to both programs and their respective media (fish and water), these pairs were examined as part of the process of summarizing and integrating the data sets. The utility of  $\delta^{15}\text{N}$  as a corollary variable for normalizing among sites also was investigated. As the last step, alternative summarization and integration techniques were illustrated using the test data sets. Results from ongoing BEST synthesis activities (Schmitt and Dethloff, 2000; Whyte and others, 2000) investigating the influence of chemical and other factors on the biological variables for fish were also utilized.

## Literature Review

As noted in the "Problem Statement" section, water-quality data are commonly censored. Statistical treatment of censored water-quality data has been discussed by Helsel and Gilliom (1986), Gilliom and Helsel (1986), and Helsel (1990). Applicable techniques from these sources include simple substitutions and estimation/replacement procedures. In addition, water-quality data are typically distributed non-normally. Both conditions make the use of parametric statistical methods problematic. Accordingly, Helsel (1987) reported on the advantages of using nonparametric procedures.

Trace elements and organic compounds in fish have been investigated in almost all NAWQA study units (<http://water.usgs.gov/nawqa/bib.html>). Many investigations concentrated on the occurrence and distribution of trace elements, organic compounds, or both in fish [see, for example, Deacon and Stephens (1998), Frenzel (2000), Knight and Powell (2001), and Chambers (2002)]. Investigations also have examined the relations between land use and contaminants in fish [for example, Long and others (2000) and Gebler (2000)]; and trace metals and fish tissue [for example, Goldstein and others (1996) and Goldstein and DeWeese (1999)]. Riva-Murray and others (2003) determined trends in concentrations of polychlorinated biphenyls in fish tissue.

Numerous studies have examined differences in biota or fish-tissue data collected at different sites or regions and illustrate some common summarization issues. For example, Brown (1998b) investigated concentrations of chlorinated organic compounds in Asiatic clams (*Corbicula fluminea*) and fish tissue in California. Tissue data were normalized by lipid content, and one-half the reporting level was substituted for less-than concentrations in tissue for use in statistical tests. Bilger and others (1999) compared local, regional, and national concentrations of organochlorine chemical residues in fish tissue to concentrations in the Lower Susquehanna River Basin. In this investigation, concentrations of total DDT (sum of *o,p'*-DDD, *o,p'*-DDE, *o,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, and *p,p'*-DDT) and total chlordane (sum of *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, and oxychlordane) were also computed using a value of one-half the MRL for less-than concentrations. One-half the reporting level has also been used in the analysis of elemental contaminant and organochlorine residue data from NCBP and BEST studies (Schmitt, 2002; Schmitt and others, 1999c; 2004; Hinck and others, 2004).

Studies integrating water-quality (water-chemistry and bed-sediment) and fish data have been described by a number of authors. Cuffney and others (2000) and Deacon and others (1999) determined the level of impairment of stream sites by assessing or characterizing physical, chemical, and biological conditions with multimetric indices and water-quality measurements. Multimetric indices developed by Cuffney and others (2000) included metals enrichment in bed sediment; non-pesticide agricultural intensity index; and pesticide contamination in filtered water, suspended sediment, bed sediment, and fish tissue. Deacon and others (1999) examined nine measures of water quality, which included information on nutrients in the water column, specific conductance, trace elements in streambed sediment, pesticides in fish tissue, fish communities, macroinvertebrate richness and composition, and measures of stream habitat, such as stream modification and bank erosion. Both studies developed fish-impairment or fish-community degradation indices based on the sum and percentages of tolerant individuals, omnivores, non-native species, and external anomalies. Fish-community metrics also were used by Brown (1998a) and May and Brown (2000) to characterize fish communities and their relations to environmental variables. Machala and others (2001) investigated biochemical responses to environmental mixtures of contaminants in the liver of chub (*Leuciscus cephalus*) by matching biochemical response data with bed-sediment contaminant data. Investigations of endocrine-disrupting chemicals in surface waters and reproductive biomarkers in fish have been reported by Bevans and others (1996), Goodbred and others (1997), and Smith (1998, 2000). Bevans and others (1996) examined occurrences and differences in measured chemical parameters that included organochlorines and semivolatile industrial compounds in the water column, bottom sediment, and tissues of common carp (*Cyprinus carpio*, henceforth carp) and reproductive biomarkers such as steroid hormone concentra-

tions and gonadal histology at five sites in southern Nevada. Differences among groups of data were examined with nonparametric tests, including a chi-squared approximation of the Kruskal-Wallis test and the Duncan multiple-range test. No statistical analysis was conducted to relate water-quality parameters to fish data in this study. Goodbred and others (1997) studied 647 carp from 25 sites in the U.S. ANOVA, analysis of covariance, and Tukey's range test were used to test for significant differences among endocrine biomarkers in carp within and between various regions of the country. Pearson's product-moment correlation analysis (*r*) was used to test for relations between contaminant groups (dissolved pesticides in water and contaminant groups in fish tissue and bed sediment) and between contaminant groups and biomarkers in male and female carp. Additional patterns in bed sediment and fish-tissue contaminants among sites were examined with principal component analysis. Relations between contaminant groups and biomarkers were examined by stepwise multiple regression analysis. In these analyses, pesticide concentrations were computed as time-weighted annual mean concentrations, all values for contaminant groups and endocrine biomarkers were  $\log_{10}$ -transformed prior to correlation analysis, and data for all sites from all regions were combined prior to the analyses (Goodbred and others, 1997). Censored or less-than values were treated as zero concentrations. Smith (1998, 2000) used correlation analyses (Pearson's *r* and Spearman's rho) and partial regression to compare and analyze endocrine biomarkers, sediment residues, fish-tissue residues, histopathology, and ancillary data for selected fish species in the Hudson River of New York. Correlation analyses were not conducted with water-quality data, however, because of the question of which summary statistic (time-weighted concentrations, monthly averages, latest concentrations prior to fish collection, and so on) best represented exposure of the fish (Stephen Smith, U.S. Geological Survey, personal communication, 2002).

## Sources of Water-Quality Data

As a first step in evaluating methods for combining results of the USGS BEST and NASQAN programs, the locations of the BEST program fish-collection stations in the CRB and RGB (table 3) were compared to locations of NASQAN water-quality stations identified from the NASQAN database (<http://water.usgs.gov/nasqan/data/finaldata.html>). Two other USGS water-quality databases were also searched for possible stations: (1) NAWQA Data Warehouse ([http://infotrek.er.usgs.gov/servlet/page?\\_pageid=543&\\_dad=portal30&\\_schema=PORTAL30](http://infotrek.er.usgs.gov/servlet/page?_pageid=543&_dad=portal30&_schema=PORTAL30)) and (2) National Water Information System (NWIS) (<http://waterdata.usgs.gov/usa/nwis/qw>). If a BEST station and a water-quality station were found to be co-located, the availability of water-quality data was determined for the parameters of interest (table 4), and all available data collected after the NASQAN re-design in 1995 and prior to the

**Table 3.** Fish-collection stations of the BEST program in the Columbia River and Rio Grande basins, 1997-98.

[USGS-NWIS, U.S. Geological Survey National Water Information System; --, no corresponding NWIS water-quality station]

BEST station number	USGS-NWIS station number	River	Nearest city or feature	Sampling date(s)	Nominal station location (latitude, longitude)
<b>Columbia River Basin</b>					
41	--	Snake	Hagerman, Idaho	10/2/1997	42°47'36.21"N, 114°56'18.10"W
42	--	Snake	Lewiston, Idaho	9/24-25/1997	46°24'54.28"N, 117°02'03.49"W
43	--	Salmon	Riggins, Idaho	9/30/1997	45°35'43.42"N, 116°16'55.00"W
44	--	Yakima	Granger, Washington	10/15-16/1997	46°20'49.31"N, 120°12'27.03"W
45	--	Willamette	Oregon City, Oregon	11/21/1997, 11/24/1997	45°19'0.47"N, 122°39'57.50"W
46	--	Columbia	Cascade Locks, Oregon	11/18/1997, 11/20/1997	45°41'23.11"N, 121°51'00.41"W
96	13353200	Snake	Ice Harbor Dam, Washington	10/8-9/1997	46°41'51.68"N, 118°53'07.88"W
97	--	Columbia	Pasco, Washington	10/10-11/1997	46°31'49.22"N, 119°16'42.07"W
98	--	Columbia	Grand Coulee, Washington	11/6-7/1997	47°57'44.85"N, 118°58'53.84"W
117	--	Flathead	Creston, Montana	10/31/1997, 11/1/1997	48°09'01.09"N, 114°11'29.71"W
501	14246900	Columbia	Beaver Army Terminal, Oregon	3/31/1998, 4/1/1998	46°10'57.86"N, 123°04'13.87"W
502	14128910	Columbia	Warrendale, Oregon	11/25-26/1997	45°38'00.82"N, 121°58'42.57"W
503	12472900	Columbia	Vernita Bridge, Washington	10/13-14/1997	46°37'28.40"N, 119°51'31.45"W
504	12400520	Columbia	Northport, Washington	11/3-4/1997	48°58'21.70"N, 117°38'48.92"W
505	14211720	Willamette	Portland, Oregon	11/14/1997, 11/17/1997	45°33'04.51"N, 122°41'43.74"W
506	--	Columbia	Marine Park - Vancouver, Washington	4/2/1998	45°35'44.21"N, 122°32'13.61"W
<b>Rio Grande Basin</b>					
16	--	Rio Grande	Mission, Texas	12/2-3/1997	26°09'28.74"N, 98°20'02.82"W
63	--	Rio Grande	Elephant Butte Reservoir, New Mexico	10/22-24/1997	33°12'48.55"N, 107°13'27.26"W
64	--	Rio Grande	Alamosa, Colorado	9/23-24/1997, 10/20-21/1997	37°25'06.42"N, 105°46'48.48"W
65	--	Pecos	Red Bluff Lake, Texas	1/21-22/1998	32°00'00.00"N, 103°58'56.28"W
511	08480400	Arroyo Colorado	Harlingen, Texas	9/30/1997, 10/2-3/1997	26°11'44.28"N, 97°36'20.52"W
512	08475000	Rio Grande	Brownsville, Texas	10/28/1997, 11/24-25/1997	25°52'12.96"N, 97°27'06.30"W
513	08461300	Rio Grande	Falcon Dam, Texas	11/18-19/1997	20°08'06.66"N, 99°08'06.42"W
514	08450900	Rio Grande	Amistad Dam, Texas	11/4-5/1997	29°26'49.06"N, 101°03'22.44"W
515	08377200	Rio Grande	Foster Ranch - Langtry, Texas	11/6/1997	29°46'40.91"N, 101°45'13.22"W
516	08364000	Rio Grande	El Paso, Texas	10/28-29/1997	31°47'55.00"N, 106°32'25.08"W

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**Table 4.** Water-quality parameters of interest with water-quality guidelines for the protection of freshwater aquatic life.

[USGS-NWIS, U.S. Geological Survey National Water Information System; MRL, minimum reporting level; --, no criterion established; Cr, chromium; CRB, Columbia River basin; RGB, Rio Grande basin; EPTC, s-ethyl dipropylthiocarbamate. Major ions and trace elements are in the dissolved form: sample water was passed through a 0.45 micrometer filter prior to analysis. Pesticides are in the dissolved form: sample water was passed through a 0.7 micrometer filter prior to analysis. Freshwater criteria for aquatic-life protection are criteria continuous concentrations in the dissolved phase from the U.S. Environmental Protection Agency (2002), unless otherwise noted]

USGS-NWIS Parameter code	Parameter name	Units	MRL	Freshwater criterion for protection of aquatic life
<b>Field parameters and major ions</b>				
	Flow (mean daily streamflow)	cubic feet per second	1	--
00061	Instantaneous discharge	cubic feet per second	1	--
00010	Water temperature	degrees Celsius	0.1	--
00400	pH	standard units	0.1	6.5-9.0
00095	Specific conductance	microsiemens per centimeter at 25 degrees Celsius	1	--
70300	Total dissolved solids	milligrams per liter	1	--
00940	Chloride, dissolved	milligrams per liter	0.1	230
<b>Trace elements</b>				
01000	Arsenic, dissolved	micrograms per liter	1	<sup>1</sup> 150
01030	Chromium, dissolved	micrograms per liter	1	Cr (III), <sup>2</sup> 74; Cr (VI), 10.582
01040	Copper, dissolved	micrograms per liter	1	<sup>3</sup> 1.4-10 (CRB), <sup>3</sup> 14-29 (RGB)
01145	Selenium, dissolved	micrograms per liter	1	4.61
01090	Zinc, dissolved	micrograms per liter	1	<sup>3</sup> 18-94 (CRB), <sup>3</sup> 180-380 (RGB)
<b>Pesticides</b>				
46342	Alachlor, dissolved	micrograms per liter	0.002	--
39632	Atrazine, dissolved	micrograms per liter	0.001	<sup>4</sup> 12
82680	Carbaryl, dissolved <sup>5</sup>	micrograms per liter	0.003	<sup>6</sup> 0.20
38933	Chlorpyrifos, dissolved	micrograms per liter	0.004	0.041
82682	Dacthal (DCPA), dissolved	micrograms per liter	0.002	--
39572	Diazinon, dissolved	micrograms per liter	0.002	<sup>7</sup> 0.08
82668	EPTC, dissolved <sup>8</sup>	micrograms per liter	0.002	--
39532	Malathion, dissolved <sup>5</sup>	micrograms per liter	0.005	0.1
39415	Metolachlor, dissolved	micrograms per liter	0.002	<sup>9</sup> 7.8
82630	Metribuzin, dissolved <sup>8</sup>	micrograms per liter	0.004	<sup>9</sup> 1.0
82679	Propanil, dissolved <sup>10</sup>	micrograms per liter	0.004	--
04035	Simazine, dissolved	micrograms per liter	0.005	<sup>6</sup> 10
82678	Triallate, dissolved <sup>8</sup>	micrograms per liter	0.001	<sup>9</sup> 0.24

<sup>1</sup>This recommended water-quality criterion was derived from data for arsenic (III) but is applied here to total arsenic in the dissolved phase.

<sup>2</sup>The freshwater criterion for this metal is expressed as a function of hardness (mg/L) in water. The value given here corresponds to a hardness of 100 mg/L. See U.S. Environmental Protection Agency (2002) for calculating criteria based on other hardness values.

<sup>3</sup>Criteria have been adjusted for hardness and reflect different hardness among the samples.

<sup>4</sup>Draft chronic criterion, from U.S. Environmental Protection Agency (2001).

<sup>5</sup>Rio Grande basin only.

<sup>6</sup>Criterion for the protection of freshwater aquatic life is a Canadian Water Quality Guideline from Canadian Council of Ministers of the Environment (1999).

<sup>7</sup>Criterion for the protection of freshwater aquatic life is from International Joint Commission Canada and United States (1978).

<sup>8</sup>Columbia River basin only.

<sup>9</sup>Interim criterion for the protection of freshwater aquatic life is a Canadian Water Quality from Canadian Council of Ministers of the Environment (1999).

<sup>10</sup>Rio Grande basin only. All concentrations but one were less than the minimum reporting level. This parameter has been excluded from the calculations of time-weighted concentrations for the Rio Grande basin

**Table 5.** NASQAN water-quality stations in the Columbia River and Rio Grande basins, 1995-99.

[USGS-NWIS, U.S. Geological Survey National Water Information System; na, not applicable]

USGS- NWIS station number	Station name	Period of record <sup>1</sup>	Number of samples <sup>2</sup>	Parameters <sup>3</sup>
<b>Columbia River Basin</b>				
12400520	Columbia River at Northport, Washington	11/25/1995-10/7/1997	28	Field parameters, major ions, trace elements, pesticides
12472900	Columbia River at Vernita Bridge near Priest Rapids Dam, Washington	1/17/1996-8/12/1997	15	Field parameters, major ions, trace elements, pesticides
13353200	Snake River at Burbank, Washington	10/13/1995-9/18/1997	31	Field parameters, major ions, trace elements, pesticides
14128910	Columbia River at Warrendale, Washington	10/21/1996-10/29/1997	16	Field parameters, major ions, trace elements, pesticides
14211720	Willamette River at Portland, Oregon	10/23/1995-10/30/1997	29	Field parameters, major ions, trace elements, pesticides
14246900	Columbia River at Beaver Army Terminal near Quincy, Oregon	10/24/1995-3/9/1998	33	Field parameters, major ions, trace elements, pesticides
<b>Rio Grande Basin</b>				
08364000	Rio Grande at El Paso, Texas	11/2/1995-9/10/1997	24	Field parameters, major ions, trace elements, pesticides
08374200	Rio Grande below Rio Conchos near Presidio, Texas	4/7/1999-9/28/1999	na	na
08377200	Rio Grande at Foster Ranch near Langtry, Texas	10/25/1995-9/10/1997	24	Field parameters, major ions, trace elements, pesticides
08447410	Pecos River near Langtry, Texas	2/7/1995-9/9/1997	27	Field parameters, major ions, trace elements, pesticides
08450900	Rio Grande below Amistad Dam, near Del Rio, Texas	5/28/1996-9/11/1997	11	Field parameters, major ions, trace elements, pesticides
08459200	Rio Grande below Laredo, Texas	1/28/1998-9/22/1999	na	na
08461300	Rio Grande below Falcon Dam, Texas	10/19/1995-9/3/1997	10	Field parameters, major ions, trace elements, pesticides
08470400	Arroyo Colorado at Harlingen, Texas	3/20/1996-9/10/1997	20	Field parameters, major ions, trace elements, pesticides
08475000	Rio Grande near Brownsville, Texas	10/17/1995-10/11/1997	17	Field parameters, major ions, trace elements, pesticides

<sup>1</sup>Does not include sample dates, if any, after time of fish collection.<sup>2</sup>Only includes samples collected prior to the time of fish collection.<sup>3</sup>Only considers parameters listed in table 4.

date of fish collection (table 3) were retrieved. The water-quality parameters included in this study were selected from more extensive data sets because they were either toxicologically significant to fish or were illustrative of the types of data to be encountered in this type of integration.

Fish sampling at BEST Station 96, Snake River at Ice Harbor Dam, Washington (in the CRB) occurred at the historic NCBP collection site (table 3) rather than at the nearby NASQAN site Snake River at Burbank, Washington (table 5). These stations were nevertheless considered to be in the same

location for this study and are described using the NASQAN name throughout this report.

*NASQAN.*—Water-quality data for all six stations in the CRB and six of eight RGB stations were available for periods of record prior to fish collection; data included field parameters, major ions, trace elements, and pesticides (table 5). Water-quality-data collection at two NASQAN stations in the RGB—Rio Grande below Laredo, Texas, and Rio Grande below Rio Conchos near Presidio, Texas—did not begin until 1998 and 1999, respectively, so these stations were excluded

from the study. The remaining 12 stations, six in each of the two basins (table 3), were included in this evaluation. The NASQAN station Pecos River near Langtry, Texas, was excluded from consideration because fish were not collected at this site. Information about the NASQAN program in the CRB and RGB is available in Kelly and Hooper (1998) and Lurry and others (1998).

*NAWQA.*—Four NAWQA study units—Upper Snake River Basin, Willamette River Basin, Central Columbia Plateau-Yakima River Basin, and Northern Rockies Intermontane Basins—are in the CRB and one—Rio Grande Valley—is in the RGB. Using the latitude/longitude of the BEST fish-collection stations, the NAWQA Data Warehouse was searched for the presence of water-quality stations in each study unit at or near the BEST fish-collection stations. When stations did coincide, water-quality data for the years immediately prior to the date of fish collection were inventoried.

For some of the NAWQA study units, the collection of water-quality data did not coincide with the test WYs of 1995-98 or the test time period of the 18 months prior to the date of fish collection at a station. For other NAWQA study units, available water-quality data for WYs 1995-98 were of limited quantity and could not be used in this evaluation. For example, only one NAWQA water-quality sample was available for the station Snake River near Hagerman, Idaho (BEST fish-collection station 41) for WYs 1995-98. Two NAWQA stations, Willamette River at Portland, Oregon, and Rio Grande at El Paso, Texas, were also NASQAN stations (table 3). For each of these stations, all available water-quality data were joint NAWQA and NASQAN data, and no additional data were available in the NAWQA Data Warehouse. Because of this and the limited quantity of NAWQA data for the test years, data specific to the NAWQA program were not used.

*Other Data Sources.*—The USGS-NWIS was searched for water-quality stations and data from Colorado, Idaho, Montana, New Mexico, Oregon, Texas, and Washington. Most of the resulting water-quality stations located near the fish-collection stations did not have adequate water-quality data for WYs 1995-98; data were either absent entirely or insufficient for statistical analysis. For example, the water-quality station Little Salmon River at Riggins, Idaho, is near BEST fish-collection Station 43, Salmon River near Riggins, Idaho (table 3). Water-quality data for the Little Salmon River were collected bimonthly or quarterly in WY 1995, but no data were collected in WYs 1996-97. At one water-quality station in the CRB and at three in the RGB that were located near fish-collection stations, periodic (monthly, bimonthly, or quarterly) data for field parameters, major ions, or both were available for WYs 1995-98. Data sets for these four stations were not as extensive as those for the NASQAN stations in terms of sampling frequency and trace-element and pesticide data, however, and these four stations were excluded from the study. For this reason and others stated in this and the previ-

ous paragraph, water-quality data from sources other than the NASQAN program were not used.

## Data Summarization and Analysis Techniques

### Water-Quality Data

Various methods for summarizing the water-quality data were considered, including flow- and time-weighted concentrations [the latter used by Goodbred and others (1997)], concentration of the last water sample before fish collection, frequency-of-detection or incidence, and total (combined) toxic units for trace elements (Wildhaber and Schmitt, 1996). Because an important consideration in this study is the length of time fish were exposed to contaminants in water, time-weighted concentrations were deemed more appropriate than flow-weighted concentrations for use in statistical correlations with fish-contaminant data. Conversely, the use of loads (for example, zinc loads in a stream) and streamflow to back calculate water-quality concentrations were determined inappropriate for this study.

Time-weighted concentrations for the water-quality parameters of interest first were determined for the 12 NASQAN stations in the CRB and RGB using techniques described in Larson and others (2004). Three separate time-weighted concentrations were computed for each station: (1) All available data (full period of record or FPR) were used to compute mean, median, and 90th percentile concentrations, (2) Data for WY 1997 (10/1/96-9/30/97) were used to compute mean, median, and 90th percentile concentrations, and (3) Natural-log-transformed data for WY 1997 were used to compute geometric means. Data for the FPR also could have been used to compute geometric means, but preliminary analyses indicated that these did not differ substantially from the WY 1997 means. For those computations involving the FPR for a station, a sampling year was defined as 12 consecutive months of data, beginning with the first date of sample collection. For all stations except Columbia River at Beaver Army Terminal, water-quality data for the 12 months preceding the collection of fish closely matched WY 1997; thus, water-quality data for WY 1997 were used to represent the 12 months preceding fish collection. This process yielded a common period of record for all stations.

Minimum sample criteria (drainage area and number of samples per year) for a station had to be met in order to compute time-weighted concentrations. In using the methods of Larson and others (2004) (table 6), smaller time gaps between samples and a greater number of samples overall are required for streams in smaller basins than for those in larger basins because runoff events and subsequent pulses of pesticides and other constituents can occur very quickly in streams of smaller

**Table 6.** Minimum sample criteria for calculation of time-weighted concentrations for selected NASQAN water-quality stations using techniques in Larson and others (2004).

[mi<sup>2</sup>, square miles; <, less than; ≥, greater than or equal to]

Drainage area class (mi <sup>2</sup> )	Required number of samples per year <sup>1</sup>
Small, <500	16
Medium, ≥500 and <5,000	12
Large, ≥5,000 and <50,000	10
Huge, ≥50,000	8

<sup>1</sup>Time-weighted concentrations were not calculated if any two samples within a year were more 120 days apart.

basins due to their flashy nature. The maximum time gap between samples was 120 days. The criteria used were subjective and, as originally developed, were designed with the goal of increasing the accuracy of annual percentage and mean percentile concentrations of pesticides while retaining as many stations in the investigation as possible (Larson and Gilliom, 2001; Larson and others, 2004).

Time-weighted mean and percentile concentrations were calculated by weighting each concentration according to the amount of the time that it represented the parameter concentration in the stream. Specifically, the weights were computed as the amount of time extending from one-half the time interval between a value and the preceding value and one-half the time interval extending from the value to the subsequent value divided by the total time being considered. The Statistical Analysis System (SAS Institute, 1998) Proc Univariate procedure was used to compute the means and percentiles from the weighted values. Less-than values were set to MRLs (table 4) for these computations. For computations of means, if fewer than 15 percent of the data were less-than values, the censored values were replaced by one-half the MRL (U.S. Environmental Protection Agency, 2000). If less-than values composed 15-50 percent of the data and there were at least 20 observations, then the log regression (LR) method (Gilliom and Helsel, 1986; Helsel and Gilliom, 1986) was used to estimate the mean. Otherwise, the mean returned by the Univariate procedure was considered to be a less-than value. For example, the mean of 3, 4, 5, and <4 was considered to be <4. For percentile concentrations, if more than *p* percent of the sample data were less-than values and there were at least 20 observations in the sample with at least 10 values above the MRL, the LR procedure was used to estimate the *p*<sup>th</sup> percentile. Otherwise, the percentile computed by the Univariate procedure was used and considered to be less-than at that value (Larson and others, 2004).

Time-weighted geometric mean concentrations for the 18 months prior to the date of fish collection were determined for the six RGB stations using less complex techniques than those

described by Larson and others (2004). Concentration data for the parameters of interest for each station were natural-log transformed and time-weighted using the methods described in the previous paragraph. The resulting time-weighted natural-log concentrations were summed over the 18-month time period, and the sum was untransformed to determine the time-weighted geometric mean. Data censored at the MRL were set at the MRL or at one-half the MRL. Use of the MRL would overestimate exposure of fish to water-borne contaminants. Data censored at concentrations greater than the MRL were omitted from the calculations. The 18-month time period was selected to yield a common length of time that fish were exposed to contaminants. Using lengths of time longer than 18 months would have caused some stations to be eliminated from the analyses.

Concentrations of the last water sample prior to the date of fish collection were retrieved for selected water-quality parameters for each station in the CRB and RGB. For many parameters, the last sample concentration for most or all stations was a censored value. Frequency-of-detection was calculated for the 18 months prior to the date of fish collection at a station for each parameter of interest. For each station, the frequency was determined by counting the number of samples in which the parameter was detected at a concentration greater than or equal to the MRL during the 18 months prior to the date of fish collection, then dividing by the total number of samples collected during the 18 months. Samples that were censored above the MRL for each parameter were excluded from frequency-of-detection calculations. Frequency-of-detection of total trace elements at a station was determined by counting the number of times each trace element (arsenic, chromium, copper, and zinc) was detected at a concentration greater than the MRL (1.0 µg/L), summing this number, and then dividing by the total number of trace-element samples at the station.

Water-quality guidelines for the protection of aquatic life have been established for most of the trace elements and pesticides of interest (table 4). Guidelines have not been established for the pesticides alachlor, Dacthal® (DCPA), *S*-ethyl dipropylthiocarbamate (EPTC), or propanil. Sources of the guidelines include the U.S. Environmental Protection Agency (USEPA) (2001, 2002), Canadian Council of Ministers of the Environment (1999), and International Joint Commission Canada and United States (IJC) (1978). For the USEPA guidelines, a criterion continuous concentration (CCC) is an estimate of the highest concentration of a parameter in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect (U.S. Environmental Protection Agency, 2002). The USEPA is revising current aquatic life criteria for copper, iron, lead, selenium, and silver and is developing new aquatic life criteria for diazinon, nonylphenol, methyl *tert*-butyl ether (MTBE), and manganese (U.S. Environmental Protection Agency, 2002). For atrazine, draft chronic and acute criteria have been established (U.S. Environmental Protection Agency, 2001). A chronic criterion is the average concentration of a parameter

to which aquatic organisms can be exposed for four days once every three years without injurious effects. An acute criterion is the average concentration over one hour to which aquatic organisms can be exposed once every three years without injurious effects. For the trace-element and pesticide parameters of interest, guidelines for the protection of aquatic life were compared to in-stream concentrations for each station in the two basins. Concentrations greater than the guidelines were identified.

Water-quality criteria for certain metals [cadmium, chromium (III), copper, lead, nickel, and zinc] are hardness-dependent. Accordingly, CCCs for copper and zinc, two of the trace elements of interest, were adjusted for hardness (as  $\text{CaCO}_3$ ) and are listed in table 4 with a range of values that reflect different hardness among the samples. Because metals are less toxic when hardness is high, a hardness of 400 milligrams per liter (mg/L) was used in the adjustment equation when the hardness for a sample was greater than 400 mg/L (U.S. Environmental Protection Agency, 2002). By doing this, the resulting adjusted criteria are more protective of aquatic life than if the actual hardness had been used in the adjustment equation. For chromium, CCCs have been established for chromium (III) and chromium (VI). The valence states of the chromium concentrations in this study were not distinguished, but the CCC of chromium (VI), which is not hardness-dependent, was used because this is the more toxic form. As such, the chromium criterion is also more protective of aquatic life because not all chromium in water is chromium (VI).

A cumulative relative frequency diagram was developed to assess how often the CCC was being exceeded for each station's FPR when the CCC for a trace element or pesticide was exceeded in more than two samples for a station. The frequency-of-exceedence value is an additional measure of the degree to which fish have been exposed to a particular contaminant.

Water-quality guidelines for the protection of aquatic life are focused on the effects of individual contaminants rather than on mixtures of contaminants. To account for the toxicity of contaminant mixtures, toxic units were calculated (Wildhaber and Schmitt, 1996). A toxic unit is defined here as the ratio of the concentration of a contaminant in a water sample to the CCC of the contaminant. For this study, the toxic unit for each trace element of interest (arsenic, chromium, copper, selenium, and zinc) in a water sample was determined individually and then summed to determine a total trace-element toxicity estimate for that sample. Finally, minimum, median, and maximum total trace-element toxicity estimates were determined for each station using all water samples at the station. When data for the individual trace elements were censored, the censored value was used in the calculations of toxic units. Censored values greater than 2  $\mu\text{g/L}$  were omitted from the calculations.

## Fish Data

Fish collected in the CRB and RGB as part of the BEST program were examined and analyzed for health-assessment indicators,  $\delta^{15}\text{N}$ , trace-element and organic contaminants, and total PCBs (table 2) (BEST, 2001; Hinck and others, 2004; Schmitt and others, 2004). The health-assessment indicators were observed or measured in individual fish whereas  $\delta^{15}\text{N}$ , elemental contaminants, organochlorine chemical residues, and 2,7,3,8-tetrachlorodibenzo-*p*-dioxin equivalents from the H4IIE bioassay (henceforth TCDD-EQ) were measured in composite fish samples (by species and gender) (Schmitt and others, 1999a and 1999b). Inorganic data for composite samples included dry- and wet-weight elemental concentrations and percent water (table 2). Organic data included concentrations of organochlorine pesticides, total PCBs, TCDD-EQ, and percent lipid (table 2). Total organochlorine pesticide concentrations for each sample were calculated as the sum of all concentrations for parameters in the "Organochlorine chemical residues" column of table 2 except for total PCBs and TCDD-EQ. Total DDT concentrations were calculated as the sum of *o,p'*-DDD, *o,p'*-DDE, *o,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, and *p,p'*-DDT. Both total organochlorine pesticide and total DDT concentrations were determined for each species and gender of fish. For concentrations reported as less than the reporting levels, both zero and one-half the reporting level were used as substitutions for the less-than concentrations.

Mean values for the fish-health observation indicators were determined for each species and gender of fish at a station by converting descriptive nomenclature to presence or absence, which was represented by zero for normal and one for abnormal (tumors, lesions, parasites, and others). Measured fish-health indicators were summarized with mean and median values for each species and gender of fish at a station and then further summarized by age. Three indicators—the gonadosomatic index (GSI) in male and female fish, and atresia and vitellogenin (vtg, an egg yolk precursor) in female fish—were also summarized by gonadal stage because these indicators change over the reproductive cycle (Schmitt, 2002).

*Final Data Set Composition.*—The procedures described in the preceding section yielded a water-quality data set of 5,046 data points from the NASQAN program. The data set for fish from the BEST program comprised 10,946 data points representing individual fish for health assessment end-points and 3,136 data points representing composite samples for trace elements, organochlorine pesticides, TCDD-EQ, and PCBs. These data sets spanned six stations in each of the CRB and RGB for WYs 1995-98, with all 12 stations included in both programs. As discussed previously, two of the NASQAN stations concurrently were stations for the NAWQA program, and all available water-quality data for the two stations were shared. No other NAWQA stations in study units comprised by the CRB and RGB contained adequate water-quality data for the period preceding collection of the



fish. Three NASQAN stations, all in the RGB, had to be eliminated. Water-quality data collection occurred after fish collection at two stations, and no fish were collected at the 3<sup>rd</sup> station. Other USGS water-quality stations in the CRB and RGG basins did not contain adequate water-quality data for the period preceding fish collection at the remaining BEST stations.

## Integration of Water-Quality and Fish Data

Potential relations between in-stream water-quality data and fish-contaminant and health-assessment data in the CRB and RGB were investigated in a two-step process. First, the fish data were graphed against time-weighted water-quality concentrations, concentrations of the last water sample before the date of fish collection, frequencies-of-detection in water, and total trace-element toxicity estimates. Data were not transformed for these analyses. Next, the strength of the associations between fish data and water-quality data were quantified by correlation analysis, specifically through the calculation of Kendall's tau using the SPLUS 2000 statistical package (Insightful Corporation, Seattle, Washington). Kendall's tau is a nonparametric rank-based procedure that measures the strength of the linear or nonlinear monotonic relation between two variables. It is resistant to outliers, and its large sample approximation produces significance-test  $p$ -values very near exact values, even for small sample sizes (Helsel and Hirsch, 1992). Other correlation analyses that were considered were Pearson's product-moment correlation and Spearman's rho. Pearson's correlation is used under the assumption that both variables are normally distributed. With small sample sizes, normally distributed data is unlikely, even if the data are transformed by procedures such as log or polynomials. The data sets used in this study were too small to have normal distributions. In contrast, Goodbred and others (1997) were able to use Pearson's product-moment correlation because their data set was large. Like Kendall's tau, Spearman's rho is a rank-based procedure. Both measure the same correlation but use different scales. With Spearman's rho, differences between data ranked further apart are given more weight than data ranked closer together whereas Kendall's tau weights all data equally (Helsel and Hirsch, 1992). In addition, large sample and rank approximations for Spearman's rho do not produce significance-test  $p$ -values near exact values for small sample sizes (Helsel and Hirsch, 1992). Because of the small sample sizes in the test data sets, Kendall's tau was selected. A significance level of  $p \leq 0.05$  was used for all correlation analyses.

## Data Refinements and Restrictions for Analysis

### Water-Quality Data Refinements

Time-weighted mean, median, and percentile concentrations for the water-quality parameters of interest were determined for one or two separate years for nine of the 12 NASQAN stations (table 7) using techniques described in Larson and others (2004). Data spanning the FPR for each station were used. These concentrations could not be determined for three stations—Willamette River (BEST Station 505) in the CRB and Rio Grande at Falcon Dam (Station 513) and Arroyo Colorado (Station 511) in the RGB—because the minimum sample criteria for drainage area, number of samples per year, or both were not met. Many of the remaining nine stations with calculated time-weighted concentrations had different periods of record for the water-quality data. Some stations had enough data for the FPR to determine time-weighted concentrations for two years, but others only had data for one year of computations. When two years of data were available, time-weighted concentrations for each year were determined. Otherwise, time-weighted concentrations for one year were determined. Time-weighted mean, median, and percentile concentrations were also computed for seven stations using WY 1997 as time (table 8). These concentrations could not be determined for five stations—Willamette River (Station 505) in the CRB; and the Rio Grande below Amistad Dam (Station 514) and Falcon Dam (Station 513), Rio Grande near Brownsville (Station 512), and Arroyo Colorado (Station 511) in the RGB—because the minimum sample criteria could not be met. The only RGB stations with sufficient data for the calculation of time-weighted concentrations for WY 1997 were Rio Grande at El Paso (Station 516) and Foster Ranch (Station 515) (table 8). In addition, some water-quality parameters of interest could not be used because of minimum sample criteria restrictions.

Summarization options for time-weighted concentrations from stations with multiple years of data were examined. For example, we examined whether the time-weighted mean or percentile concentration for one time period (for example, 1/1/96-12/30/97) could be averaged with the mean or percentile concentration for a second time period (1/1/97-10/7/97) to yield a single time-weighted value for the FPR (1/1/96-10/7/97; dates for the station Columbia River at Northport) (table 7). We determined that time-weighted mean concentrations representing more than one time period could be averaged together to obtain a time-weighted mean for the FPR provided that the individual time periods have the same number of samples. For time periods with different numbers of samples and for time-weighted percentiles, the mean value for the averages of the individual years does not equal the mean for the FPR. This issue proved to be irrelevant, however; most

**Table 7.** Time-weighted mean, median, and percentile concentrations of selected water-quality parameters for selected NASQAN water-quality stations in the Columbia River and Rio Grande basins for each station's full period of record.

[Dates in parentheses after station name refer to period of record in table 5; µg/L, micrograms per liter; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; EPTC, s-ethyl dipropylthiocarbamate. Time-weighted mean, median, and percentile concentrations were determined using techniques described in Larson and others (2004)]

Water-quality parameter (units)	Sample year	Begin date	Number of months	Number of samples	Number of less-than values	Time-weighted concentration		
						Mean	Median (50th percentile)	90th percentile
<b>Columbia River Basin</b>								
<b>Columbia River at Northport, Washington (11/25/1995-10/7/1997)</b>								
Atrazine (µg/L)	1	1/1/1996	11	15	13	<0.001	<0.001	0.002
Atrazine (µg/L)	2	1/1/1997	8	11	9	<0.001	<0.001	0.003
Chloride (mg/L)	1	1/1/1996	11	16	0	0.7	0.8	0.8
Chloride (mg/L)	2	1/1/1997	7	10	0	0.7	0.7	1
Chromium (µg/L)	1	1/1/1996	11	16	16	<1	<1	<1
Chromium (µg/L)	2	1/1/1997	8	11	5	<1.128	1	2
Copper (µg/L)	1	1/1/1996	11	16	4	<1.268	1	2
Copper (µg/L)	2	1/1/1997	8	11	5	<1.1	<1	1
Dacthal (µg/L)	1	1/1/1996	11	15	15	<0.002	<0.002	<0.002
Dacthal (µg/L)	2	1/1/1997	8	11	9	<0.002	<0.002	0.002
pH (standard units)	1	1/1/1996	11	16	0	8.1	8.1	8.2
pH (standard units)	2	1/1/1997	7	10	0	8.2	8.2	8.2
Simazine (µg/L)	1	1/1/1996	11	15	14	<0.005	<0.005	<0.005
Simazine (µg/L)	2	1/1/1997	8	11	11	<0.005	<0.005	<0.005
Specific conductance (µS/cm)	1	1/1/1996	11	16	0	139	138	152
Specific conductance (µS/cm)	2	1/1/1997	7	10	0	133	125	149
Total dissolved solids (mg/L)	1	1/1/1996	11	16	0	80	80	88
Total dissolved solids (mg/L)	2	1/1/1997	8	11	0	77	72	88
Water temperature (°C)	1	1/1/1996	11	16	0	8.8	6.8	15.5
Water temperature (°C)	2	1/1/1997	7	10	0	10.2	13	17.6
Zinc (µg/L)	1	1/1/1996	11	16	0	4	3	6
Zinc (µg/L)	2	1/1/1997	8	11	0	2	2	3
<b>Columbia River at Vernita Bridge near Priest Rapids Dam, Washington (1/17/1996-8/12/1997)</b>								
Arsenic (µg/L)	1	5/1/1996	8	8	8	<1	<1	<1
Atrazine (µg/L)	1	5/1/1996	8	8	6	<0.001	<0.001	0.002
Chloride (mg/L)	1	5/1/1996	8	8	0	1.0	0.9	1.5
Chlorpyrifos (µg/L)	1	5/1/1996	8	8	7	<0.004	<0.004	0.005
Chromium (µg/L)	1	5/1/1996	8	8	7	<1.02	<1	1
Copper (µg/L)	1	5/1/1996	8	8	3	<1.382	1	3
Dacthal (µg/L)	1	5/1/1996	8	8	7	<0.002	<0.002	<0.002
EPTC (µg/L)	1	5/1/1996	8	8	7	<0.002	<0.002	0.003

**Table 7.** Time-weighted mean, median, and percentile concentrations of selected water-quality parameters for selected NASQAN water-quality stations in the Columbia River and Rio Grande basins for each station's full period of record.—Continued

[Dates in parentheses after station name refer to period of record in table 5; µg/L, micrograms per liter; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; EPTC, s-ethyl dipropylthiocarbamate. Time-weighted mean, median, and percentile concentrations were determined using techniques described in Larson and others (2004)]

Water-quality parameter (units)	Sample year	Begin date	Number of months	Number of samples	Number of less-than values	Time-weighted concentration		
						Mean	Median (50th percentile)	90th percentile
Metolachlor (µg/L)	1	5/1/1996	8	8	8	<0.002	<0.002	<0.002
pH (standard units)	1	5/1/1996	8	8	0	7.9	8	8
Simazine (µg/L)	1	5/1/1996	8	8	8	<0.005	<0.005	<0.005
Specific conductance (µS/cm)	1	5/1/1996	8	8	0	140	135	157
Total dissolved solids (mg/L)	1	5/1/1996	8	8	0	88	88	100
Triallate (µg/L)	1	5/1/1996	8	8	7	<0.001	<0.001	0.005
Water temperature (°C)	1	5/1/1996	8	8	0	10.2	9.5	19.0
Zinc (µg/L)	1	5/1/1996	8	8	2	<2.17	2	4
<b>Snake River at Burbank, Washington (10/13/1995-9/18/1997)</b>								
Alachlor (µg/L)	1	10/1/1995	11	15	10	<0.002	<0.002	0.004
Alachlor (µg/L)	2	10/1/1996	10	14	9	<0.003	<0.002	0.004
Arsenic (µg/L)	1	10/1/1995	10	14	0	2	2	3
Arsenic (µg/L)	2	10/1/1996	10	14	1	2	2	3
Atrazine (µg/L)	1	10/1/1995	11	15	2	<0.005	0.004	0.008
Atrazine (µg/L)	2	10/1/1996	10	14	0	0.006	0.005	0.008
Chloride (mg/L)	1	10/1/1995	12	17	0	5.7	5.2	9.7
Chloride (mg/L)	2	10/1/1996	10	14	0	7.1	6.8	12
Chromium (µg/L)	1	10/1/1995	10	15	12	<1.752	<5	5
Chromium (µg/L)	2	10/1/1996	10	14	9	<1.099	<1	1
Copper (µg/L)	1	10/1/1995	10	14	8	<1.113	<1	1
Copper (µg/L)	2	10/1/1996	10	14	9	<1.193	<1	2
Dacthal (µg/L)	1	10/1/1995	11	15	5	<0.002	0.002	0.003
Dacthal (µg/L)	2	10/1/1996	10	14	6	<0.002	<0.002	0.003
EPTC (µg/L)	1	10/1/1995	11	15	8	<0.003	<0.002	0.007
EPTC (µg/L)	2	10/1/1996	10	14	6	<0.003	<0.002	0.009
Metolachlor (µg/L)	1	10/1/1995	11	15	7	<0.004	0.002	0.007
Metolachlor (µg/L)	2	10/1/1996	10	14	6	<0.004	0.002	0.006
Metribuzin (µg/L)	1	10/1/1995	11	15	14	<0.004	<0.004	<0.004
Metribuzin (µg/L)	2	10/1/1996	10	14	12	<0.004	<0.004	<0.004
pH (standard units)	1	10/1/1995	12	17	0	7.9	7.9	8.1
pH (standard units)	2	10/1/1996	10	14	0	7.9	8	8.1
Simazine (µg/L)	1	10/1/1995	11	15	13	<0.005	<0.005	<0.005
Simazine (µg/L)	2	10/1/1996	10	14	13	<0.005	<0.005	<0.005
Specific conductance (µS/cm)	1	10/1/1995	12	17	0	177	171	265
Specific conductance (µS/cm)	2	10/1/1996	10	14	0	218	217	325

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**Table 7.** Time-weighted mean, median, and percentile concentrations of selected water-quality parameters for selected NASQAN water-quality stations in the Columbia River and Rio Grande basins for each station's full period of record.—Continued

[Dates in parentheses after station name refer to period of record in table 5; µg/L, micrograms per liter; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; EPTC, s-ethyl dipropylthiocarbamate. Time-weighted mean, median, and percentile concentrations were determined using techniques described in Larson and others (2004)]

Water-quality parameter (units)	Sample year	Begin date	Number of months	Number of samples	Number of less-than values	Time-weighted concentration		
						Mean	Median (50th percentile)	90th percentile
Total dissolved solids (mg/L)	1	10/1/1995	12	17	0	113	110	159
Total dissolved solids (mg/L)	2	10/1/1996	10	13	0	132	130	192
Triallate (µg/L)	1	10/1/1995	11	15	9	<0.004	<0.001	0.008
Triallate (µg/L)	2	10/1/1996	10	14	8	<0.003	<0.001	0.008
Water temperature (°C)	1	10/1/1995	12	17	0	12.0	11.5	21
Water temperature (°C)	2	10/1/1996	10	14	0	11.7	12.5	20
Zinc (µg/L)	1	10/1/1995	10	14	11	<1	<3	3
Zinc (µg/L)	2	10/1/1996	10	14	11	<1	<1	1
<b>Columbia River at Warrendale, Washington (10/21/1996-10/29/1997)</b>								
Alachlor (µg/L)	1	10/1/1996	9	15	12	<0.002	<0.002	<0.002
Arsenic (µg/L)	1	10/1/1996	9	15	4	<1.035	1	1
Atrazine (µg/L)	1	10/1/1996	9	15	1	0.003	0.004	0.005
Chloride (mg/L)	1	10/1/1996	9	15	0	2.619	2.2	5.4
Chlorpyrifos (µg/L)	1	10/1/1996	9	15	13	<0.004	<0.004	0.005
Chromium (µg/L)	1	10/1/1996	9	15	9	<1.035	<1	1
Copper (µg/L)	1	10/1/1996	9	15	2	<1.365	1	2
Dacthal (µg/L)	1	10/1/1996	9	15	7	<0.002	<0.002	0.002
EPTC (µg/L)	1	10/1/1996	9	15	7	<0.003	<0.002	0.004
Metolachlor (µg/L)	1	10/1/1996	9	15	8	<0.002	<0.002	0.004
Metribuzin (µg/L)	1	10/1/1996	9	15	12	<0.004	<0.004	0.005
pH (standard units)	1	10/1/1996	9	15	0	7.9	7.9	8.1
Simazine (µg/L)	1	10/1/1996	9	15	11	<0.005	<0.005	0.005
Specific conductance (µS/cm)	1	10/1/1996	9	15	0	142	142	191
Total dissolved solids (mg/L)	1	10/1/1996	9	15	0	92	94	126
Triallate (µg/L)	1	10/1/1996	9	15	11	<0.003	<0.001	0.014
Water temperature (°C)	1	10/1/1996	9	15	0	11.8	12.1	21.4
Zinc (µg/L)	1	10/1/1996	9	15	6	<1.601	<1	4
<b>Columbia River at Beaver Army Terminal near Quincy, Oregon (10/24/1995-3/9/1998)</b>								
Arsenic (µg/L)	1	11/1/1995	10	12	11	<1	<1	<1
Arsenic (µg/L)	2	11/1/1996	8	14	6	<1.039	1	1
Atrazine (µg/L)	1	11/1/1995	11	14	2	0.01	0.007	0.023
Atrazine (µg/L)	2	11/1/1996	8	14	1	0.016	0.005	0.078
Chloride (mg/L)	1	11/1/1995	10	12	0	2.9	3.1	3.6
Chloride (mg/L)	2	11/1/1996	8	14	0	3.5	3	6.7
Chlorpyrifos (µg/L)	1	11/1/1995	11	14	13	<0.004	<0.004	<0.004

**Table 7.** Time-weighted mean, median, and percentile concentrations of selected water-quality parameters for selected NASQAN water-quality stations in the Columbia River and Rio Grande basins for each station's full period of record.—Continued

[Dates in parentheses after station name refer to period of record in table 5; µg/L, micrograms per liter; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; EPTC, s-ethyl dipropylthiocarbamate. Time-weighted mean, median, and percentile concentrations were determined using techniques described in Larson and others (2004)]

Water-quality parameter (units)	Sample year	Begin date	Number of months	Number of samples	Number of less-than values	Time-weighted concentration		
						Mean	Median (50th percentile)	90th percentile
Chlorpyrifos (µg/L)	2	11/1/1996	8	14	11	<0.004	<0.004	0.004
Chromium (µg/L)	1	11/1/1995	11	13	12	<1	<1	<1
Chromium (µg/L)	2	11/1/1996	8	14	9	<1.088	<1	1
Copper (µg/L)	1	11/1/1995	11	13	2	<1.597	2	2
Copper (µg/L)	2	11/1/1996	8	14	2	1	1	2
Dacthal (µg/L)	1	11/1/1995	11	14	9	<0.002	<0.002	0.002
Dacthal (µg/L)	2	11/1/1996	8	14	6	<0.002	<0.002	0.002
EPTC (µg/L)	1	11/1/1995	11	14	8	<0.002	<0.002	0.004
EPTC (µg/L)	2	11/1/1996	8	14	7	<0.002	<0.002	0.004
Metolachlor (µg/L)	1	11/1/1995	11	14	4	<0.004	0.003	0.007
Metolachlor (µg/L)	2	11/1/1996	8	14	3	0.006	<0.004	0.023
Metribuzin (µg/L)	1	11/1/1995	11	14	12	<0.004	<0.004	<0.004
Metribuzin (µg/L)	2	11/1/1996	8	14	10	<0.006	0.004	0.013
pH (standard units)	1	11/1/1995	11	13	0	7.7	7.6	8.1
pH (standard units)	2	11/1/1996	8	14	0	7.7	7.8	8
Simazine (µg/L)	1	11/1/1995	11	14	3	<0.007	0.005	0.013
Simazine (µg/L)	2	11/1/1996	8	14	6	<0.009	0.005	0.034
Specific conductance (µS/cm)	1	11/1/1995	11	13	0	121	123	136
Specific conductance (µS/cm)	2	11/1/1996	8	14	0	130	125	183
Total dissolved solids (mg/L)	1	11/1/1995	10	12	0	77	77	84
Total dissolved solids (mg/L)	2	11/1/1996	8	14	0	86	79	123
Triallate (µg/L)	1	11/1/1995	11	14	10	<0.002	<0.001	0.005
Triallate (µg/L)	2	11/1/1996	8	14	8	<0.003	<0.001	0.011
Water temperature (°C)	1	11/1/1995	11	13	0	12.2	10.3	20.5
Water temperature (°C)	2	11/1/1996	8	14	0	12.7	11.5	21.7
Zinc (µg/L)	1	11/1/1995	11	13	3	<1.659	2	3
Zinc (µg/L)	2	11/1/1996	8	14	7	<1.642	1	3
<b>Rio Grande Basin</b>								
<b>Rio Grande at El Paso, Texas (11/2/1995-9/10/1997)</b>								
Arsenic (µg/L)	2	11/1/1996	12	12	0	3	3	4
Atrazine (µg/L)	2	11/1/1996	12	12	4	<0.002	0.003	0.004
Carbaryl (µg/L)	2	11/1/1996	12	12	11	<0.004	<0.008	<0.008
Chloride (mg/L)	1	11/1/1995	12	13	0	142	120	310
Chloride (mg/L)	2	11/1/1996	12	12	0	170	98.1	400
Chlorpyrifos (µg/L)	2	11/1/1996	12	12	7	<0.005	<0.004	0.004

## 22 Approach for Integrating BEST and NASQAN

**Table 7.** Time-weighted mean, median, and percentile concentrations of selected water-quality parameters for selected NASQAN water-quality stations in the Columbia River and Rio Grande basins for each station's full period of record.—Continued

[Dates in parentheses after station name refer to period of record in table 5; µg/L, micrograms per liter; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; EPTC, s-ethyl dipropylthiocarbamate. Time-weighted mean, median, and percentile concentrations were determined using techniques described in Larson and others (2004)]

Water-quality parameter (units)	Sample year	Begin date	Number of months	Number of samples	Number of less-than values	Time-weighted concentration		
						Mean	Median (50th percentile)	90th percentile
Chromium (µg/L)	2	11/1/1996	12	12	3	<1.895	2	3
Copper (µg/L)	2	11/1/1996	12	12	4	<1.592	<2	2
Dacthal (µg/L)	2	11/1/1996	12	12	1	0.003	0.003	0.004
Diazinon (µg/L)	2	11/1/1996	12	12	9	<0.002	<0.005	0.005
Malathion (µg/L)	2	11/1/1996	12	12	11	<0.007	<0.005	<0.005
Metolachlor (µg/L)	2	11/1/1996	12	12	2	<0.004	0.004	0.006
pH (standard units)	1	11/1/1995	11	12	0	8.3	8.3	8.5
pH (standard units)	2	11/1/1996	12	12	0	8.4	8.5	8.6
Selenium (µg/L)	2	11/1/1996	12	12	12	<1	<1	<1
Simazine (µg/L)	2	11/1/1996	12	12	4	<0.008	0.008	0.012
Specific conductance (µS/cm)	1	11/1/1995	11	12	0	1290	1110	2300
Specific conductance (µS/cm)	2	11/1/1996	12	12	0	1450	1060	2660
Total dissolved solids (mg/L)	1	11/1/1995	12	13	0	832	698	1510
Total dissolved solids (mg/L)	2	11/1/1996	12	12	0	926	656	1740
Water temperature (°C)	1	11/1/1995	11	12	0	16.0	16.5	24
Water temperature (°C)	2	11/1/1996	12	12	0	16.6	16	25
Zinc (µg/L)	2	11/1/1996	12	12	1	3	2	5
<b>Rio Grande at Foster Ranch near Langtry, Texas (10/25/1995-9/10/1997)</b>								
Arsenic (µg/L)	2	11/1/1996	8	11	1	<1.89	2	3
Atrazine (µg/L)	2	11/1/1996	8	11	7	<0.001	<0.001	0.003
Chloride (mg/L)	2	11/1/1996	8	11	0	142	120	250
Chromium (µg/L)	2	11/1/1996	8	11	2	<1.759	2	2
Copper (µg/L)	2	11/1/1996	8	11	5	<1.388	<1	2
Dacthal (µg/L)	2	11/1/1996	8	11	8	<0.002	<0.002	0.002
Diazinon (µg/L)	2	11/1/1996	8	11	9	<0.003	<0.002	0.008
Metolachlor (µg/L)	2	11/1/1996	8	11	11	<0.002	<0.002	<0.002
pH (standard units)	2	11/1/1996	8	11	0	7.8	7.8	8.1
Selenium (µg/L)	2	11/1/1996	8	11	5	<1.095	1	2
Simazine (µg/L)	2	11/1/1996	8	11	10	<0.005	<0.005	0.005
Specific conductance (µS/cm)	2	11/1/1996	8	11	0	1280	1230	1790
Total dissolved solids (mg/L)	2	11/1/1996	8	11	0	850	804	1140
Water temperature (°C)	2	11/1/1996	8	11	0	20.0	19	27.5
Zinc (µg/L)	2	11/1/1996	8	11	6	<1.719	1	3

**Table 7.** Time-weighted mean, median, and percentile concentrations of selected water-quality parameters for selected NASQAN water-quality stations in the Columbia River and Rio Grande basins for each station's full period of record.—Continued

[Dates in parentheses after station name refer to period of record in table 5; µg/L, micrograms per liter; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; EPTC, s-ethyl dipropylthiocarbamate. Time-weighted mean, median, and percentile concentrations were determined using techniques described in Larson and others (2004)]

Water-quality parameter (units)	Sample year	Begin date	Number of months	Number of samples	Number of less-than values	Time-weighted concentration		
						Mean	Median (50th percentile)	90th percentile
<b>Rio Grande below Amistad Dam, near Del Rio, Texas (5/28/1996-9/11/1997)</b>								
Arsenic (µg/L)	1	6/1/1996	8	8	0	3	2	5
Atrazine (µg/L)	1	6/1/1996	8	8	2	<0.003	0.003	0.004
Chloride (mg/L)	1	6/1/1996	8	8	0	174	161	200
Chromium (µg/L)	1	6/1/1996	8	8	1	<1.574	1	3
Copper (µg/L)	1	6/1/1996	8	8	2	<1.186	1	2
Dacthal (µg/L)	1	6/1/1996	8	8	7	<0.002	<0.002	<0.002
Diazinon (µg/L)	1	6/1/1996	8	8	7	<0.004	<0.002	0.01
pH (standard units)	1	6/1/1996	8	8	0	7.8	7.8	7.9
Simazine (µg/L)	1	6/1/1996	8	8	6	<0.004	<0.005	0.005
Specific conductance (µS/cm)	1	6/1/1996	8	8	0	1270	1210	1360
Total dissolved solids (mg/L)	1	6/1/1996	8	8	0	846	798	862
Water temperature (°C)	1	6/1/1996	8	8	0	17.9	17.5	25
Zinc (µg/L)	1	6/1/1996	8	8	1	3	2	6
<b>Rio Grande near Brownsville, Texas (10/17/1995-10/11/1997)</b>								
Arsenic (µg/L)	1	3/1/1996	9	11	0	4	3	7
Atrazine (µg/L)	1	3/1/1996	9	11	0	0.013	0.009	0.027
Carbaryl (µg/L)	1	3/1/1996	9	11	11	<0.003	<0.003	<0.003
Chloride (mg/L)	1	3/1/1996	9	11	0	216	210	280
Chlorpyrifos (µg/L)	1	3/1/1996	9	11	9	<0.005	<0.004	0.004
Chromium (µg/L)	1	3/1/1996	9	11	3	<1.245	1	2
Copper (µg/L)	1	3/1/1996	9	11	0	2	2	3
Dacthal (µg/L)	1	3/1/1996	9	11	6	<0.005	0.003	0.021
Diazinon (µg/L)	1	3/1/1996	9	11	10	<0.003	<0.002	0.005
Malathion (µg/L)	1	3/1/1996	9	11	11	<0.005	<0.005	<0.005
Metolachlor (µg/L)	1	3/1/1996	9	11	7	<0.003	<0.002	0.004
pH (standard units)	1	3/1/1996	9	11	0	8.2	8.2	8.2
Simazine (µg/L)	1	3/1/1996	9	11	10	<0.005	<0.005	0.005
Specific conductance (µS/cm)	1	3/1/1996	9	11	0	1600	1590	1810
Total dissolved solids (mg/L)	1	3/1/1996	9	11	0	956	938	1140
Water temperature (°C)	1	3/1/1996	9	11	0	24.3	24	30.5
Zinc (µg/L)	1	3/1/1996	9	11	0	3	2	4

**Table 8.** Time-weighted mean, median, and percentile concentrations of selected water-quality parameters for selected NASQAN water-quality stations in the Columbia River and Rio Grande basins for water year 1997.

[water year 1997, October 1, 1996 through September 30, 1997; µg/L, micrograms per liter; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; EPTC, s-ethyl dipropylthiocarbamate. Time-weighted mean, median, and percentile concentrations were determined using techniques described in Larson and others (2004)]

Water-quality parameter (units)	Number of months	Number of samples	Number of less-than values	Time-weighted concentration			
				Mean	Geometric Mean	Median (50th percentile)	90th percentile
<b>Columbia River Basin</b>							
<b>Columbia River at Northport, Washington</b>							
Atrazine (µg/L)	9	12	10	<0.001	<0.001	<0.001	0.003
Chloride (mg/L)	8	11	0	0.7	0.7	0.8	1
Chromium (µg/L)	9	12	7	<1.068	<1.057	<1	1.5
Copper (µg/L)	9	12	6	<1.1	<1.084	<1	1.3
Dacthal (µg/L)	9	12	11	<0.002	<0.002	<0.002	<0.002
pH (standard units)	8	11	0	8.2	8.2	8.2	8.2
Simazine (µg/L)	9	12	12	<0.005	<0.005	<0.005	<0.005
Specific conductance (µS/cm)	8	11	0	136	136	138	149
Total dissolved solids (mg/L)	9	12	0	79	78	77	88
Water temperature (°C)	8	11	0	9.1	7.4	6.9	17.6
Zinc (µg/L)	9	12	0	2.942	2.815	3	4
<b>Columbia River at Vernita Bridge near Priest Rapids Dam, Washington</b>							
Arsenic (µg/L)	9	11	10	<1.038	<1.031	<1	<1
Atrazine (µg/L)	9	11	7	<0.001	<0.001	<0.001	0.002
Chloride (mg/L)	9	11	0	1.0	0.9	0.9	1.5
Chlorpyrifos (µg/L)	9	11	10	<0.004	<0.004	<0.004	<0.004
Chromium (µg/L)	9	11	8	<1.038	<1.034	<1	1.2
Copper (µg/L)	9	11	5	<1.125	<1.107	<1	1.5
Dacthal (µg/L)	9	11	7	<0.002	<0.002	<0.002	0.002
EPTC (µg/L)	9	11	8	<0.003	<0.002	<0.002	0.003
Metolachlor (µg/L)	9	11	10	<0.002	<0.002	<0.002	<0.002
pH (standard units)	9	11	0	7.9	7.9	8.0	8.1
Simazine (µg/L)	9	11	10	<0.005	<0.005	<0.005	<0.005
Specific conductance (µS/cm)	9	11	0	135	134	135	152
Total dissolved solids (mg/L)	9	11	0	85	84	86	100
Triallate (µg/L)	9	11	10	<0.001	<0.001	<0.001	<0.001
Water temperature (°C)	9	11	0	10.6	8.8	10.8	19.0
Zinc (µg/L)	9	11	1	<2.547	<2.162	2	4
<b>Snake River at Burbank, Washington</b>							
Alachlor (µg/L)	10	14	9	<0.003	<0.002	<0.002	0.004
Arsenic (µg/L)	10	14	1	2.064	1.972	2	3
Atrazine (µg/L)	10	14	0	0.006	0.005	0.005	0.008
Chloride (mg/L)	10	14	0	7.1	6.1	6.8	12.0



**Table 8.** Time-weighted mean, median, and percentile concentrations of selected water-quality parameters for selected NASQAN water-quality stations in the Columbia River and Rio Grande basins for water year 1997.—Continued

[water year 1997, October 1, 1996 through September 30, 1997; µg/L, micrograms per liter; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; EPTC, s-ethyl dipropylthiocarbamate. Time-weighted mean, median, and percentile concentrations were determined using techniques described in Larson and others (2004)]

Water-quality parameter (units)	Number of months	Number of samples	Number of less-than values	Time-weighted concentration			
				Mean	Geometric Mean	Median (50th percentile)	90th percentile
Chromium (µg/L)	10	14	9	<1.099	<1.074	<1	1.2
Copper (µg/L)	10	14	9	<1.193	<1.155	<1	2
Dacthal (µg/L)	10	14	6	<0.002	<0.002	<0.002	0.003
EPTC (µg/L)	10	14	6	<0.003	<0.003	<0.002	0.009
Metolachlor (µg/L)	10	14	6	<0.004	<0.004	0.002	0.006
Metribuzin (µg/L)	10	14	12	<0.004	<0.004	<0.004	<0.004
pH (standard units)	10	14	0	7.9	7.9	8.0	8.1
Simazine (µg/L)	10	14	13	<0.005	<0.005	<0.005	<0.005
Specific conductance (µS/cm)	10	14	0	218	201	217	325
Total dissolved solids (mg/L)	10	13	0	132	123	130	192
Triallate (µg/L)	10	14	8	<0.003	<0.002	<0.001	0.008
Water temperature (°C)	10	14	0	11.7	10.0	12.5	20.0
Zinc (µg/L)	10	14	11	<1.065	<1.042	<1	1
<b>Columbia River at Warrendale, Washington</b>							
Alachlor (µg/L)	9	15	12	<0.002	<0.002	<0.002	<0.002
Arsenic (µg/L)	9	15	4	<1.035	<1.03	1	1.1
Atrazine (µg/L)	9	15	1	0.003	0.004	0.004	0.005
Chloride (mg/L)	9	15	0	2.6	2.4	2.2	5.4
Chlorpyrifos (µg/L)	9	15	13	<0.004	<0.004	<0.004	0.005
Chromium (µg/L)	9	15	9	<1.035	<1.034	<1	1.1
Copper (µg/L)	9	15	2	<1.365	<1.297	1.2	2
Dacthal (µg/L)	9	15	7	<0.002	<0.002	<0.002	0.002
EPTC (µg/L)	9	15	7	<0.003	<0.002	<0.002	0.004
Metolachlor (µg/L)	9	15	8	<0.002	<0.002	<0.002	0.004
Metribuzin (µg/L)	9	15	12	<0.004	<0.004	<0.004	0.005
pH (standard units)	9	15	0	7.9	7.9	7.9	8.1
Simazine (µg/L)	9	15	11	<0.005	<0.004	<0.005	0.005
Specific conductance (µS/cm)	9	15	0	142	139	142	191
Total dissolved solids (mg/L)	9	15	0	92	91	94	126
Triallate (µg/L)	9	15	11	<0.003	<0.002	<0.001	0.014
Water temperature (°C)	9	15	0	11.8	9.9	12.1	21.4
Zinc (µg/L)	9	15	6	<1.601	<1.376	<1	3.7

**Table 8.** Time-weighted mean, median, and percentile concentrations of selected water-quality parameters for selected NASQAN water-quality stations in the Columbia River and Rio Grande basins for water year 1997.—Continued

[water year 1997, October 1, 1996 through September 30, 1997; µg/L, micrograms per liter; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; EPTC, s-ethyl dipropylthiocarbamate. Time-weighted mean, median, and percentile concentrations were determined using techniques described in Larson and others (2004)]

Water-quality parameter (units)	Number of months	Number of samples	Number of less-than values	Time-weighted concentration			
				Mean	Geometric Mean	Median (50th percentile)	90th percentile
<b>Columbia River at Beaver Army Terminal near Quincy, Oregon</b>							
Arsenic (µg/L)	9	15	7	<1.039	<1.035	1	1.1
Atrazine (µg/L)	9	15	1	0.014	0.008	0.005	0.078
Chloride (mg/L)	9	15	0	3.5	3.3	3.1	6.7
Chlorpyrifos (µg/L)	9	15	12	<0.004	<0.004	<0.004	0.004
Chromium (µg/L)	9	15	10	<1.088	<1.067	<1	1.2
Copper (µg/L)	9	15	3	<1.177	<1.156	1	1.6
Dacthal (µg/L)	9	15	7	<0.002	<0.002	<0.002	0.002
EPTC (µg/L)	9	15	8	<0.002	<0.002	<0.002	0.004
Metolachlor (µg/L)	9	15	3	0.006	0.005	0.004	0.023
Metribuzin (µg/L)	9	15	11	<0.006	<0.005	<0.004	0.013
pH (standard units)	9	15	0	7.7	7.7	7.8	8
Simazine (µg/L)	9	15	6	<0.008	<0.005	0.005	0.034
Specific conductance (µS/cm)	9	15	0	131	129	130	183
Total dissolved solids (mg/L)	9	15	0	87	86	84	123
Triallate (µg/L)	9	15	9	<0.003	<0.002	<0.001	0.011
Water temperature (°C)	9	15	0	12.1	10.5	11.5	21.7
Zinc (µg/L)	9	15	7	<1.564	<1.377	1	3
<b>Rio Grande Basin</b>							
<b>Rio Grande at El Paso, Texas</b>							
Arsenic (µg/L)	12	12	0	3.107	3.022	3	4
Atrazine (µg/L)	12	12	3	<0.003	<0.003	0.003	0.004
Carbaryl (µg/L)	12	12	10	<0.004	<0.003	<0.003	0.005
Chloride (mg/L)	12	12	0	176	143	98	400
Chlorpyrifos (µg/L)	12	12	7	<0.005	<0.004	<0.004	0.004
Chromium (µg/L)	12	12	3	<1.807	<1.73	2	2.1
Copper (µg/L)	12	12	4	<1.622	<1.478	<2	2
Dacthal (µg/L)	12	12	1	0.003	0.004	0.003	0.006
Diazinon (µg/L)	12	12	8	<0.002	<0.002	<0.002	0.004
Malathion (µg/L)	12	12	10	<0.009	<0.007	<0.005	0.026
Metolachlor (µg/L)	12	12	2	<0.005	<0.004	0.004	0.008
pH (standard units)	12	12	0	8.5	8.5	8.5	8.6
Selenium (µg/L)	12	12	12	<1	<1	<1	<1
Simazine (µg/L)	12	12	3	<0.007	<0.007	0.008	0.012
Specific conductance (µS/cm)	12	12	0	1470	1350	1060	2660

**Table 8.** Time-weighted mean, median, and percentile concentrations of selected water-quality parameters for selected NASQAN water-quality stations in the Columbia River and Rio Grande basins for water year 1997.—Continued

[water year 1997, October 1, 1996 through September 30, 1997; µg/L, micrograms per liter; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; EPTC, s-ethyl dipropylthiocarbamate. Time-weighted mean, median, and percentile concentrations were determined using techniques described in Larson and others (2004)]

Water-quality parameter (units)	Number of months	Number of samples	Number of less-than values	Time-weighted concentration			
				Mean	Geometric Mean	Median (50th percentile)	90th percentile
Total dissolved solids (mg/L)	12	12	0	942	852	656	1740
Water temperature (°C)	12	12	0	15.9	14.7	13.5	25.0
Zinc (µg/L)	12	12	1	2.832	2.37	2.1	5
<b>Rio Grande at Foster Ranch near Langtry, Texas</b>							
Arsenic (µg/L)	8	11	1	<1.788	<1.664	<2	2.9
Atrazine (µg/L)	8	11	7	<0.001	<0.001	<0.001	0.003
Chloride (mg/L)	8	11	0	153	124	133	250
Chromium (µg/L)	8	11	2	<1.844	<1.74	2	2.4
Copper (µg/L)	8	11	5	<1.388	<1.303	<1	2.1
Dacthal (µg/L)	8	11	8	<0.002	<0.002	<0.002	0.002
Diazinon (µg/L)	8	11	9	<0.004	<0.003	<0.002	0.008
Metolachlor (µg/L)	8	11	11	<0.002	<0.002	<0.002	<0.002
pH (standard units)	8	11	0	7.9	7.9	7.8	8.1
Selenium (µg/L)	8	11	5	<1.095	<.081	<1	1.5
Simazine (µg/L)	8	11	10	<0.005	<0.005	<0.005	0.005
Specific conductance (µS/cm)	8	11	0	1330	1250	1250	1790
Total dissolved solids (mg/L)	8	11	0	884	842	815	1140
Water temperature (°C)	8	11	0	18.5	16.9	18.0	27.5
Zinc (µg/L)	8	11	6	<1.889	<1.667	1.4	3

mean and median time-weighted concentrations representing multiple years of CRB and RGB water quality were reported as less-than concentrations, which could not be condensed into single values. Because an exact concentration value is not known for a less-than concentration, these concentrations cannot be averaged. Substitution of zero or one-half the MRL for censored values was also considered but subsequently rejected because the percentage of replaced observations would have exceeded the recommended maximum (15%) for substitution (U.S. Environmental Protection Agency, 2000). In such instances, time-weighted concentrations for WY 1997 (table 8) were combined with the fish data for correlation analyses.

Specifically, we used the 90th percentile time-weighted concentrations for WY 1997, as determined using the techniques described by Larson and others (2004), in the CRB correlation analyses. Although the 90th percentile concentrations overestimate exposure of fish to water-borne contaminants as compared to mean or median concentrations, these values were used to facilitate computations in this example because of the large amount of censored data. The 90th percentile

values for specific conductance, arsenic, atrazine, copper, total trace elements (sum of 90th percentile concentrations for arsenic, chromium, copper, and zinc), and zinc were used. Two parameters of interest, chloride and total dissolved solids, were highly correlated ( $p \leq 0.05$ ) with specific conductance; therefore, we used only specific conductance. The 90th percentile concentrations of chromium were excluded because all concentrations were very similar ( $\pm 0.1$  µg/L). Selenium was excluded because most or all concentrations were less than the reporting level.

Only specific conductance could be used in the CRB correlation analyses for the last water sample before the date of fish collection, (table 9). All other parameters of interest had at least one concentration that was less than the respective MRL for the four stations with appropriate fish data, resulting in insufficient data for analysis. Frequencies-of-detection of arsenic, atrazine, chromium, copper, EPTC, total trace elements, and zinc in the CRB for the 18 months prior to the date of fish collection also were used in the correlation analyses

**Table 9.** Concentration of last water sample before date of fish collection for selected NASQAN water-quality stations in the Columbia River and Rio Grande basins.

[ $\mu\text{S/cm}$ , microsiemens per centimeter at 25 degrees Celsius;  $\mu\text{g/L}$ , micrograms per liter; <, less than; E, estimated. Table only includes stations with carp]

Station name	Specific conductance ( $\mu\text{S/cm}$ )	Arsenic ( $\mu\text{g/L}$ )	Chromium ( $\mu\text{g/L}$ )	Copper ( $\mu\text{g/L}$ )	Zinc ( $\mu\text{g/L}$ )	Atrazine ( $\mu\text{g/L}$ )
<b>Columbia River Basin</b>						
Columbia River at Vernita Bridge near Priest Rapids Dam, Washington	122	<1.0	1.0	<1.0	1.8	<0.001
Snake River at Burbank, Washington	217	2.3	<1.0	1.5	1.0	0.007
Columbia River at Warrendale, Washington	165	1.0	1.3	1.2	<1.0	E 0.004
Columbia River at Beaver Army Terminal near Quincy, Oregon	144	<1.0	1.5	<1.0	2.2	0.012
<b>Rio Grande Basin</b>						
Rio Grande at El Paso, Texas	1040	3.4	1.2	2.0	2.7	<0.001
Rio Grande at Foster Ranch near Langtry, Texas	1090	2.2	<1.0	<1.0	<1.0	<0.001
Rio Grande below Amistad Dam, near Del Rio, Texas	1220	2.9	1.4	<1.0	<1.0	<0.001
Rio Grande below Falcon Dam, Texas	1130	2.9	<1.0	1.3	5.8	0.007
Arroyo Colorado at Harlingen, Texas	4760	5.1	<2.0	3.0	4.4	0.252
Rio Grande near Brownsville, Texas	819	3.4	1.8	1.5	2.3	0.224

(table 10). Selenium was not detected in the CRB during this period (table 10).

Concentrations of most constituents were greater in the RGB than in the CRB. Nevertheless, and as discussed previously, time-weighted concentrations could not be determined for most RGB stations when the data requirements of Larson and others (2004) were applied. Consequently, we relaxed the data requirements by eliminating minimum sample criteria for drainage area and number of samples per year and used data for all six stations. Time-weighted geometric mean concentrations of arsenic, copper, zinc, total trace elements (the sum of arsenic, chromium, copper, and zinc concentrations), and atrazine were determined for the 18 months prior to the date of fish collection for each station (table 11). The time-weighted geometric mean concentration for chromium was not determined because almost 37 percent of the data comprised censored values. As in the CRB, most or all selenium concentrations in the RGB were less than the reporting level, and selenium was therefore excluded from the calculations for total trace elements.

Other RGB water-quality parameters used in the correlation analyses included the last sample values of specific conductance and arsenic, and frequencies-of-detection of atrazine, chromium, copper, total trace elements, and zinc for the 18 months prior to the date of fish collection (tables 9 and

10). Eighteen-month frequencies-of-detection of arsenic and selenium were excluded because arsenic was detected in every sample from five of six stations and selenium was not detected at three of six stations (table 10).

Trace-element and pesticide data for the two basins were also compared to guidelines for the protection of freshwater aquatic life (table 4). Trace-element concentrations greater than USEPA hardness-adjusted trace element CCCs only occurred for copper in four (13.8%) samples, all from Willamette River (Station 505) in the CRB. The copper concentrations and related hardness-adjusted CCCs (in parentheses) were 3.0 (1.4), 2.0 (1.8), 3.0 (1.9), and 4.0 (2.7)  $\mu\text{g/L}$ . For two other samples, the copper concentration and hardness-adjusted CCC for each were nearly the same at 2.0 and 2.03  $\mu\text{g/L}$ , respectively. Pesticide concentrations greater than or equal to the USEPA or IJC pesticide aquatic life CCCs only occurred in the RGB. These included three stations and three pesticides: Arroyo Colorado (Station 511), diazinon (0.11 and 0.105  $\mu\text{g/L}$ ) and malathion (0.84  $\mu\text{g/L}$ ); Rio Grande below Falcon Dam (Station 513), chlorpyrifos (0.061  $\mu\text{g/L}$ ); and Rio Grande at Foster Ranch (Station 515), diazinon (0.16  $\mu\text{g/L}$ ).

A cumulative relative frequency diagram was developed for copper at Station 505 over the FPR (fig. 2) to measure the degree to which fish were exposed to concentrations greater than or equal to relevant aquatic life criteria. This was the

**Table 10.** Frequencies-of-detection of selected water-quality parameters for selected NASQAN water-quality stations in the Columbia River and Rio Grande basins for the 18 months prior to the date of fish collection.

[%; percent; EPTC, s-ethyl dipropylthiocarbamate; --, no data. Total trace elements are arsenic, chromium, copper, and zinc]

Station name	18-month frequency-of-detection (%)							
	Arsenic	Chromium	Copper	Selenium	Total trace elements	Zinc	Atrazine	EPTC
<b>Columbia River Basin</b>								
Columbia River at Northport, Washington	4.76	28.6	61.9	0.00	47.6	100.0	14.3	0.00
Columbia River at Vernita Bridge near Priest Rapids Dam, Washington	7.14	21.4	64.3	0.00	44.6	85.7	28.6	21.4
Snake River at Burbank, Washington	95.7	29.2	39.1	0.00	43.0	21.7	95.7	65.2
Columbia River at Warrendale, Washington	75.0	43.8	87.5	0.00	67.2	56.2	93.8	50.0
Willamette River at Portland, Oregon	0.00	5.56	50.0	0.00	36.1	88.9	100.0	35.3
Columbia River at Beaver Army Terminal near Quincy, Oregon	50.0	38.9	72.2	0.00	57.7	55.6	94.4	38.9
<b>Rio Grande Basin</b>								
Rio Grande at El Paso, Texas	100.0	76.9	83.3	0.00	88.7	92.9	75.0	--
Rio Grande at Foster Ranch near Langtry, Texas	94.4	72.2	66.7	61.1	73.2	61.1	27.8	--
Rio Grande below Amistad Dam, near Del Rio, Texas	100.0	90.0	70.0	0.00	82.5	70.0	70.0	--
Rio Grande below Falcon Dam, Texas	100.0	25.0	75.0	12.5	75.0	100.0	75.0	--
Arroyo Colorado at Harlingen, Texas	100.0	90.9	100.0	94.7	98.4	100.0	100.0	--
Rio Grande near Brownsville, Texas	100.0	64.3	92.9	0.00	87.5	92.9	100.0	--

only station at which trace-element or pesticide concentrations met or exceeded the respective CCC in more than two samples. The cumulative relative frequency of copper concentrations greater than or equal to the copper CCC was about 25 percent (fig. 2).

The final water components used in the correlation analyses were minimum, median, and maximum estimates of total trace-element toxicity (toxic units; Wildhaber and Schmitt, 1996) for the 18 months prior to the date of fish collection (table 12). Toxic units data for all stations in both basins were used.

## Fish Data Refinements

Use of the fish-contaminant data and health-assessment indicators was restricted in this study to subsets of data. As a first restriction, only data for male carp in the CRB and male and female carp in the RGB were used. In the CRB, male carp were collected at the most (four of six) stations. All other species and female carp were collected at three or fewer stations, which was insufficient for the analyses. For male carp in the CRB, data were also insufficient to further divide by gonadal stage and age, so the correlation analyses were conducted using all stages and ages combined. In the RGB, carp was the only species collected at all six stations. Male carp of stage-3 (all ages) and stage-3, age-2 were included in the analyses. Data for female carp were similarly restricted to stage-2. No

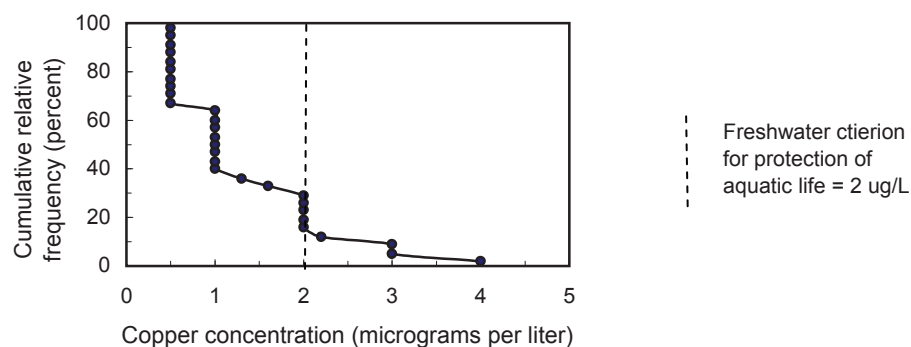
**Table 11.** Time-weighted geometric mean concentrations of water-quality parameters of interest for selected NASQAN water-quality stations in the Rio Grande basin for the 18 months prior to the date of fish collection.

[ug/L, micrograms per liter; --, no data. Dates in parentheses after station name refer to the 18-month time-period prior to the data of fish collection. Total trace elements are arsenic, chromium, copper, and zinc]

Water-quality parameter	Number of samples	Number of less-than values	Geometric Mean <sup>1</sup> (µg/L)	Geometric Mean <sup>2</sup> (µg/L)
<b>Rio Grande at El Paso, Texas (4/29/1996-10/28/1997)</b>				
Atrazine	16	4	0.003	0.002
Arsenic	14	0	3.02	--
Copper	13	2	1.67	1.53
Total trace elements	53	6	10.0	9.48
Zinc	14	1	2.99	2.86
<b>Rio Grande at Foster Ranch near Langtry, Texas (5/7/1996-11/6/1997)</b>				
Arsenic	18	0	2.06	--
Copper	18	6	1.44	1.04
Total trace elements	71	18	7.23	6.49
Zinc	18	7	1.84	1.44
<b>Rio Grande below Amistad Dam, near Del Rio, Texas (5/5/1996-11/4/1997)</b>				
Atrazine	10	3	0.002	0.002
Arsenic	11	0	2.57	--
Copper	11	3	1.16	0.925
Total trace elements	44	7	7.32	6.89
Zinc	11	3	2.12	1.67
<b>Rio Grande below Falcon Dam, Texas (5/19/1996-11/18/1997)</b>				
Atrazine	8	2	0.004	0.004
Arsenic	8	0	2.82	--
Copper	8	2	1.16	1.02
Total trace elements	32	8	9.01	8.49
Zinc	8	0	3.39	--
<b>Arroyo Colorado at Harlingen, Texas (3/31/1996-9/30/1997)</b>				
Atrazine	19	0	0.336	--
Arsenic	19	0	6.46	--
Copper	15	0	4.42	--
Total trace elements	63	1	20.76	18.47
Zinc	18	0	6.80	--
<b>Rio Grande near Brownsville, Texas (4/29/1996-10/28/1997)</b>				
Atrazine	14	0	0.012	--
Arsenic	14	0	4.38	--
Copper	14	1	1.55	1.38
Total trace elements	56	7	9.94	9.56
Zinc	14	1	2.28	2.02

<sup>1</sup>Minimum reporting level substituted for less-than concentrations. No substitution needed for arsenic.

<sup>2</sup>One-half the minimum reporting level substituted for less-than concentrations. No substitution needed for arsenic.



**Figure 2.** Cumulative relative frequency of copper concentrations above U.S. Environmental Protection Agency freshwater criterion continuous concentration for protection of aquatic life, Willamette River at Portland, Columbia River basin, September 1995-October 1997 (U.S. Environmental Protection Agency, 1999).

other stages or ages of male or female carp were present at all six stations.

Elemental contaminant data for fish were first restricted to the elements of interest for water: arsenic, chromium, copper, selenium, and zinc. Correlation analyses were performed using dry-weight concentrations of arsenic, chromium, copper, and zinc in male carp in the CRB, and chromium, copper, and zinc in male and female carp in the RGB. Correlation analyses using concentrations of total organochlorine pesticides in fish also were limited to male carp in the CRB and male and female carp in the RGB. Analyses using total DDT concentrations were limited to female carp in the RGB because most of the total organochlorine pesticides in male carp were total DDT. Total PCBs were detected only in fish from the CRB. In the correlation analyses, both zero and one-half the reporting level were substituted for censored values of trace elements and organic contaminants in fish.

The fish health-assessment indicators examined in this study included both observations and measurements (table 2). Two observation indicators (external lesions and fin anomalies) were selected as examples for evaluation. Both were included in analyses for the CRB whereas only fin anomalies were included for the RGB. For each observation indicator, species-station mean values were used for correlation analyses because most median values were zero. Some observation indicators not selected also could have been studied in the same manner; others had mean values of zero for many stations and were therefore eliminated from consideration. Median values of the fish-health measurement indicators were used in the correlation analyses.

For the CRB, correlation analyses were conducted using the fish-health observation and measurement indicators for male carp (all stages and ages combined). For the RGB, correlation analyses using the observation indicators were performed for male carp with all stages and ages combined whereas analyses using the measurement indicators were performed separately for male and female carp and were further separated by stage for both genders and also by age for males.

The observation indicators for male carp by stage and age and for female carp in the RGB also could have been summarized in the same manner as the male carp with all stages and ages combined.

In general we did not compare data among stations in the CRB or RGB or compare the two basins; such comparisons are presented elsewhere (Schmitt and others, 2004; Hinck and others, 2004) and are beyond the scope of this investigation. The exception is stable isotope data, which are compared among sites and basins.

## Results

Only a small number of stations in each basin (four in CRB, five to six in RGB) met the requirements for data integration; the test data sets contained too few observations for in-depth analysis and the power of the statistical test was low. The results of the analyses reported here are therefore for illustration purposes to show how a larger data set from the two programs could be combined and interpreted in larger studies.

As noted in the "Integration of Water-Quality and Fish Data" section, Kendall's tau is based on the ranks of data rather than actual values. For this study, the ranking of most water-quality and fish data did not change when different substitution values were used for less-than concentrations, and there was no effect on Kendall's tau. Ranked values did change when different substitution values were used for less-than concentrations in the calculation of the total trace-element geometric mean concentrations in water and total organochlorine concentrations in female carp in the RGB. Substitution values are included in the discussion of correlation results for these two parameters.

Arsenic, chromium, copper, and zinc concentrations in male carp from the CRB were not significantly cor-

**Table 12.** Minimum, median, and maximum estimates of total trace-element toxicity for selected NASQAN water-quality stations in the Columbia River and Rio Grande basins for the 18 months prior to the date of fish collection.

[ug/L, micrograms per liter. Total trace element is arsenic, chromium, copper, selenium, and zinc]

Station name	Total trace-element toxicity estimate (µg/L)		
	Minimum	Median	Maximum
<b>Columbia River Basin</b>			
Columbia River at Northport, Washington	0.493	0.577	0.749
Columbia River at Vernita Bridge near Priest Rapids Dam, Washington	0.498	0.546	0.896
Snake River at Burbank, Washington	0.447	0.584	0.983
Columbia River at Warrendale, Washington	0.475	0.588	1.04
Willamette River at Portland, Oregon	0.717	0.789	2.23
Columbia River at Beaver Army Terminal near Quincy, Oregon	0.497	0.610	0.905
<b>Rio Grande Basin</b>			
Rio Grande at El Paso, Texas	0.250	0.490	0.614
Rio Grande at Foster Ranch near Langtry, Texas	0.365	0.479	0.690
Rio Grande below Amistad Dam, near Del Rio, Texas	0.377	0.442	0.613
Rio Grande below Falcon Dam, Texas	0.388	0.406	0.494
Arroyo Colorado at Harlingen, Texas	0.352	0.709	1.05
Rio Grande near Brownsville, Texas	0.374	0.440	0.576

related ( $p \geq 0.05$ ) with frequencies of detection of these elements in water for the 18 months prior to the date of fish collection (table 13). Similarly, chromium, copper, and zinc concentrations in male and female carp from the RGB were also not significantly correlated ( $p \geq 0.05$ ) with the 18-month detection frequencies of these elements in water (table 13). Similar to previously reported findings (Hinck and others, 2004), correlations between concentrations of total organochlorine pesticides and total PCBs in fish with fish-health observation indicators (external lesions and fin anomalies) in CRB male carp were not statistically significant ( $p \geq 0.05$ ) (table 14). Most of the remaining correlations between water-quality data and external lesions and fin anomalies were also not statistically significant ( $p \geq 0.05$ ) (table 14). However, in the CRB significant positive correlations ( $p \leq 0.05$ ) were detected between atrazine in water (time-weighted 90th percentile concentration) and external lesions and between zinc in water (time-weighted 90th percentile concentration and 18-month frequency of detection) and fin anomalies (table 14). A value of 1.00 for Kendall's tau in the atrazine relation (table 14) indicates that successive samples of both variables increased consistently and did not oscillate. An

equally significant negative correlation (Kendall's tau = -1.0,  $p \leq 0.05$ ) was detected between the 18-month frequency of detection for atrazine and fin anomalies in the CRB (table 14). This result is opposite of our expectation, which was increasing fin anomalies with atrazine detections, and may be a result of small sample size; with few samples, the chance of spurious correlations increases because statistical power is low.

In the RGB, concentrations of total organochlorine pesticides in fish and fin anomalies were not significantly correlated ( $p \geq 0.05$ ) for male carp (table 14). Correlations also were not significant ( $p \geq 0.05$ ) between four categories of water-quality data (time-weighted geometric mean and percentile concentrations, last-sample concentrations, and detection frequencies in water) and fin anomalies for male carp.

Results of the Kendall's tau correlation analyses between fish-contaminant and water-quality data and fish-health measurement indicators are shown in table 15. Use of the indicator GSI, which is related to gonadal stage, was restricted to stage-3, age-2 male carp in the RGB because this was the only category for male or female carp with sufficient data to summarize by stage. In the CRB, statistically significant correlations ( $p \leq 0.05$ ) between fish-contaminant and



**Table 13.** Kendall's tau correlation matrix of frequencies-of-detection of trace elements in water for the 18 months prior to the date of fish collection and trace-element concentrations in carp at selected NASQAN and BEST stations in the Columbia River and Rio Grande basins.

[*p*, *p*-value; --, no data. Significance level of correlation test was  $p \leq 0.05$ . Number of stations: Columbia River basin, 4; Rio Grande basin, 6]

Water-quality parameter	Arsenic in carp tau ( $\rho$ )	Chromium in carp tau ( $\rho$ )	Copper in carp tau ( $\rho$ )	Zinc in carp tau ( $\rho$ )
<b>Columbia River Basin</b>				
<b>Male</b>				
Arsenic, 18-month frequency-of-detection	0.33 (0.50)	--	--	--
Chromium, 18-month frequency-of-detection	--	-0.33 (0.50)	--	--
Copper, 18-month frequency-of-detection	--	--	-0.33 (0.50)	--
Zinc, 18-month frequency-of-detection	--	--	--	0.33 (0.50)
<b>Rio Grande Basin</b>				
<b>Male</b>				
Chromium, 18-month frequency-of-detection	--	-0.07 (0.85)	--	--
Copper, 18-month frequency-of-detection	--	--	-0.33 (0.35)	--
Zinc, 18-month frequency-of-detection	--	--	--	-0.20 (0.56)
<b>Female</b>				
Chromium, 18-month frequency-of-detection	--	-0.20 (0.57)	--	--
Copper, 18-month frequency-of-detection	--	--	-0.47 (0.19)	--
Zinc, 18-month frequency-of-detection	--	--	--	0.07 (0.85)

water-quality data and fish-health measurement indicators in male carp (all stages and ages) were detected between a few parameters and the splenosomatic index (SSI) and condition factor (CF) (table 15). Statistically significant negative correlations ( $p \leq 0.05$ ) occurred between the concentration of total PCBs and SSI and CF in male carp. SSI and CF were positively correlated ( $p \leq 0.05$ ) with the time-weighted 90th percentile concentration of total trace elements and maximum estimate of total trace-element toxicity in water. The maximum total toxicity estimates probably overestimate exposure of fish to water-borne contaminants, as do the time-weighted 90th percentile concentrations. The SSI can vary depending on a number of factors, including species, gender, age, gonad development, nonspecific stressors, and water quality. Acute, nonspecific stressors and chronic exposure to a number of chemical contaminants can decrease SSI whereas infection can cause spleen enlargement, which increases SSI (Schmitt and Dethloff, 2000). Condition factor varies directly with nutrition but can also increase or decrease in response to chemical exposure (Schmitt and Dethloff, 2000). Because SSI and CF are non-specific indicators and can increase or decrease as a result of contaminant exposure, they are typically used together with other data in a weight-of-evidence assessment (for example, Schmitt and others, 2004).

Statistically significant negative correlations ( $p \leq 0.05$ ) also occurred between the 18-month detection frequencies of

copper and total trace elements in water and the percent of tissue occupied by macrophage aggregates in CRB carp (table 15). Macrophage aggregates, which occur in the spleen, kidney, and liver, are immune system biomarkers (Schmitt and Dethloff, 2000). Macrophage aggregate numbers have generally been reported to increase with exposure to contaminants, whereas only a few studies have reported decreasing numbers or no significant contaminant effect. The negative relation between the 18-month detection frequencies of copper and total trace elements with percent of tissue occupied by macrophage aggregates is therefore counter-intuitive; further study would be required to determine if exposure to copper or other trace elements can reduce aggregate density.

For male carp in the RGB, a statistically significant positive correlation ( $p \leq 0.05$ ) was documented between the last-sample concentration of arsenic and ethoxyresorufin *O*-deethylase (EROD) activity (table 15). EROD activity can be influenced by water temperature, gonadal stage, age, and a variety of chemicals and chemical mixtures including organic, organometallic, and metallic compounds (Whyte and others, 2000). EROD activity tends to increase following exposure to certain planar hydrocarbons (Schmitt and Dethloff, 2000; Whyte and others, 2000). For correlations between 18-month time-weighted geometric mean concentrations of total trace elements in water and all fish-health measurement indicators for male carp, Kendall's tau differed when

**Table 14.** Kendall's tau correlation matrix of fish-contaminant and water-quality parameters of interest and mean fish-health observation indicators for male carp at selected NASQAN and BEST stations in the Columbia River and Rio Grande basins.

[EL, external lesions; FINS, fin anomalies;  $p$ ,  $p$ -value; PCBs, polychlorinated biphenyls; --, no data; EPTC, *s*-ethyl dipropylthiocarbamate. All concentrations in water are time-weighted concentrations. Correlations that are significant at  $p \leq 0.05$  are shown in **bold**. Total trace elements for 18-month geometric mean concentrations in water are arsenic, chromium, copper, and zinc. Total trace elements for 18-month frequencies-of-detection in water are arsenic, chromium, copper, selenium, and zinc. Number of stations: Columbia River basin, 4; Rio Grande basin, 6]

Fish-contaminant and water-quality parameters	Mean fish-health observation indicator		
	Columbia River Basin		Rio Grande Basin
	EL tau ( $p$ )	FINS tau ( $p$ )	FINS tau ( $p$ )
Total organochlorine pesticides concentration in fish	-0.33 (0.50)	0.00 (1.00)	0.27 (0.44)
Total PCBs concentration in fish	0.00 (1.00)	0.33 (0.50)	--
Arsenic, 90th percentile concentration in water	0.50 (0.28)	-0.83 (0.07)	--
Arsenic, 18-month geometric mean concentration in water	--	--	0.27 (0.44)
Arsenic, concentration of last sample in water before fish collection	--	--	0.20 (0.55)
Arsenic, 18-month frequency-of-detection in water	0.33 (0.50)	-0.67 (0.17)	--
Atrazine, 90th percentile concentration in water	<b>1.00 (0.04)</b>	-0.67 (0.17)	--
Atrazine, 18-month frequency-of-detection in water	0.67 (0.17)	<b>-1.00 (0.04)</b>	0.13 (0.69)
Chromium, 18-month frequency-of-detection in water	0.33 (0.50)	0.00 (1.00)	0.13 (0.70)
Copper, 90th percentile concentration in water	0.33 (0.50)	-0.67 (0.17)	--
Copper, 18-month geometric mean concentration in water <sup>1</sup>	--	--	0.53 (0.13)
Copper, 18-month frequency-of-detection in water	0.00 (1.00)	0.33 (0.50)	0.27 (0.44)
EPTC, 18-month frequency-of-detection in water	0.33 (0.50)	-0.67 (0.17)	--
Specific conductance, 90th percentile concentration in water	0.33 (0.50)	-0.67 (0.17)	--
Specific conductance, concentration of last sample in water before fish collection	0.33 (0.50)	-0.67 (0.17)	-0.13 (0.70)
Total trace elements, 90th percentile concentration in water	0.00 (1.00)	-0.33 (0.50)	--
Total trace elements, 18-month geometric mean concentration in water <sup>1</sup>	--	--	0.27 (0.44)
Total trace-elements, 18-month frequency-of-detection in water	0.00 (1.00)	0.33 (0.50)	0.13 (0.70)
Total trace-element toxicity estimate for water, minimum	-0.33 (0.50)	0.67 (0.17)	-0.40 (0.25)
Total trace-element toxicity estimate for water, median	0.67 (0.17)	-0.33 (0.50)	0.40 (0.25)
Total trace-element toxicity estimate for water, maximum	0.00 (1.00)	-0.33 (0.50)	0.53 (0.13)
Zinc, 90th percentile concentration in water	-0.67 (0.17)	<b>1.00 (0.04)</b>	--
Zinc, 18-month geometric mean concentration in water <sup>1</sup>	--	--	0.00 (1.00)
Zinc, concentration of last sample in water before fish collection	--	--	-0.07 (0.85)
Zinc, 18-month frequency-of-detection in water	-0.67 (0.17)	<b>1.00 (0.04)</b>	-0.07 (0.85)

<sup>1</sup>Minimum reporting level substituted for less-than concentrations.

**Table 15.** Kendall's tau correlation matrix of fish-contaminant and water-quality parameters of interest and median fish-health measurement indicators for male and female carp at selected NASQAN and BEST stations in the Columbia River and Rio Grande basins.

[EROD, ethoxyresorfin-O-deethylase; MA, macrophage aggregate; % Tis, percent of tissue occupied by macrophage aggregates; GSI, gonadosomatic index; SSI, splenosomatic index; CF, condition factor; HAI, health-assessment index; *p*, *p*-value; --, no data; PCBs, polychlorinated biphenyls; EPTC, *s*-ethyl dipropylthiocarbamate. All concentrations in water are time-weighted concentrations. Correlations that are significant at *p*≤0.05 are shown in **bold**. Total trace elements are arsenic, chromium, copper, and zinc. Number of stations: Columbia River basin, 4; Rio Grande basin, 6, except for 5 stations for SSI and male carp (all stages and ages) and geometric mean concentrations for male carp (stage 3, age 2)]

	Median fish-health measurement indicator										
	Fish-contaminant and water-quality parameters		EROD	MA	% Tis	GSI'	SSI	CF	HAI		
	tau (ρ)	tau (ρ)	tau (ρ)	tau (ρ)	tau (ρ)	tau (ρ)	tau (ρ)	tau (ρ)	tau (ρ)	tau (ρ)	
<b>Columbia River Basin</b>											
<b>Male carp, all stages and ages</b>											
Total organochlorine pesticides concentration in fish	--	0.50 (0.28)	0.67 (0.17)	--	-0.67 (0.17)	-0.67 (0.17)	-0.67 (0.17)	-0.17 (0.72)	-0.17 (0.72)		
Total PCBs concentration in fish	--	0.17 (0.72)	0.33 (0.50)	--	<b>-1.00 (0.04)</b>	<b>-1.00 (0.04)</b>	<b>-1.00 (0.04)</b>	-0.50 (0.28)	-0.50 (0.28)		
Arsenic, 90th percentile concentration in water	--	0.00 (1.00)	0.17 (0.72)	--	0.50 (0.28)	0.50 (0.28)	0.50 (0.28)	0.00 (1.00)	0.00 (1.00)		
Arsenic, 18-month frequency-of-detection in water	--	0.17 (0.72)	0.00 (1.00)	--	0.67 (0.17)	0.67 (0.17)	0.67 (0.17)	0.17 (0.72)	0.17 (0.72)		
Atrazine, 90th percentile concentration in water	--	-0.50 (0.28)	0.00 (1.00)	--	0.00 (1.00)	0.00 (1.00)	0.00 (1.00)	-0.50 (0.28)	-0.50 (0.28)		
Atrazine, 18-month frequency-of-detection in water	--	-0.17 (0.72)	0.33 (0.50)	--	0.33 (0.50)	0.33 (0.50)	0.33 (0.50)	-0.17 (0.72)	-0.17 (0.72)		
Chromium, 18-month frequency-of-detection in water	--	-0.50 (0.28)	-0.67 (0.17)	--	0.67 (0.17)	0.67 (0.17)	0.67 (0.17)	0.17 (0.72)	0.17 (0.72)		
Copper, 90th percentile concentration in water	--	0.17 (0.72)	0.67 (0.17)	--	0.00 (1.00)	0.00 (1.00)	0.00 (1.00)	-0.50 (0.28)	-0.50 (0.28)		
Copper, 18-month frequency-of-detection in water	--	-0.50 (0.28)	<b>-1.00 (0.04)</b>	--	0.33 (0.50)	0.33 (0.50)	0.33 (0.50)	0.17 (0.72)	0.17 (0.72)		
EPTC, 18-month frequency-of-detection in water	--	0.17 (0.72)	0.00 (1.00)	--	0.67 (0.17)	0.67 (0.17)	0.67 (0.17)	0.17 (0.72)	0.17 (0.72)		
Specific conductance, 90th percentile concentration in water	--	0.17 (0.72)	0.00 (1.00)	--	0.67 (0.17)	0.67 (0.17)	0.67 (0.17)	0.17 (0.72)	0.17 (0.72)		
Specific conductance, concentration of last sample in water before fish collection	--	0.17 (0.72)	0.00 (1.00)	--	0.67 (0.17)	0.67 (0.17)	0.67 (0.17)	0.17 (0.72)	0.17 (0.72)		
Total trace elements, 90th percentile concentration in water	--	-0.17 (0.72)	-0.33 (0.50)	--	<b>1.00 (0.04)</b>	<b>1.00 (0.04)</b>	<b>1.00 (0.04)</b>	0.50 (0.28)	0.50 (0.28)		
Total trace-elements, 18-month frequency-of-detection in water	--	-0.50 (0.28)	<b>-1.00 (0.04)</b>	--	0.33 (0.50)	0.33 (0.50)	0.33 (0.50)	0.17 (0.72)	0.17 (0.72)		
Total trace-element toxicity estimate for water, minimum	--	-0.17 (0.72)	0.00 (1.00)	--	-0.67 (0.17)	-0.67 (0.17)	-0.67 (0.17)	-0.17 (0.72)	-0.17 (0.72)		
Total trace-element toxicity estimate for water, median	--	-0.83 (0.07)	-0.33 (0.50)	--	0.33 (0.50)	0.33 (0.50)	0.33 (0.50)	-0.17 (0.72)	-0.17 (0.72)		
Total trace-element toxicity estimate for water, maximum	--	-0.17 (0.72)	-0.33 (0.50)	--	<b>1.00 (0.04)</b>	<b>1.00 (0.04)</b>	<b>1.00 (0.04)</b>	0.50 (0.28)	0.50 (0.28)		
Zinc, 90th percentile concentration in water	--	0.17 (0.72)	-0.33 (0.50)	--	-0.33 (0.50)	-0.33 (0.50)	-0.33 (0.50)	0.17 (0.72)	0.17 (0.72)		
Zinc, 18-month frequency-of-detection in water	--	0.17 (0.72)	-0.33 (0.50)	--	-0.33 (0.50)	-0.33 (0.50)	-0.33 (0.50)	0.17 (0.72)	0.17 (0.72)		

**Table 15.** Kendall's tau correlation matrix of fish-contaminant and water-quality parameters of interest and median fish-health measurement indicators for male and female carp at selected NASQAN and BEST stations in the Columbia River and Rio Grande basins.—Continued

[EROD, ethoxyresorfin-*O*-deethylase; MA, macrophage aggregate; % Tis, percent of tissue occupied by macrophage aggregates; GSI, gonadosomatic index; SSI, splenosomatic index; CF, condition factor; HAI, health-assessment index; *p*, *p*-value; --, no data; PCBs, polychlorinated biphenyls; EPTC, *s*-ethyl dipropylthiocarbamate. All concentrations in water are time-weighted concentrations. Correlations that are significant at  $p \leq 0.05$  are shown in **bold**. Total trace elements are arsenic, chromium, copper, and zinc. Number of stations: Columbia River basin, 4; Rio Grande basin, 6, except for 5 stations for SSI and male carp (all stages and ages) and geometric mean concentrations for male carp (stage 3, age 2)]

	Median fish-health measurement indicator							
	EROD tau ( <i>p</i> )	MA tau ( <i>p</i> )	% Tis tau ( <i>p</i> )	GSI <sup>1</sup> tau ( <i>p</i> )	SSI tau ( <i>p</i> )	CF tau ( <i>p</i> )	HAI tau ( <i>p</i> )	
<b>Rio Grande Basin</b>								
<b>Male carp, all stages and ages</b>								
Total organochlorine pesticides concentration in fish	0.33 (0.35)	-0.20 (0.57)	-0.20 (0.57)	--	0.07 (0.85)	-0.07 (0.85)	0.13 (0.70)	
Arsenic, 18-month geometric mean concentration in water	0.40 (0.25)	0.20 (0.57)	0.20 (0.57)	--	0.00 (1.00)	-0.47 (0.19)	0.13 (0.70)	
Arsenic, concentration of last sample in water before fish collection	<b>0.87 (0.01)</b>	0.07 (0.85)	0.07 (0.85)	--	0.07 (0.85)	-0.47 (0.17)	0.00 (1.00)	
Atrazine, 18-month frequency-of-detection in water	0.40 (0.23)	0.20 (0.56)	0.20 (0.56)	--	0.00 (1.00)	-0.47 (0.17)	0.13 (0.69)	
Chromium, 18-month frequency-of-detection in water	0.13 (0.70)	-0.33 (0.35)	-0.33 (0.35)	--	-0.20 (0.62)	-0.20 (0.57)	-0.13 (0.70)	
Copper, 18-month geometric mean concentration in water <sup>2</sup>	0.27 (0.44)	0.33 (0.35)	0.33 (0.35)	--	0.00 (1.00)	-0.60 (0.09)	0.27 (0.44)	
Copper, 18-month frequency-of-detection in water	0.40 (0.25)	0.20 (0.57)	0.20 (0.57)	--	0.00 (1.00)	-0.47 (0.19)	0.13 (0.70)	
Specific conductance, concentration of last sample in water before fish collection	0.20 (0.57)	-0.60 (0.09)	-0.60 (0.09)	--	-0.07 (0.85)	0.33 (0.35)	0.00 (1.00)	
Total trace elements, 18-month geometric mean concentration in water <sup>2</sup>	0.53 (0.13)	0.07 (0.85)	0.07 (0.85)	--	0.20 (0.62)	-0.33 (0.35)	0.00 (1.00)	
Total trace elements, 18-month geometric mean concentration, in water <sup>3</sup>	0.40 (0.25)	0.20 (0.57)	0.20 (0.57)	--	0.00 (1.00)	-0.47 (0.19)	0.13 (0.70)	
Total trace-elements, 18-month frequency-of-detection in water	0.67 (0.06)	-0.07 (0.85)	-0.07 (0.85)	--	0.20 (0.62)	-0.47 (0.19)	-0.13 (0.70)	
Total trace-element toxicity estimate for water, minimum	-0.40 (0.25)	-0.20 (0.57)	-0.20 (0.57)	--	0.00 (1.00)	0.47 (0.19)	-0.13 (0.70)	
Total trace-element toxicity estimate for water, median	0.13 (0.70)	-0.07 (0.85)	-0.07 (0.85)	--	-0.20 (0.62)	-0.47 (0.19)	0.13 (0.70)	
Total trace-element toxicity estimate for water, maximum	0.00 (1.00)	0.07 (0.85)	0.07 (0.85)	--	-0.40 (0.33)	-0.33 (0.35)	0.27 (0.44)	
Zinc, 18-month geometric mean concentration in water <sup>2</sup>	0.27 (0.44)	-0.20 (0.57)	-0.20 (0.57)	--	0.20 (0.62)	-0.07 (0.85)	0.13 (0.70)	
Zinc, 18-month frequency-of-detection in water	0.13 (0.69)	-0.20 (0.56)	-0.20 (0.56)	--	0.20 (0.60)	-0.07 (0.85)	0.13 (0.69)	
<b>Male carp, stage 3</b>								
Arsenic, 18-month geometric mean concentration in water	<b>0.73 (0.04)</b>	0.33 (0.35)	0.47 (0.19)	--	0.07 (0.85)	-0.60 (0.09)	0.20 (0.56)	
Arsenic, concentration of last sample in water before fish collection	<b>0.87 (0.01)</b>	0.20 (0.56)	0.33 (0.33)	--	0.20 (0.56)	-0.60 (0.08)	0.07 (0.84)	
Atrazine, 18-month frequency-of-detection in water	0.60 (0.08)	0.33 (0.33)	0.47 (0.17)	--	-0.07 (0.85)	-0.47 (0.17)	0.20 (0.55)	
Chromium, 18-month frequency-of-detection in water	0.47 (0.19)	-0.20 (0.57)	-0.07 (0.85)	--	0.07 (0.85)	-0.33 (0.35)	-0.07 (0.85)	

**Table 15.** Kendall's tau correlation matrix of fish-contaminant and water-quality parameters of interest and median fish-health measurement indicators for male and female carp at selected NASOAN and BEST stations in the Columbia River and Rio Grande basins.—Continued

[EROD, ethoxyresorfin-*O*-deethylase; MA, macrophage aggregate; % Tis, percent of tissue occupied by macrophage aggregates; GSI, gonadosomatic index; SSI, splenosomatic index; CF, condition factor; HAI, health-assessment index; *p*, *p*-value; --, no data; PCBs, polychlorinated biphenyls; EPTC, *s*-ethyl dipropylthiocarbamate. All concentrations in water are time-weighted concentrations. Correlations that are significant at  $p \leq 0.05$  are shown in **bold**. Total trace elements are arsenic, chromium, copper, and zinc. Number of stations: Columbia River basin, 4; Rio Grande basin, 6, except for 5 stations for SSI and male carp (all stages and ages) and geometric mean concentrations for male carp (stage 3, age 2)]

	Median fish-health measurement indicator						
	EROD tau ( <i>p</i> )	MA tau ( <i>p</i> )	% Tis tau ( <i>p</i> )	GSI <sup>1</sup> tau ( <i>p</i> )	SSI tau ( <i>p</i> )	CF tau ( <i>p</i> )	HAI tau ( <i>p</i> )
Copper, 18-month geometric mean concentration in water <sup>2</sup>	0.60 (0.09)	0.47 (0.19)	0.60 (0.09)	--	-0.07 (0.85)	<b>-0.73 (0.04)</b>	0.33 (0.33)
Copper, 18-month frequency-of-detection in water	<b>0.73 (0.04)</b>	0.33 (0.35)	0.47 (0.19)	--	0.07 (0.85)	-0.60 (0.09)	0.20 (0.56)
Specific conductance, concentration of last sample in water before fish collection	0.20 (0.57)	-0.47 (0.19)	-0.33 (0.35)	--	0.07 (0.85)	0.20 (0.57)	0.07 (0.84)
Total trace elements, 18-month geometric mean concentration in water <sup>2</sup>	<b>0.87 (0.01)</b>	0.20 (0.57)	0.33 (0.35)	--	0.20 (0.57)	-0.47 (0.19)	0.07 (0.85)
Total trace elements, 18-month geometric mean concentration, in water <sup>3</sup>	<b>0.73 (0.04)</b>	0.33 (0.35)	0.47 (0.19)	--	-0.60 (0.09)	0.07 (0.85)	0.20 (0.56)
Total trace-elements, 18-month frequency-of-detection in water	<b>1.00 (&lt;0.01)</b>	0.07 (0.85)	0.20 (0.57)	--	0.33 (0.35)	-0.60 (0.09)	-0.07 (0.85)
Total trace-element toxicity estimate for water, minimum	-0.47 (0.19)	-0.07 (0.85)	-0.20 (0.57)	--	-0.07 (0.85)	0.60 (0.09)	-0.20 (0.56)
Total trace-element toxicity estimate for water, median	0.47 (0.19)	0.07 (0.85)	0.20 (0.57)	--	0.07 (0.85)	-0.60 (0.09)	0.20 (0.56)
Total trace-element toxicity estimate for water, maximum	0.33 (0.35)	0.20 (0.57)	0.33 (0.35)	--	-0.07 (0.85)	-0.47 (0.19)	0.33 (0.33)
Zinc, 18-month geometric mean concentration in water <sup>2</sup>	0.60 (0.09)	-0.07 (0.85)	0.07 (0.85)	--	0.20 (0.57)	-0.20 (0.57)	0.20 (0.56)
Zinc, 18-month frequency-of-detection in water	0.47 (0.17)	-0.07 (0.85)	0.07 (0.85)	--	0.20 (0.56)	-0.20 (0.56)	0.20 (0.55)
<b>Male carp, stage 3, age 2</b>							
Arsenic, 18-month geometric mean concentration in water	0.60 (0.14)	0.00 (1.00)	0.40 (0.33)	-0.20 (0.62)	0.20 (0.62)	-0.20 (0.62)	0.50 (0.21)
Arsenic, concentration of last sample in water before fish collection	<b>0.80 (0.04)</b>	0.00 (1.00)	0.40 (0.30)	0.00 (1.00)	0.40 (0.30)	0.00 (1.00)	0.40 (0.29)
Atrazine, 18-month frequency-of-detection in water	0.50 (0.21)	-0.10 (0.80)	0.30 (0.45)	-0.10 (0.80)	0.10 (0.80)	-0.10 (0.80)	0.60 (0.12)
Chromium, 18-month frequency-of-detection in water	0.20 (0.62)	0.00 (1.00)	0.00 (1.00)	0.20 (0.62)	0.20 (0.62)	0.20 (0.62)	-0.50 (0.21)
Copper, 18-month geometric mean concentration in water <sup>2</sup>	0.40 (0.33)	0.20 (0.62)	0.60 (0.14)	-0.40 (0.33)	0.00 (1.00)	-0.40 (0.33)	0.10 (0.80)
Copper, 18-month frequency-of-detection in water	0.60 (0.14)	0.00 (1.00)	0.40 (0.33)	-0.20 (0.62)	0.20 (0.62)	-0.20 (0.62)	0.50 (0.21)
Specific conductance, concentration of last sample in water before fish collection	-0.20 (0.62)	-0.40 (0.33)	<b>-0.80 (0.05)</b>	0.60 (0.14)	0.20 (0.62)	0.60 (0.14)	-0.10 (0.80)
Total trace elements, 18-month geometric mean concentration in water <sup>2</sup>	<b>0.80 (0.05)</b>	-0.20 (0.62)	0.20 (0.62)	0.00 (1.00)	0.40 (0.33)	0.00 (1.00)	0.50 (0.21)
Total trace elements, 18-month geometric mean concentration, in water <sup>3</sup>	0.60 (0.14)	0.00 (1.00)	0.40 (0.33)	-0.20 (0.62)	0.20 (0.62)	-0.20 (0.62)	0.50 (0.21)
Total trace-elements, 18-month frequency-of-detection in water	<b>1.00 (0.01)</b>	0.00 (1.00)	0.40 (0.33)	0.20 (0.62)	0.60 (0.14)	0.20 (0.62)	0.30 (0.45)

**Table 15.** Kendall's tau correlation matrix of fish-contaminant and water-quality parameters of interest and median fish-health measurement indicators for male and female carp at selected NASQAN and BEST stations in the Columbia River and Rio Grande basins.—Continued

	Median fish-health measurement indicator							
	EROD tau (p)	MA tau (p)	% Tis tau (p)	GSI' tau (p)	SSI tau (p)	CF tau (p)	HAI tau (p)	
Total trace-element toxicity estimate for water, minimum	-0.40 (0.33)	-0.60 (0.14)	-0.60 (0.14)	0.40 (0.33)	0.00 (1.00)	0.40 (0.33)	0.30 (0.45)	
Total trace-element toxicity estimate for water, median	0.20 (0.62)	0.40 (0.33)	0.40 (0.33)	-0.20 (0.62)	0.20 (0.62)	-0.20 (0.62)	-0.50 (0.21)	
Total trace-element toxicity estimate for water, maximum	0.00 (1.00)	0.60 (0.14)	0.20 (0.62)	-0.40 (0.33)	0.00 (1.00)	-0.40 (0.33)	-0.70 (0.08)	
Zinc, 18-month geometric mean concentration in water <sup>2</sup>	0.40 (0.33)	-0.60 (0.14)	-0.20 (0.62)	0.40 (0.33)	0.40 (0.33)	0.40 (0.33)	<b>0.90 (0.02)</b>	
Zinc, 18-month frequency-of-detection in water	0.30 (0.45)	-0.50 (0.21)	-0.10 (0.80)	0.30 (0.45)	0.30 (0.45)	0.30 (0.45)	<b>0.90 (0.02)</b>	
<b>Female carp, all stages and ages</b>								
Total organochlorine pesticides concentration in fish <sup>4</sup>	0.07 (0.85)	0.07 (0.85)	0.07 (0.85)	--	-0.33 (0.35)	-0.20 (0.57)	0.20 (0.56)	
Total organochlorine pesticides concentration in fish <sup>3</sup>	-0.07 (0.85)	-0.07 (0.85)	-0.07 (0.85)	--	-0.20 (0.57)	-0.33 (0.35)	0.33 (0.33)	
Arsenic, 18-month geometric mean concentration in water	0.47 (0.19)	0.20 (0.57)	0.20 (0.57)	--	-0.47 (0.19)	-0.33 (0.35)	-0.20 (0.56)	
Arsenic, concentration of last sample in water before fish collection	0.47 (0.17)	0.20 (0.56)	0.20 (0.56)	--	-0.33 (0.33)	-0.20 (0.56)	-0.20 (0.56)	
Atrazine, 18-month frequency-of-detection in water	0.33 (0.33)	0.20 (0.56)	0.20 (0.56)	--	-0.47 (0.17)	-0.20 (0.56)	-0.20 (0.55)	
Chromium, 18-month frequency-of-detection in water	0.47 (0.19)	-0.07 (0.85)	-0.07 (0.85)	--	0.07 (0.85)	-0.07 (0.85)	-0.07 (0.85)	
Copper, 18-month geometric mean concentration in water <sup>2</sup>	0.33 (0.35)	0.33 (0.35)	0.33 (0.35)	--	-0.60 (0.09)	-0.47 (0.19)	0.20 (0.56)	
Copper, 18-month frequency-of-detection in water	0.47 (0.19)	0.20 (0.57)	0.20 (0.57)	--	-0.47 (0.19)	-0.33 (0.35)	-0.20 (0.56)	
Specific conductance, concentration of last sample in water before fish collection	0.20 (0.58)	-0.33 (0.35)	-0.33 (0.35)	--	0.07 (0.85)	0.20 (0.57)	0.20 (0.56)	
Total trace elements, 18-month geometric mean concentration in water <sup>2</sup>	0.33 (0.35)	0.07 (0.85)	0.07 (0.85)	--	-0.33 (0.35)	-0.20 (0.57)	-0.07 (0.85)	
Total trace elements, 18-month geometric mean concentration, in water <sup>3</sup>	0.47 (0.19)	0.20 (0.57)	0.20 (0.57)	--	-0.47 (0.19)	-0.33 (0.35)	-0.20 (0.56)	
Total trace-elements, 18-month frequency-of-detection in water	0.47 (0.19)	0.20 (0.57)	0.20 (0.57)	--	-0.20 (0.57)	-0.07 (0.85)	-0.20 (0.56)	
Zinc, 18-month geometric mean concentration in water <sup>2</sup>	0.07 (0.85)	-0.20 (0.57)	-0.20 (0.57)	--	-0.33 (0.35)	0.07 (0.85)	0.20 (0.56)	
Zinc, 18-month frequency-of-detection in water	0.07 (0.85)	-0.20 (0.56)	-0.20 (0.56)	--	-0.33 (0.34)	0.07 (0.85)	0.13 (0.69)	
<b>Female carp, stage 2</b>								
Arsenic, 18-month geometric mean concentration in water	0.47 (0.19)	0.20 (0.57)	0.07 (0.85)	--	-0.47 (0.19)	-0.33 (0.35)	<b>-0.73 (0.04)</b>	
Arsenic, concentration of last sample in water before fish collection	0.47 (0.17)	0.20 (0.56)	-0.07 (0.85)	--	-0.33 (0.33)	-0.20 (0.56)	<b>-0.87 (0.01)</b>	

[EROD, ethoxyresorofin-O-deethylase; MA, macrophage aggregate; % Tis, percent of tissue occupied by macrophage aggregates; GSI, gonadosomatic index; SSI, splenosomatic index; CF, condition factor; HAI, health-assessment index; p, p-value; --, no data; PCBs, polychlorinated biphenyls; EPTC, s-ethyl dipropylthiocarbamate. All concentrations in water are time-weighted concentrations. Correlations that are significant at  $p \leq 0.05$  are shown in **bold**. Total trace elements are arsenic, chromium, copper, and zinc. Number of stations: Columbia River basin, 4; Rio Grande basin, 6, except for 5 stations for SSI and male carp (all stages and ages) and geometric mean concentrations for male carp (stage 3, age 2)]

**Table 15.** Kendall's tau correlation matrix of fish-contaminant and water-quality parameters of interest and median fish-health measurement indicators for male and female carp at selected NASQAN and BEST stations in the Columbia River and Rio Grande basins.—Continued

[EROD, ethoxyresorfin-O-deethylase; MA, macrophage aggregate; % Tis, percent of tissue occupied by macrophage aggregate; GSI, gonadosomatic index; SSI, splenosomatic index; CF, condition factor; HAI, health-assessment index; *p*, *p*-value; --, no data; PCBs, polychlorinated biphenyls; EPTC, *s*-ethyl dipropylthiocarbamate. All concentrations in water are time-weighted concentrations. Correlations that are significant at  $p \leq 0.05$  are shown in **bold**. Total trace elements are arsenic, chromium, copper, and zinc. Number of stations: Columbia River basin, 4; Rio Grande basin, 6, except for 5 stations for SSI and male carp (all stages and ages) and geometric mean concentrations for male carp (stage 3, age 2)]

	Median fish-health measurement indicator													
	Fish-contaminant and water-quality parameters													
	EROD	MA	% Tis	GSI <sup>1</sup>	SSI	CF	HAI	EROD	MA	% Tis	GSI <sup>1</sup>	SSI	CF	HAI
	tau ( <i>p</i> )	tau ( <i>p</i> )	tau ( <i>p</i> )	tau ( <i>p</i> )	tau ( <i>p</i> )	tau ( <i>p</i> )	tau ( <i>p</i> )	tau ( <i>p</i> )	tau ( <i>p</i> )	tau ( <i>p</i> )	tau ( <i>p</i> )	tau ( <i>p</i> )	tau ( <i>p</i> )	tau ( <i>p</i> )
Atrazine, 18-month frequency-of-detection in water	0.33 (0.33)	0.20 (0.56)	0.07 (0.85)	--	-0.47 (0.17)	-0.20 (0.56)	-0.60 (0.08)	0.33 (0.33)	0.20 (0.56)	0.07 (0.85)	--	-0.47 (0.17)	-0.20 (0.56)	-0.60 (0.08)
Chromium, 18-month frequency-of-detection in water	0.47 (0.19)	-0.07 (0.85)	-0.20 (0.57)	--	0.07 (0.85)	-0.07 (0.85)	-0.47 (0.19)	0.47 (0.19)	-0.07 (0.85)	-0.20 (0.57)	--	0.07 (0.85)	-0.07 (0.85)	-0.47 (0.19)
Copper, 18-month geometric mean concentration in water <sup>2</sup>	0.33 (0.35)	0.33 (0.35)	0.20 (0.57)	--	-0.60 (0.09)	-0.47 (0.19)	-0.60 (0.09)	0.33 (0.35)	0.33 (0.35)	0.20 (0.57)	--	-0.60 (0.09)	-0.47 (0.19)	-0.60 (0.09)
Copper, 18-month frequency-of-detection in water	0.47 (0.19)	0.20 (0.57)	0.07 (0.85)	--	-0.47 (0.19)	-0.33 (0.35)	<b>-0.73 (0.04)</b>	0.47 (0.19)	0.20 (0.57)	0.07 (0.85)	--	-0.47 (0.19)	-0.33 (0.35)	<b>-0.73 (0.04)</b>
Specific conductance, concentration of last sample in water before fish collection	0.20 (0.57)	-0.33 (0.35)	-0.60 (0.09)	--	0.07 (0.85)	0.20 (0.57)	-0.20 (0.57)	0.20 (0.57)	-0.33 (0.35)	-0.60 (0.09)	--	0.07 (0.85)	0.20 (0.57)	-0.20 (0.57)
Total trace elements, 18-month geometric mean concentration in water <sup>2</sup>	0.33 (0.35)	0.07 (0.85)	-0.07 (0.85)	--	-0.33 (0.35)	-0.20 (0.57)	<b>-0.87 (0.01)</b>	0.33 (0.35)	0.07 (0.85)	-0.07 (0.85)	--	-0.33 (0.35)	-0.20 (0.57)	<b>-0.87 (0.01)</b>
Total trace elements, 18-month geometric mean concentration, in water <sup>3</sup>	0.47 (0.19)	0.20 (0.57)	0.07 (0.85)	--	-0.47 (0.19)	-0.33 (0.35)	<b>-0.73 (0.04)</b>	0.47 (0.19)	0.20 (0.57)	0.07 (0.85)	--	-0.47 (0.19)	-0.33 (0.35)	<b>-0.73 (0.04)</b>
Total trace-elements, 18-month frequency-of-detection in water	0.47 (0.19)	0.20 (0.57)	0.07 (0.85)	--	-0.20 (0.57)	-0.07 (0.85)	<b>-1.00 (&lt;0.01)</b>	0.47 (0.19)	0.20 (0.57)	0.07 (0.85)	--	-0.20 (0.57)	-0.07 (0.85)	<b>-1.00 (&lt;0.01)</b>
Zinc, 18-month geometric mean concentration in water <sup>2</sup>	0.07 (0.85)	-0.20 (0.57)	-0.33 (0.35)	--	-0.33 (0.35)	0.07 (0.85)	-0.60 (0.09)	0.07 (0.85)	-0.20 (0.57)	-0.33 (0.35)	--	-0.33 (0.35)	0.07 (0.85)	-0.60 (0.09)
Zinc, 18-month frequency-of-detection in water	0.07 (0.85)	-0.20 (0.56)	-0.33 (0.33)	--	-0.33 (0.33)	0.07 (0.85)	-0.47 (0.17)	0.07 (0.85)	-0.20 (0.56)	-0.33 (0.33)	--	-0.33 (0.33)	0.07 (0.85)	-0.47 (0.17)

<sup>1</sup>Immature gonad stage.  
<sup>2</sup>Minimum reporting level substituted for less-than concentrations.  
<sup>3</sup>One-half the minimum reporting level substituted for less-than concentrations.  
<sup>4</sup>Zero substituted for less-than concentrations.

either zero or one-half the reporting level was substituted for censored trace-element concentrations, but the correlations were nevertheless statistically insignificant ( $p \geq 0.05$ , table 15).

Statistically significant positive correlations ( $p \leq 0.05$ ) for stage-3 RGB male carp were detected between five categories of water-quality data (18-month time-weighted geometric mean concentrations of arsenic and total trace elements, last-sample arsenic concentration, and 18-month detection frequencies of copper and total trace elements in water) and EROD activity (table 15). Kendall's tau changed with use of the different substitution values for total trace-element concentrations but nevertheless remained significant ( $p \leq 0.05$ ). A significant negative correlation ( $p \leq 0.05$ ) was detected between the 18-month time-weighted geometric mean concentration of copper and CF.

In stage-3, age-2 male carp from the RGB, EROD activity was positively correlated ( $p \leq 0.05$ ) with the last-sample arsenic concentration and with the 18-month time-weighted geometric mean concentration (MRL substitution) and detection frequency of total trace elements in water (table 15). Significant positive correlations ( $p \leq 0.05$ ) were also detected between 18-month time-weighted geometric mean concentration and detection frequency of zinc in water and the health-assessment index (HAI) (table 15). The HAI is based on the fish-health observation indicators. Each structure or organ observed (for example, eye or gill) is given a numeric value, and these numbers are summed to yield a single HAI value for each fish. Higher HAI values indicate greater cumulative stress (Schmitt and Dethloff, 2000). A statistically significant negative correlation ( $p \leq 0.05$ ) was detected between last sample specific conductance and the percent of spleen tissue occupied by macrophage aggregates. As with the negative associations involving copper and other trace elements and percent of tissue occupied macrophage aggregates noted for the CRB, documentation of the negative association between specific conductance and percent of tissue occupied by the aggregates in the RGB would require further investigation.

Among the twelve BEST stations included in our analyses, vtg was detected in at least one male carp from three stations in the CRB (Vernita Bridge, Snake River at Burbank, and Warrendale) and three in the RGB (Foster Ranch, Amistad Dam, and Arroyo Colorado). However, correlation analyses relating fish-contaminant or water-quality data to vtg concentrations in male carp were not conducted because most vtg concentrations were less than the detection limit.

No statistically significant correlations were detected for female carp (all stages and ages) from the RGB (table 15). Values of Kendall's tau differed slightly when substitution values were used in the calculations of total organochlorine pesticide concentrations in the fish and time-weighted geometric mean concentrations of total trace elements in water, but the overall results (statistically insignificant correlations) did not change. For stage-2 female carp, the last-sample arsenic concentration, 18-month time-weighted geometric

mean concentrations of arsenic and copper, and 18-month detection frequencies of copper and total trace elements in water were negatively correlated ( $p \leq 0.05$ ) with the HAI. These results are contrary to expectations; HAI should increase (get worse) with exposure to chemical contaminants. Because so many factors and combinations of factors can affect fish health, the negative correlations between the constituents in water and HAI may be reflecting the effects of other chemicals or factors on fish health or may be the result of the small sample size.

## Stable Isotopes

The final techniques evaluated for integrating the BEST and NASQAN data sets were the examination of stable nitrogen isotopes in fish and particulate organic matter (POM) in water, and ratios of carbon to nitrogen (C:N) in the POM. In biota, the ratio of the abundance of naturally occurring stable (non-radioactive) isotopes of nitrogen ( $^{15}\text{N}$ : $^{14}\text{N}$ , or  $\delta^{15}\text{N}$ ) reflects nitrogen sources to the ecosystem and trophic relations within the ecosystem (Schmitt and Dethloff, 2000). The  $\delta^{15}\text{N}$  of POM in water reflects the relative contributions of terrestrial and in-stream sources of nitrogen in the POM. These various sources often have distinctive isotopic compositions and also distinctive C:N values (Kendall and others, 2001). As part of the BEST and NASQAN sampling efforts in the CRB and RGB, fish were analyzed for  $\delta^{15}\text{N}$  and POM samples were analyzed for  $\delta^{15}\text{N}$  and C:N (atomic).

Correlation analyses of  $\delta^{15}\text{N}$  of POM in water and  $\delta^{15}\text{N}$  of fish were examined using Kendall's tau correlation coefficient. The Kruskal-Wallis test was used in comparisons of the isotope data. The latter test is an analysis of variance, nonparametric rank-based procedure that is appropriate for small data sets. Other analysis of variance procedures, such as ANOVA, could not be used because the assumption of normality could not be met.

Mean values and ranges of  $\delta^{15}\text{N}$  and C:N in POM in water in the CRB and RGB are shown in table 16. The  $\delta^{15}\text{N}$  values for POM were significantly ( $p \leq 0.05$ ) lower in the CRB than in the RGB, and most C:N values in POM were greater in the CRB. Based on the  $\delta^{15}\text{N}$  and C:N values, POM sources in both basins included plankton, fresh terrestrial plant material, aquatic plants, and soil organic matter (Kendall and others, 2001). The POM values of  $\delta^{15}\text{N}$  reflected the sources of nitrogen—low values for mineral sources and high values for animal sources. Relative to the other sites in their respective basins, animal nitrogen inputs were small at the Northport and Vernita Bridge stations in the CRB and at Amistad Dam in the RGB, as reflected by relatively low mean  $\delta^{15}\text{N}$  of POM (table 16). In contrast, animal nitrogen was evident at the Falcon Dam, Arroyo Colorado, and Brownsville stations in the RGB, where mean  $\delta^{15}\text{N}$  of POM was greater (table 16).



**Table 16.** Mean values and ranges of  $\delta^{15}\text{N}$  of POM and C:N POM in water and ranges of  $\delta^{15}\text{N}$  of fish at selected NASQAN and BEST stations in the Columbia River and Rio Grande basins, water year 1997.

[water year 1997, October 1, 1996 through September 30, 1997; POM, particulate organic matter; C, carbon; N, nitrogen; ‰, permil (parts per thousand); at., atomic; --, no data. Values for  $\delta^{15}\text{N}$  mean and C:N for water are modified from Kendall et al. 2001;  $\delta^{15}\text{N}$  data for fish are from Carol Kendall, U.S. Geological Survey, unpublished data]

Station	Water				Fish			
	$\delta^{15}\text{N}$ of POM mean (‰)	$\delta^{15}\text{N}$ of POM range (‰)	C:N POM mean (at.)	C:N POM range (at.)	$\delta^{15}\text{N}$ range (‰) Bottom feeders <sup>2</sup>	$\delta^{15}\text{N}$ range (‰) Piscivores <sup>3</sup>	Bottom feeders <sup>2</sup>	Piscivores <sup>3</sup>
	<b>Columbia River Basin</b>							
Columbia River at Northport, Washington	-0.8	-3.1 – 3.8	19.4	8.4 – 39.7	6.1 – 7.2	8.0 – 8.3	7.4	9.0
Columbia River at Vernita Bridge near Priest Rapids Dam, Washington	0.4	-1.6 – 4.7	7.0	5.4 – 9.2	10.1 – 10.2	11.8 – 12.6	9.8	11.8
Snake River at Burbank, Washington	3.2	0.4 – 5.4	9.2	6.8 – 14.3	12.0 – 12.2	15.1 – 15.2	9.2	11.9
Columbia River at Warrendale, Washington	3.8	1.8 – 6.4	12.5	7.5 – 16.9	9.1 – 10.0	13.2 – 13.6	5.8	9.6
Willamette River at Portland, Oregon	2.7	0.5 – 5.6	9.8	7.5 – 16.0	11.0 – 11.5	14.0 – 14.4	8.6	11.5
Columbia River at Beaver Army Terminal near Quincy, Oregon	3.1	-0.6 – 4.8	9.4	7.3 – 12.4	10.8 – 11.1	13.2	7.9	10.1
	<b>Rio Grande Basin</b>							
Rio Grande at El Paso, Texas	7.9	5.0 – 10.4	7.6	6.9 – 8.2	13.6 – 14.5	13.8 – 14.2	6.1	6.1
Rio Grande at Foster Ranch near Langtry, Texas	5.1	3.2 – 7.9	7.8	5.7 – 9.8	13.4 – 14.0	--	8.6	--
Rio Grande below Amistad Dam, near Del Rio, Texas	2.0	1.1 – 3.0	5.6	3.2 – 8.0	15.9 – 17.2	17.5 – 19.0	14.5	16.3
Rio Grande below Falcon Dam, Texas	9.6	8.8 – 10.2	7.5	6.0 – 9.5	15.1 – 15.2	18.0 – 18.1	5.5	8.5
Arroyo Colorado at Harlingen, Texas	12.0	8.6 – 14.4	11.4	7.1 – 30.2	14.8 – 15.7	16.4 – 17.6	3.2	5.0
Rio Grande near Brownsville, Texas	8.4	5.0 – 14.0	9.2	6.1 – 16.6	12.1 – 13.4	17.7 – 17.9	4.3	9.4

<sup>1</sup> Mean  $\delta^{15}\text{N}$  of fish minus mean  $\delta^{15}\text{N}$  of POM in water.

<sup>2</sup> Common carp (*Cyprinus carpio*) and largescale sucker (*Catostomus macrocheilus*).

<sup>3</sup> Largemouth bass (*Micropterus salmoides*), smallmouth bass (*Micropterus dolomieu*), rainbow trout (*Oncorhynchus mykiss*), channel catfish (*Ictalurus punctatus*), and northern pikeminnow (*Ptychocheilus oregonensis*).

**Table 17.** Kendall's tau correlation matrix of mean trophic positions and mean total organics concentrations for fish species at selected NASQAN and BEST stations in the Columbia River and Rio Grande basins, water year 1997.

[water year 1997, October 1, 1996 through September 30, 1997; OCs, organochlorine pesticides; PCBs, polychlorinated biphenyls;  $p$ ,  $p$ -value; -- no data. Correlations that are significant at  $p \leq 0.05$  are shown in **bold**. Number of data pairs: Columbia River basin, 15; Rio Grande basin, 12]

Mean trophic positions per basin	Mean total OCs tau ( $p$ )	Mean total DDT tau ( $p$ )	Mean total PCBs tau ( $p$ )
Mean trophic positions, Columbia River basin	0.15 (0.43)	0.16 (0.40)	<b>0.50 (0.01)</b>
Mean trophic positions, Rio Grande basin	<b>-0.55 (0.01)</b>	<b>-0.55 (0.01)</b>	--

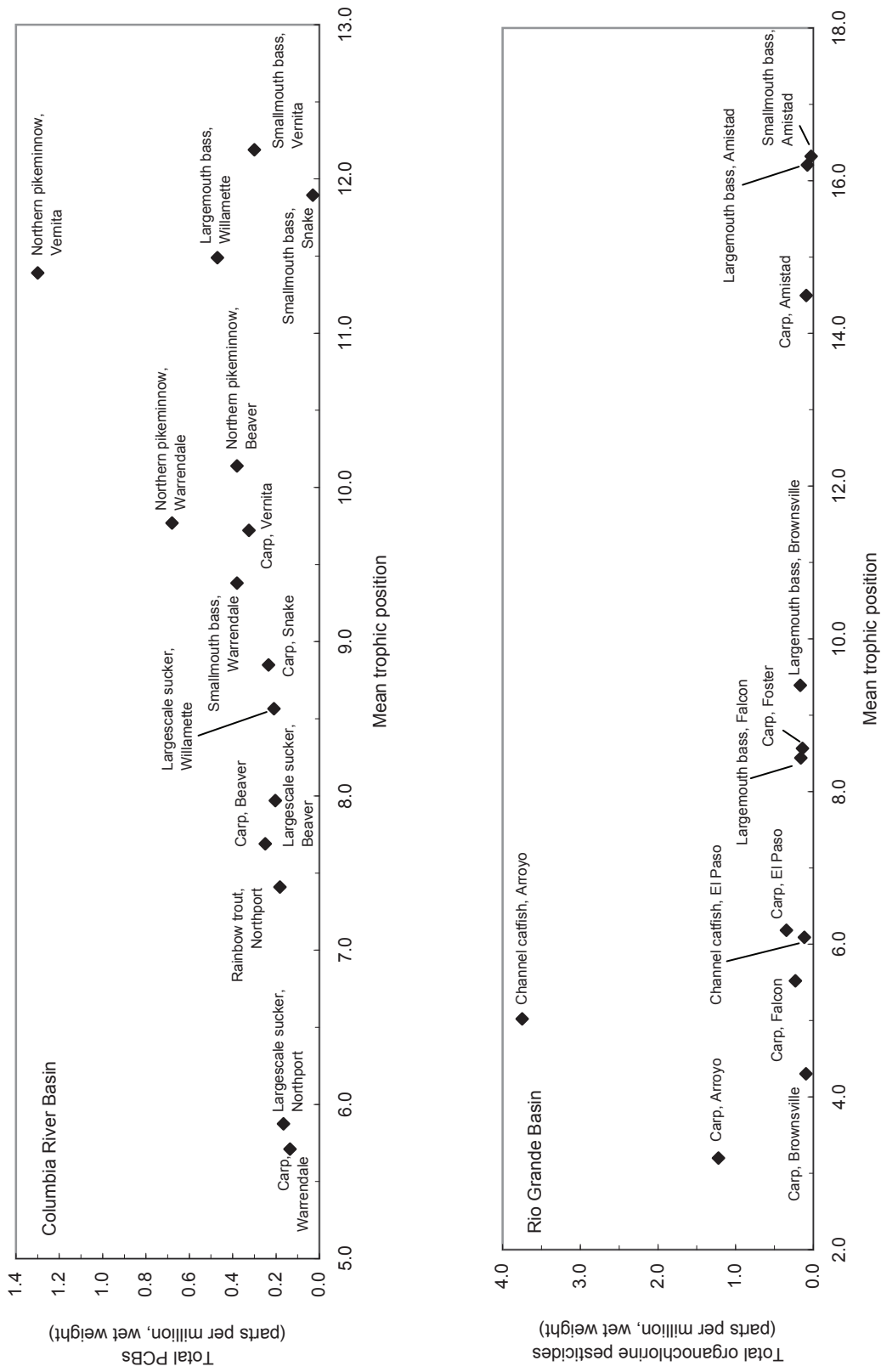
The spread of  $\delta^{15}\text{N}$  in benthivorous fish [carp and largescale sucker (*Catostomus macrocheilus*)] and piscivorous fish [largemouth bass (*Micropterus salmoides*), smallmouth bass (*Micropterus dolomieu*), rainbow trout (*Oncorhynchus mykiss*), channel catfish (*Ictalurus punctatus*), and northern pikeminnow (*Ptychocheilus oregonensis*)] are also shown in table 16. The  $\delta^{15}\text{N}$  of benthivores and piscivores were significantly ( $p \leq 0.05$ ) lower in the CRB than in the RGB, reflecting the significantly ( $p \leq 0.05$ ) lower values of  $\delta^{15}\text{N}$  of POM and Kjeldahl nitrogen (organic plus ammonia nitrogen) in waters of the CRB and greater nitrogen enrichment in the RGB. However, when these data were normalized by subtracting the mean  $\delta^{15}\text{N}$  of POM in water from the mean  $\delta^{15}\text{N}$  of fish, the resulting mean trophic positions (mean  $\delta^{15}\text{N}$  of fish minus mean  $\delta^{15}\text{N}$  of POM in water) of the benthivorous fish did not differ significantly between basins, as measured by the Kruskal-Wallis test. Trophic positions of the piscivores (adjusted  $\delta^{15}\text{N}$ ) also did not differ significantly between basins (table 16). The trophic position of the nominal piscivores was significantly ( $p \leq 0.05$ ) higher than that of the nominal benthivores in the CRB, but not in the RGB. These results indicate that there is considerably more dietary overlap among the fishes sampled in RGB than in those from the CRB.

The strengths of the associations between mean trophic position and mean concentrations of bio-accumulative contaminants (total organochlorine pesticides, total DDT, or total PCBs) for each species at a station in the CRB and RGB were examined using Kendall's tau. Statistically significant correlations ( $p \leq 0.05$ ) were documented between mean trophic position and mean total PCB concentrations in CRB fish, and between mean trophic position and mean concentrations of total organochlorine pesticides and total DDT in RGB fish (table 17). Values of Kendall's tau were only moderate (about 0.50), however, and reflected the influence of outliers in the data (fig. 3). When mean trophic positions greater than 11.0 were omitted from the CRB analysis, Kendall's tau increased to 0.80, and the positive correlation between mean trophic positions and mean total PCB concentrations in fish became stronger ( $p \leq 0.01$ ). However, it is important to note that there was no *a priori* reason to eliminate these means from consideration, other than the fact that the adjusted  $\delta^{15}\text{N}$  values were larger than most. For the RGB, the elimination of mean total

organochlorine and mean total DDT concentrations in fish greater than 1.0 part per million (equivalent to 1 microgram per gram) resulted in a Kendall's tau of -0.42 and no significant relation ( $p = 0.09$ ) between these contaminants and mean trophic positions. Similar results were obtained when one-half the reporting level of the bio-accumulative contaminants was substituted for censored values. In contrast to the outliers eliminated from the CRB analysis, the values excluded from the RGB analysis all represented samples from the Arroyo Colorado that reflected relatively localized sources of contamination.

As illustrated by the situation described in the previous paragraph, analyses of correlations between mean trophic position and bio-accumulative contaminants in fish on a basin-wide scale are probably not very relevant. Significant correlations (positive or negative) between  $\delta^{15}\text{N}$  of fish and any contaminants across all stations in a basin are not necessarily expected unless the correlation is a result of a large-scale pollutant; for example, atmospheric mercury. Instead, the expectation is that  $\delta^{15}\text{N}$  and bio-accumulative contaminants in fish will co-vary at a station; that is, some of the differences between fish exposed to the same concentrations of a bioaccumulable contaminant can be explained by differences in trophic position, as measured by  $\delta^{15}\text{N}$ . The examination of the different taxa present at a station is probably more relevant than the basin-wide analyses.

As noted by Schmitt and Dethloff (2000),  $\delta^{15}\text{N}$  of POM in water may be useful for interpreting the results of reproductive biomarkers. Among all BEST stations sampled in 1997-98 ( $n=26$ ), vtg was detected in at least one male carp from four stations in the CRB (Vernita Bridge, Warrendale, Snake River at Burbank, and Willamette at Oregon City) and six in the RGB (Alamosa, Elephant Butte, Foster Ranch, Mission, Amistad Dam, and Arroyo Colorado in the RGB). Concentrations were especially high (mid-vitellogenic female range) in two carp from Arroyo Colorado in the RGB (Schmitt and others, 2004), and several vtg concentrations in male carp from Warrendale in the CRB (Hinck and others, 2004) were greater than most other concentrations. These two stations also had the highest  $\delta^{15}\text{N}$  of POM in water in their respective basins. The elevated POM values indicate inputs of animal sources of nitrogen such as livestock or sewage, which may also be



**Figure 3.** Relation between mean total PCB concentrations and mean trophic position, by fish species, in the Columbia River basin; and mean total organochlorine pesticide concentrations and mean trophic position in the Rio Grande basin.

sources of endocrine-modulating chemicals [for example natural and synthetic estrogens, alkylphenol polyethoxylates (APEs), and pharmaceuticals] to aquatic systems (Schmitt and Dethloff, 2000; Folmar and others, 1996; Tyler and others, 1998; Kolpin and others, 2002). Conversely, Vernita Bridge (CRB) and Amistad Dam (RGB) had the lowest  $\delta^{15}\text{N}$  of POM in water in their respective basins, but vtg was nevertheless detected in male carp from both stations. At these two stations, other or additional factors may be involved, including contaminants not included in our analysis.

## Discussion and Recommendations

This study was initiated in 2001 to investigate alternative techniques for summarizing and integrating water-quality data of the NASQAN program with fish-contaminant and fish-health data of the BEST program. Test data sets from both programs for stations in the CRB and RGB with water-quality data for WYs 1995-98 and fish data for 1997-98 were used in the study. Integration of the two data sets through the calculation of Kendall's tau correlation coefficient and the Kruskal-Wallis test showed that statistically significant correlations ( $p \leq 0.05$ ) occurred between NASQAN water-quality data and BEST fish data in both basins. The following parameters were found to be significantly correlated with one or more other parameters: arsenic, atrazine, copper, specific conductance, total trace elements and their toxicity estimate, and zinc in water; total organochlorine pesticides and total PCBs in fish; external lesions and fin anomalies; EROD activity, percent of tissue occupied by macrophage aggregates, splenosomatic index, condition factor, and health-assessment index; and trophic position ( $\delta^{15}\text{N}$  of fish minus  $\delta^{15}\text{N}$  of POM in water). A few significant negative correlations, including those between water-quality data and fish-health observation and measurement indicators for both basins and between trophic position and fish-contaminant data for the RGB, were counter-intuitive in a biological sense. For these results, the small sample sizes may have resulted in spurious correlations, or water-quality parameters may have mimicked the effects of other parameters or factors.

Results presented in this report have value to the BEST program. We specifically address issues related to the quantity of water-quality and fish data, water-quality parameters and summarization and integration techniques, guidelines for the protection of freshwater aquatic life, substitutions for censored data, use of water and fish trace element and  $\delta^{15}\text{N}$  data, and additional parameters that could be included in future studies. Of the 25 BEST stations sampled in the CRB and RGB, only 12 were near NASQAN stations that had sufficient water-quality data for the study. Because only six stations in each basin were investigated in this study and not all of these stations could be used in correlation analyses, the power of the

statistical tests was low and the analyses were conducted for illustrative purposes. With the inclusion of additional stations, the power of the statistical tests would increase. If integration of the programs and their data is to become an objective, collection of fish and water data should be conducted at as many stations in common as possible. Prior to station selection for the BEST program, the NASQAN data should be examined for parameters of interest to the BEST program, sampling frequency and period of record for the parameters of interest, and streamflow data. This also would pertain to NAWQA stations that might be selected by the BEST program. The period of record for the water-quality data for either the NASQAN or NAWQA stations should run through the time fish are collected.

As stated in the "Background" section of this report, BEST sampled NAWQA stations in the MRB during 1995; however, these stations could not be included in this study because most water-quality data for the NAWQA stations were collected after the fish sampling had occurred. The NAWQA program could represent a source of water-quality data for future integrated studies because data have been collected continuously at some stations (long-term trend sites) since the 1990s. Nevertheless, a potential drawback to the use of NAWQA water-quality data for integration with BEST fish data is the lack of trace-element data for surface-water samples. In the 1990s, only a few NAWQA study units, such as the Upper Colorado River Basin and the Northern Rockies Intermontane Basins, included trace elements in surface-water analyses. The NAWQA program currently analyses trace elements in ground water, streambed sediment, and fish and clam tissue but not in surface water. In our study, the trace elements arsenic, chromium, copper, and zinc in water were important components of the correlation analyses. In addition, these are potentially toxic to aquatic organisms at environmental concentrations which, with the exception of arsenic, do not tend to bioaccumulate. Therefore, their measurement in surface water is an important monitoring and assessment component. Nevertheless, it is likely that these data will continue to be available only for NASQAN stations.

An important consideration in our study was the amount of time that fish were potentially exposed to water-borne contaminants. Time-weighted concentrations were therefore determined to be more appropriate than flow-weighted concentrations. Time-weighted concentrations of the parameters of interest first were determined for a station's FPR and for WY 1997 using techniques described by Larson and others (2004). Time-weighted concentrations for some stations could not be determined because minimum sample criteria could not be met. Many of the time-weighted mean, geometric mean, and median concentrations of the parameters of interest in water that could be determined were less than the parameters' MRL. Because of this, the use of time-weighted 90th percentile concentrations was examined and is believed to be an adequate statistical representation for concentrations in water. Although the 90th percentile concentration may overestimate the long-term (that is, chronic) exposure of fish to contami-

nants, it might represent a reasonable estimate of short-term (acute) exposure.

Data for WY 1997 were used to evaluate the use of a common period of record for all stations. This was unsatisfactory because it further reduced the data available. At some stations additional water-quality data were collected between the end of WY 1997 and the date of fish collection; restricting water-quality data to WY 1997 eliminated this data. An alternative would have been the use of water-quality data for the 12 months prior to the date of fish collection for all stations. This approach should be considered in future studies.

Time-weighted concentrations also were determined using less restrictive data requirements than those needed for use of techniques in Larson and others (2004). By ignoring minimum sample criteria for drainage area and number of samples per year, we could determine time-weighted geometric mean concentrations of the parameters of interest for all six stations in the RGB for the 18 months prior to the date of fish collection. This technique was similar to the method used by Goodbred and others (1997) to determine time-weighted concentrations and is an alternative technique when minimum sample criteria eliminate stations from the computations.

Selenium, one of the trace-element parameters of interest, was either not detected or was detected at concentrations above the MRL in only a few samples for most stations. Detections greater than the MRL were only common at the Arroyo Colorado station in the RGB. Geologic and irrigation conditions in the Arroyo Colorado watershed were appropriate for selenium to occur in the water column. Except for situations such as this, the nation-wide detection of selenium in water at most stations may be too low to include in integrated studies.

For this study, some correlations involving concentrations of arsenic, specific conductance, and zinc in the last water sample prior to fish collection were statistically significant ( $p \leq 0.05$ ). The validity of using the last-sample concentration as a summarization technique for water-quality data would depend on the appropriateness of this technique for bioexposure. With a short (1- or 2-month) time lapse between the last water-quality sample and fish collection, the last-sample concentration would reflect, at best, acute exposure of fish to water-borne contaminants rather than chronic or long-term exposure.

Frequency-of-detection for the 18 months prior to the data of fish collection also was used as a summarization technique for the water-quality parameters of interest. Some correlations between frequencies-of-detection and the fish data were statistically significant ( $p \leq 0.05$ ). In our study, the frequency-of-detection of a parameter of interest was determined by counting the number of samples in which the concentration of the parameter was at or above the MRL and dividing this number by the total number of samples. As such, the detection frequency depends on both sampling design and analytical sensitivity. Also, there can be some instances where frequency-of-detection is large and concentrations are low or frequency-of-detection is small and concentrations are

elevated. For example, it is possible for the detection frequency of atrazine at a station to be 70 percent for the period of interest, but concentrations might only range between 0.005 and 0.01  $\mu\text{g/L}$ . Such concentrations might be too low to affect fish, but this would not be reflected in the frequency-of-detection. Conversely, a frequency-of-detection of 6 percent would not adequately represent exposure if concentrations in a few samples were greater than criteria for the protection of aquatic life. Consequently, frequency-of-detection is not a valid summarization technique for use in integrated studies.

Guidelines for the protection of aquatic life were used as an additional technique for integrating NASQAN water-quality data and BEST fish data. Based on comparisons of trace-element and pesticide concentrations in water for each station to guidelines for the protection of freshwater aquatic life, water quality in the RGB was more impaired than water quality in the CRB in terms of the pesticides chlorpyrifos, diazinon, and malathion. Fish-health data at those stations with chlorpyrifos, diazinon, and malathion concentrations greater than or equal to aquatic life criteria could be examined more closely if additional information were available on toxic effects of each pesticide to particular fish species rather than to all aquatic life. If one species is more susceptible to a chlorpyrifos concentration of 1  $\mu\text{g/L}$ , for example, than another species, this information possibly could be used as an additional tool for examining fish health at stations with elevated concentrations of chlorpyrifos. A similar approach could be used for exceedences of trace-element criteria concentrations and estimates of total trace-element toxicity. An additional approach was used for copper concentrations in water. A cumulative relative frequency diagram was developed for one station to illustrate the extent to which fish at that station had been exposed to copper concentrations greater than or equal to the aquatic life criterion.

When censored or less-than concentrations were indicated for water-quality or fish data, the MRL and one-half the MRL or one-half the MRL and zero, respectively, were substituted for the less-than concentrations. For most parameters, the ranking of data did not change with substitution, and the results for Kendall's tau remained unchanged. However, ranks did change for the geometric mean total trace-element concentrations in water and total organochlorine concentrations in female carp in the RGB when different substitution values were used. As a result, correlations of total trace-element concentrations in water with fin anomalies and HAI scores and of total organochlorine pesticide concentrations in female carp with HAI scores also changed. For bioexposure, though, one-half the reporting level or an imputed value (for example, Helsel, 1990) would probably be more appropriate than zero for fish, which would imply no exposure, or the MRL for water, which may overestimate exposure. In each instance where Kendall's tau changed with substitution, the significance of the correlations remained the same.

As noted in the "Purpose and Approach" section, only selected trace elements and  $\delta^{15}\text{N}$  were common to both the NASQAN and BEST programs and the respective water and

fish media. As a test of integrating the two data sets, correlations between occurrences of four trace elements (arsenic, chromium, copper, and zinc) in water were paired with corresponding concentrations in fish. However, and as noted previously, trace-element occurrences in water may not be appropriate for use in a situation such as this because, with the exception of arsenic, these elements do not tend to accumulate in fish. Nevertheless, all four can be toxic to fish at environmentally relevant concentrations, and it is therefore important to account for them in an integrated assessment. Trace-element concentrations are generally greater and less temporally variable in streambed sediments than in water, and correlations between concentrations of trace elements in sediments and fish may therefore represent a better technique for examining bioexposure. Streambed sediments are not collected as part of the NASQAN program but are collected and analyzed for trace elements as part of the NAWQA program. Analyses of correlations between concentrations of most trace-element concentrations in water and fish could be excluded from future integrated studies.

$\delta^{15}\text{N}$  was used as a corollary variable for normalizing among CRB and RGB stations.  $\delta^{15}\text{N}$  of POM in water was compared between the two basins and between individual stations as an indicator of nitrogen sources. The trophic positions of benthivorous and piscivorous species were compared between the two basins and within a basin, as were trophic positions and concentrations of bio-accumulative organic contaminants in fish. As a result of these analyses, we feel that the latter comparison of trophic positions and bio-accumulative contaminants in fish between basins could be excluded from future investigations because relations between the two groups should only occur if it reflects a large-scale pollutant such as atmospheric mercury. Finally,  $\delta^{15}\text{N}$  POM values in water indicative of animal-derived nitrogen inputs co-occurred with reproductive biomarker effects in both basins. Overall, results of the analyses of  $\delta^{15}\text{N}$  of POM in water and fish indicate that  $\delta^{15}\text{N}$  generally was useful for comparing stations between the two basins and within each basin, and the use of  $\delta^{15}\text{N}$  should continue.

This study was conducted to evaluate the feasibility of combining fish-contaminant and fish-health data of the BEST program with water-quality data of the NASQAN program. As such, the concentrations of the fish and water contaminants investigated at the small number of stations included in the study do not span the range likely to be represented by a larger-scale study. The range of fish-health variables was similarly narrow. These narrow ranges and small numbers of stations undoubtedly contributed to the results (or lack thereof) reported here. Nevertheless, they represent suitable examples of the types of data to be encountered and problems inherent in their analysis. Moreover, and as noted elsewhere (Schmitt, 2002), studies such as these are exclusively exploratory, not explanatory. Correlations quantify associations between measured variables rather than determine cause and effect; regardless of the number of samples and variables and statistical tools available, only carefully planned and controlled field

and laboratory research can identify cause and effect relations. The foundation of biomarker-based monitoring is the understanding of the factors that influence the biomarkers based on such research; for example, interpretation of biomarker findings is based more on knowledge of the biomarkers than on empirical correlations. Such correlations typically generate more questions than answers but may suggest testable hypotheses to be evaluated through subsequent laboratory and more focused field studies. Moreover, simple correlations are inherently deceptive because many variables are inter-correlated and cannot be controlled or otherwise accounted for. Finally, the notion of biological responses rising or falling monotonically with the concentration of one or more contaminants in fish collected over broad expanses of time and space is grossly simplistic. Curvilinear and asymptotic relations on environmental gradients are common, and many variables are inter-related. Given these factors, results of investigations such as ours should be considered exploratory, with results used as a starting point for additional focused laboratory or field studies to better define causation.

In the process of integrating the fish and water data we have identified substantial previously recognized and unrecognized difficulties. Nevertheless, data sets combined and summarized in the manner described here would represent a comprehensive assessment of fish exposure to contaminants and the effects of exposure on fish irrespective of the program or programs from which the data originate. We offer the following additional recommendations and comments to guide and improve future integrated assessments:

**1. Analytical methods.** The NASQAN water samples were analyzed at the USGS National Water Quality Laboratory. The five trace elements used in this study all had MRLs of 1.0  $\mu\text{g/L}$  or greater. More recent NASQAN samples have been analyzed using laboratory methods with lower reporting levels. Currently (2005), all five trace elements have MRLs less than 1.0  $\mu\text{g/L}$ : arsenic, 0.2  $\mu\text{g/L}$ ; chromium, 0.8  $\mu\text{g/L}$ ; copper and selenium, 0.4  $\mu\text{g/L}$ ; and zinc 0.6  $\mu\text{g/L}$ . With lower reporting levels the number of censored observations should be reduced, which may alleviate some of the problems arising from the use of censored data we identified.

**2. Sampling frequency.** Water was sampled too infrequently at some stations to accurately characterize time-weighted concentrations; more frequent sampling at these stations may have allowed the determination of the time-weighted concentrations. However, it is difficult to make an overall recommendation for an adequate sampling frequency. Such a recommendation would depend in a large part on the time period being examined and how concentrations vary at a station. Monthly sampling during low-flow conditions and more frequent

sampling during high-flow conditions, as is done at many NASQAN and NAWQA stations, over a long enough time period could represent the range of conditions that typically occur over a hydrograph. Even this may not be adequate for determining time-weighted concentrations for pesticides and trace elements if they are episodic, however. For documenting waterborne exposure of fish to pesticides and elevated aqueous concentrations, it is important to sample water during the first flush of pesticides following application. Because the timing of the flush cannot be predicted and determining the time to sample is difficult, the degree to which fish exposure is represented by time-weighted concentrations is questionable. Conversely, trace-element concentrations are typically greater during low-flow conditions, and more frequent sampling during high-flow conditions may not be needed. Although costly and time consuming, a period of over-sampling could be used as a starting point for determining sampling frequency at a station or possibly one nearby. At present there are few stations in the United States that are over-sampled, especially on large rivers.

**3. Station density.** A simplified recommendation for the density of stations per basin is also difficult to make. For an integrated study, the density of stations would largely depend on data availability and the homogeneity of the stations across the basin, other factors being equal. Assuming that data availability was adequate for the stations in question, similarities or differences between the stations would determine the station density. If a basin is relatively uniform with respect to such factors as type and source(s) of contaminants, contaminant concentrations, land use, physical conditions (temperature, pH, and so on), and stream modification, few stations would be needed and they could be distributed more-or-less uniformly throughout the basin. Conversely, a heterogeneous basin would require more stations. Sampling density and distribution could be different in a basin with urban areas and areas with different agricultural crops than in an agricultural basin with a single crop or in a basin with a number of mining areas.

**4. Estimates of total trace-element toxicity.** Toxic units were used in this report to estimate total trace-element toxicity, the combined toxicity of multiple trace elements in water. These estimates were easy to compute and use in correlation analysis, but interpretation of the results is more difficult. Although fish at any site are likely to be exposed to a mixture of contaminants, interactions among them can vary. Mixtures can be less than, equal to, or greater than

the sum of the toxicities of the individual contaminants. Moreover, there is considerable debate within the scientific community about how mixtures of contaminants interact to affect aquatic biota; for example, how multiple pesticides or a mixture of pesticides and trace elements interact to affect fish. As noted by Wildhaber and Schmitt (1996), an estimate such as total trace-element toxicity, which assumes strictly additive toxicity, should be used cautiously and only as a comparative tool.

**5. Correlations between parameters.** Results presented in this report indicate that some correlations will have limited value in future integrated studies. For example, because they do not bioaccumulate in fish, correlations between concentrations of most trace elements in water and fish could be excluded. The exceptions would be arsenic, selenium, and mercury, with the caveat that a high degree of analytical sensitivity is necessary for their inclusion to avoid problems associated with large numbers of censored values. Correlations between trophic conditions (as reflected by  $\delta^{15}\text{N}$ ) and bio-accumulative contaminants in fish could also be excluded for most contaminants because relations between the two groups are not necessarily expected unless they describe a large-scale pollutant such as atmospheric mercury.

**6. Passive accumulative samplers.** An alternative or additional method for determining the amount of contamination in water is the use of sampling devices that are broadly defined as passive accumulative samplers. These include the semipermeable membrane device (SPMD) for hydrophobic organic compounds (Huckins and others, 1993), the polar organic chemical integrative sampler (POCIS) for hydrophilic organic compounds (Alvarez and others, 2004), and the stabilized liquid membrane device (SLMD) for labile metals (Brumbaugh and others, 1999). Passive accumulators are typically placed in the water for a predetermined period, generally about a month. Upon removal, the contents are analyzed for contaminants and time-weighted mean concentrations can be readily determined. Passive accumulators eliminate many of the previously discussed problems associated with water sampling; very low aqueous concentrations of potential analytes are concentrated by the samplers, and sampling spans the range of concentrations that occurred over the full range of hydrologic conditions present during the deployment period. Although passive accumulators sample contaminants such as hydrophobic chemicals and metals that may also be accumulated

by fish, passive accumulators typically accumulate greater concentrations and larger numbers of chemicals because they lack metabolic and excretory capacity. Concentrations in passive accumulators may therefore represent short-term exposure more accurately than concentrations in fish. In an integrated study, passive accumulators could be a valuable tool for determining contaminant concentrations in water and thereby documenting exposure. Passive accumulators do not sequester all chemicals equally well, however; for example, the SMLD can accurately gauge exposure to waterborne lead, zinc, cadmium, copper, and similar metals, but is less well suited for bioaccumulative elemental contaminants such as arsenic, selenium, and mercury. Consequently, a battery of passive accumulators would be required to completely characterize waterborne exposure (see, for example, Petty and others, 2004), and fish would still have to be analyzed for bioaccumulative elemental contaminants and biomarkers to fully gauge both exposure and effects. Additional information on passive accumulators is presented by Huckins and others (1993), Ellis and others (1995), Capel (1996), Brumbaugh and others (1999), McCarthy and Gale (2001), Alvarez and others (2004), and Petty and others (2004).

### 7. Additional measurements and parameters.

Additional water-quality parameters, such as contaminant concentrations in suspended and streambed sediments and elemental ratios, may be of value in future integrated assessments. Questions that could be addressed with suspended-sediment data include the following: Are suspended-sediment contaminant concentrations related to streambed-sediment concentrations? And are either suspended-sediment or streambed-sediment concentrations related to fish-contaminant concentrations or fish health? For these questions, suspended-sediment data could also be used as a proxy for erosion and runoff that may yield substances harmful to fish. Elemental ratios (based on molar concentrations) could also be examined in some biotic and abiotic sample matrices to account for the effects of geochemical and biochemical processes on measured concentrations and to reduce otherwise unexplained variation (see, for example, Settle and Patterson, 1980; Schmitt and Finger, 1987). Benthic macroinvertebrates represent an important route of contaminant transfer from sediments to fish and other biota in rivers and streams; contaminant concentrations in streambed sediments or benthic macroinvertebrates could therefore be used to assess bioexposure. Sediment-quality guidelines, although not enforceable, also provide a means for further evaluating streambed-

sediment data. In depositional environments such as reservoirs, information on historic sediment and water quality can also be obtained from sediment cores (for example, Van Metre and others, 1997; Greve and others, 2001). Examination of sediments could include determining the degree to which contaminant concentrations are correlated with concentrations in fish and with fish-health indicators. It is important to note that the issues we identified for summarizing water-quality data for combination with fish data also apply for integration with streambed-sediment data because sediment is also typically sampled less frequently than water.

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