

CONCENTRATION AND DISTRIBUTION OF SELENIUM ASSOCIATED WITH IRRIGATION DRAINAGE IN THE WESTERN UNITED STATES

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ABSTRACT

Concentrations, distribution and sources of selenium from irrigated lands were studied between 1986 and 1990 at 20 reconnaissance project areas in western States under the Department of the Interior's National Irrigation Water Quality Program. Samples of water, bottom sediment, whole-body fish, and bird livers for analysis of selenium concentrations were collected before, during, and after irrigation season from streams, canals, lakes, and groundwater in each project area. Selenium concentrations in water ranged from less than the reporting limit of 1 microgram per liter in 42 percent of the 586 samples collected to 4,800 micrograms per liter from a well in the Pine River Area in southern Colorado. Selenium concentrations in 223 samples of bottom sediment ranged from less than the reporting limit of 0.1 microgram per gram to 85 micrograms per gram in a sample from the Middle Green River Basin in Utah. Selenium concentrations in whole-body fish (all species) ranged from 0.1 to 50 micrograms per gram dry weight with the maximum concentration observed in a carp from the Gunnison River Basin in western Colorado. Selenium concentrations in bird livers (all species) ranged from less than 0.32 to 170 micrograms per gram dry weight with the maximum concentration observed in the liver of an avocet from the Kendrick Reclamation Project Area in Wyoming.

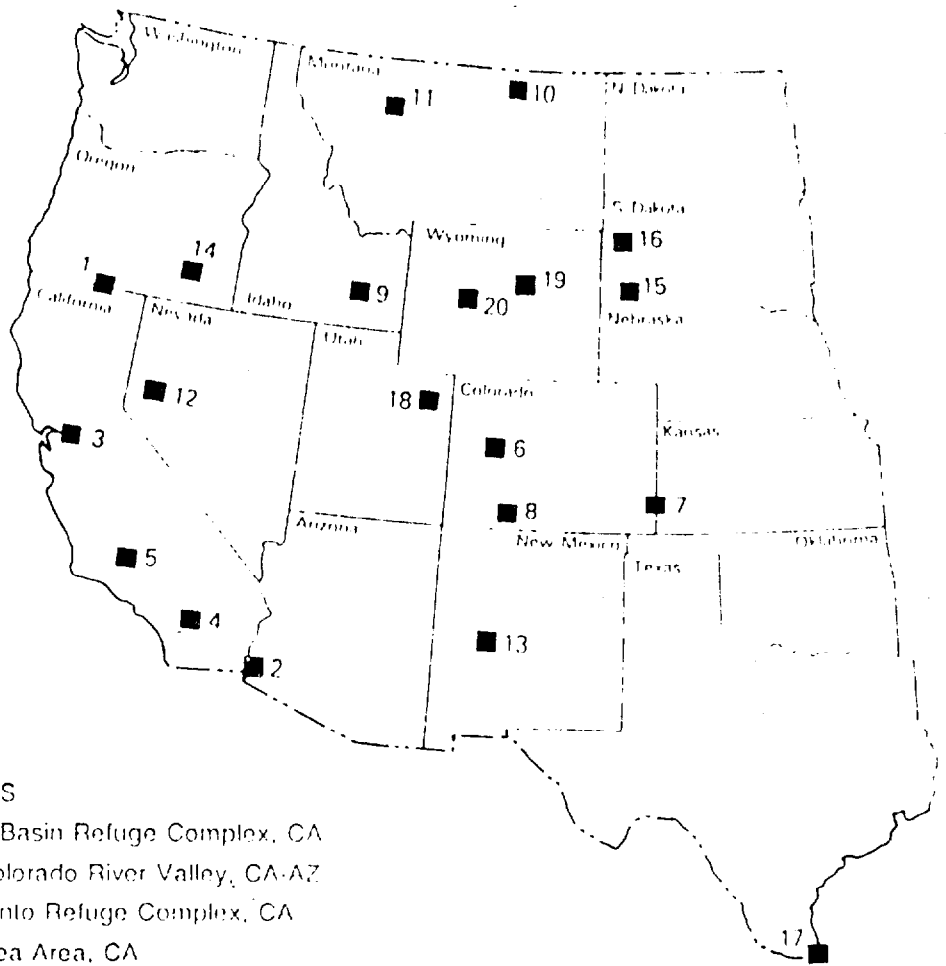
INTRODUCTION

Water quality problems related to elevated concentrations of dissolved solids in irrigation drainwater occur in many areas of the United States. In 1983, the link between irrigation drainwater and elevated concentrations of selenium was made after waterfowl deaths, deformities, and reproductive failures at Kesterson Reservoir in California were observed. The Department of the Interior in 1985 began the National Irrigation Water Quality Program (NIWQP) to determine whether problems of selenium and other inorganic or organic trace constituents in irrigation drainwater similar to those at Kesterson Reservoir existed in other western States.

Reconnaissance investigations were completed for 20 areas (Figure 1) between the years 1986 and 1990. Reconnaissance investigations are field-sampling studies to determine levels of potentially toxic constituents in the water, bottom sediment, and biota of the study areas. Samples generally were collected before, during, and after the irrigation season. Samples were analyzed for major and trace constituents and in some cases, for pesticides.

CONCENTRATIONS AND DISTRIBUTION OF SELENIUM

Selenium has been detected in samples of water, bottom sediment, or biota from all 20 reconnaissance study areas. Although selenium is the constituent that has the greatest potential for toxic effects on biota in most of the study areas, other trace constituents are of concern in some areas.



STUDY SITES

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| 1. Klamath Basin Refuge Complex, CA | 14. Malheur National Wildlife Refuge, OR |
| 2. Lower Colorado River Valley, CA-AZ | 15. Angostura Reclamation Unit, SD |
| 3. Sacramento Refuge Complex, CA | 16. Belle Fourche Reclamation Project, SD |
| 4. Salton Sea Area, CA | 17. Lower Rio Grande and Laguna Atascosa National Wildlife Refuge, TX |
| 5. Tulare Lake Bed Area, CA | 18. Middle Green River Basin, UT |
| 6. Gunnison River Basin, CO | 19. Kendrick Reclamation Project Area, WY |
| 7. Middle Arkansas River Basin, CO-KS | 20. Riverton Reclamation Project, WY |
| 8. Pine River Area, CO | |
| 9. American Falls Reservoir, ID | |
| 10. Milk River Basin, MT | |
| 11. Sun River Area, MT | |
| 12. Stillwater Wildlife Management Area, NV | |
| 13. Middle Rio Grande and Bosque del Apache National Wildlife Refuge, NM | |

Figure 1: Locations of reconnaissance areas, National Irrigation Water Quality Program, 1986-1990

Table 1. Selenium concentrations in water from reconnaissance study areas. (Units are micrograms per liter ($\mu\text{g/l}$). Analytical reporting limit is 1 $\mu\text{g/l}$. Study areas are keyed to Figure 1.)

Study Area	Abbreviated Name	Number of Samples	Range of observed concentrations ($\mu\text{g/l}$)	Median	Number of observations less than reporting limit
1	Klamath	16	< 1	< 1	13
2	Lower Colorado	14	< 1 - 2	2	3
3	Sacramento	28	< 1	< 1	27
4	Salton Sea	12	1 - 300	19	0
5	Tulare	12	< 1 - 390	35	5
6	Gunnison	37	< 1 - 320	12	5
7	Arkansas River	26	1 - 52	6	0
8	Pine River	69	< 1 - 4800	2	26
9	American Falls	18	< 1 - 6	< 1	13
10	Milk River	16	< 1 - 1	< 1	15
11	Sun River	27	< 1 - 580	2	8
12	Stillwater	78	< 1 - 1	< 1	71
13	Middle Rio Grande	29	< 1 - 1	< 1	28
14	Malheur	22	< 1	< 1	22
15	Angostura	34	< 1 - 16	3	2
16	Belle Fourche	41	< 1 - 34	3	2
17	Lower Rio Grande	16	< 1 - 2	< 1	10
18	Green River	43	< 1 - 140	17	8
19	Kendrick	24	< 1 - 300	8	4
20	Riverton	26	< 1 - 12	2	4

Selenium in Water

Analytical results of selenium in water for all sampling sites from 20 reconnaissance study areas are presented in Table 1. Sampling sites in each area include irrigation drainwater, irrigation supply, ground water, receiving water sites (streams, wetlands, etc.) and reference sites. For comparison between study areas, results of water samples from all sources in each area are grouped for discussion with the understanding that they provide the widest spectrum of selenium concentrations that may occur in water in that area. Analytical results were provided by the U.S. Geological Survey Water Resources Division Central Laboratory in Denver, Colorado. Study areas in Table 1 are keyed by number and abbreviated name to Figure 1. Results presented in Table 1 and in all following tables are from data available in U.S. Geological Survey files and/or in the following publications: Study area 1, Sorenson and Schwarzbach (1991); 2, Radtke and others (1988); 4, Setmire and others (1988);

5, Schroeder and others (1988); 9, Low and Mullins (1990); 10, Lambing and others (1988); 11, Knapton and others (1988); 12, Hoffman and others (1990); 15, Green and Sowards (1991); 16, Roddy and others (1991); 17, Wells and others (1988); 18 Stephens and others (1988); 19, Peterson and others (1988); and 20, Peterson and others (1991). Reconnaissance investigation reports are in preparation or in review for study areas 3,6,7,8,13, and 14. These reports like those referenced above are planned for release as U.S. Geological Survey Water-Resources Investigations Reports.

Selenium concentrations in a total of 590 water samples from all reconnaissance study areas range from less than the reporting limit of 1 ug/l to 4800 ug/l in a sample collected from a shallow well in the Pine River Area. A total of 271 samples (46 percent) from 18 of the 20 areas had concentrations of less than the detection limit and the minimum selenium concentration for all areas was at or below the reporting limit. At the Klamath, Sacramento, and Malheur study areas, no selenium was detected in any water samples. At the Milk River, Stillwater, Lower Colorado, Middle Rio Grande and Lower Rio Grande areas, maximum selenium concentrations were 2 ug/l or less. Selenium concentrations were less than 5 ug/l in approximately 70 percent of all samples from all areas. The median selenium concentration was less than 1 ug/l at the Klamath, Sacramento, American Falls, Milk River, Stillwater, Malheur and Lower Rio Grande areas. The median value of 35 ug/l selenium for the Tulare area exceeds the U.S. Environmental Protection Agency (EPA) (1987) acute criterion for protection of freshwater aquatic life of 20 ug/l. The median values of 19, 12, and 17 ug/l selenium for the Salton Sea, Gunnison, and Middle Green areas, respectively, exceed the EPA (1986b) drinking water standard of 10 ug/l. Fewer than 10 percent of all samples from all areas had concentrations of selenium greater than 20 ug/l and these concentrations were found in samples from only nine areas. Large concentrations of selenium (>100 ug/l) were found in 18 samples (3 percent) from seven areas (Salton Sea, Tulare, Gunnison, Pine River, Sun River, Middle Green, and Kendrick).

In general, selenium concentrations in water in those areas where large concentrations (>100 ug/l) were found were not distributed evenly throughout the area and tended to be found principally in drainwater, ground water, or wetlands and associated ponds in or near areas of known selenium "hot spots." For example, in the Pine River area, out of a total of 69 samples, ten samples of ground water were collected with selenium concentrations ranging from 30 to 4800 ug/l. Ground water sampling on the other hand was biased to a known seleniferous area. Conversely, 26 out of the 59 samples collected at surface water sites in the Pine River area had selenium concentrations less than the detection limit of 1 ug/l. The median concentration for all samples from the Pine River area was 2 ug/l.

Selenium in Bottom Sediment

Analytical results of selenium in bottom sediment (Table 2) represent only the fine material (<0.062 millimeters in diameter) in surficial sediment (upper 50 millimeters). Samples were collected from streams and wetlands during conditions of low streamflow in each area, most frequently following irrigation season (October-November). Samples were sieved either in the field or in the laboratory and results were determined on both the fine material and the larger-size material between 0.062 millimeters and 2 millimeters in diameter. Because of the greater surface exposure of fine material, most transport of trace

constituents by sediment probably occurs in this phase. Only these data are discussed herein. Study areas in Table 2 are keyed by number to Figure 1. Analyses of bottom sediment samples were provided by the U.S. Geological Survey Geologic Division Laboratory in Denver, Colorado.

A total of 221 bottom sediment samples were collected from all areas and analyzed for total selenium concentrations. Compared to an upper limit of the expected 95 percent baseline range of 1.4 micrograms per gram ($\mu\text{g/g}$) dry weight (Feltz and others, 1991) for selenium in soils of the western United states, selenium concentrations in about 22 percent of the samples exceeded the baseline. Selenium concentrations in bottom sediment from all sites in the Klamath, Sacramento, Pine River, Milk River, Sun River, Stillwater, Malheur, and

Table 2. Total selenium concentrations in bottom sediment less than 0.262 millimeters from reconnaissance study area. (Units are micrograms per gram ($\mu\text{g/g}$) dry weight. Analytical reporting limit is 0.1 $\mu\text{g/g}$.)

Study Area	Abbreviated Name	Number of Samples	Range of observed concentrations ($\mu\text{g/g}$)	Median	Number of observations less than reporting limit
1	Klamath	13	0.1 - 0.7	0.6	0
2	Lower Colorado	12	<0.1 - 7.1	0.9	1
3	Sacramento	13	0.1 - 1.4	0.2	0
4	Salton Sea	17	0.1 - 3.3	0.7	0
5	Tulare	9	<0.1 - 19	0.2	1
6	Gunnison	6	1.5 - 41	2.2	0
7	Arkansas River	13	0.5 - 5.4	1.3	0
8	Pine River	10	0.2 - 0.8	0.5	1
9	American Falls	9	0.1 - 1.9	0.4	1
10	Milk River	6	0.3 - 6.7	0.4	1
11	Sun River	14	0.3 - 0.6	0.8	0
12	Stillwater	17	<0.1 - 1.2	0.5	1
13	Middle Rio Grande	11	0.2 - 0.4	0.3	0
14	Malheur	5	0.1 - 0.6	0.2	1
15	Angostura	9	0.6 - 14	1.0	0
16	Belle Fourche	10	0.5 - 2.8	0.9	0
17	Lower Rio Grande	15	0.3 - 0.7	0.4	0
18	Green River	9	<0.1 - 85	7.1	1
19	Kendrick	9	0.9 - 25	2.5	0
20	Riverton	14	0.1 - 3.0	0.4	0

Lower Rio Grande areas did not exceed the baseline. Conversely, selenium concentrations in all samples collected from the Gunnison area and nearly all samples from the Middle Green and Kendrick areas did exceed the baseline.

Median selenium concentrations for these three areas are 2.2, 7.1, and 2.5 ug/g respectively. Median concentrations do not exceed the baseline for any of the other areas. The maximum concentration of 85 ug/g was found in a sample from the Middle Green River Basin in Utah (area 18).

In some areas, elevated selenium concentrations in bottom sediment tend to correspond to elevated selenium concentrations in water (Gunnison, Middle Arkansas, Middle Green, and Kendrick areas). In the Klamath, Sacramento, and Malheur areas, where selenium concentrations in all water samples were less than the reporting limit, median concentrations of selenium in bottom sediment ranged from 0.2 - 0.6 ug/g and maximum concentrations ranged from 0.4 - 0.7 ug/g, all of which are considerably less than the baseline. These concentrations of selenium probably can be considered naturally occurring and at background levels.

Selenium in Fish

Analytical results of selenium in whole-body fish samples for all sampling sites from all reconnaissance study areas are presented in Table 3. Study areas are keyed by number to Figure 1 and all values represent selenium concentrations in micrograms per gram dry weight for whole-body fish samples. Results from all species from cold-water sport fish to warm-water bottom feeders collected from each area are combined in the data table. Analytical results were provided by Fish and Wildlife Service laboratories or their contract laboratories.

A total of 911 individual or composite fish samples from all areas were analyzed for total selenium concentrations. Concentrations ranged from 0.1 ug/g dry weight in a Utah sucker from the American Falls Reservoir to 50 ug/g dry weight in a carp from the Gunnison River Basin. Baumann and May (1984) indicate a threshold concentration of about 8.0 ug/g dry weight selenium for adverse reproductive effects in fish. Approximately 16 percent of all samples from all areas had concentrations exceeding 8 ug/g selenium, dry weight. Selenium concentrations for all samples from all sites in the Sacramento, Klamath, Tulare, American Falls, Milk River, Middle Rio Grande, Malheur, Belle Fourche, and Lower Rio Grande were less than 8 ug/g. In contrast, selenium concentrations in 58 percent of all samples collected from the Middle Arkansas area (median 11 ug/g) and in 80 percent of all samples collected from the Middle Green area (median 20 ug/g) were greater than 8 ug/g.

Although it was assumed that species-to-species differences in selenium uptake might occur, concentrations of selenium generally varied narrowly among all species collected at the same sampling site in areas where high concentrations of selenium in fish samples occurred. In many cases, however, average concentrations in all fish at one site varied widely with average concentrations in all fish at a different site in the same area. This indicates that all species of fish tend to accumulate selenium similarly in their body tissues and that the availability or nonavailability of selenium to the food chain is responsible for the differences in accumulation of selenium in fish among sites.

Table 3 Selenium concentrations in fish (all species) from reconnaissance study areas. Units are micrograms per dry weight ($\mu\text{g/g}$). [Analytical reporting limit is 0.1 $\mu\text{g/g}$.]

Study Area	Abbreviated Name	Number of Samples	Range of observed concentrations ($\mu\text{g/g}$)	Median	Percent of samples with concentrations $> 8.0 \mu\text{g/g}$
1	Klamath	19	0.43 - 1.2	0.70	0
2	Lower Colorado	31	2.4 - 16	6.1	32
3	Sacramento	27	0.50 - 2.0	1.4	0
4	Salton Sea	25	3.5 - 20	7.7	48
5	Tulare	33	0.60 - 4.3	1.5	0
6	Gunnison	55	1.3 - 50	5.0	27
7	Arkansas River	59	2.1 - 20	11	58
8	Pine River	153	0.92 - 16	4.2	16
9	American Falls	10	0.1 - 2.6	1.0	0
10	Milk River	2	2.3 - 2.5	2.4	0
11	Sun River	8	2.2 - 48	2.5	25
12	Stillwater	98	0.69 - 11	1.7	3.1
13	Middle Rio Grande	14	0.57 - 1.7	0.96	0
14	Malheur	11	0.66 - 3.1	2.0	0
15	Angostura	126	2.1 - 13	4.4	8.6
16	Belle Fourche	128	1.4 - 5.3	2.8	0
17	Lower Rio Grande	22	0.59 - 3.4	1.7	0
18	Green River	10	3.1 - 31	20	80
19	Kendrick	11	1.9 - 49	6.1	27
20	Riverton	69	0.48 - 15	5.9	28

Generally, for areas and sites within areas where elevated concentrations of selenium occurred in fish samples, elevated concentrations also occurred in water and bottom sediment. A comparison of median values indicated that concentrations of selenium in fish were higher than in water and in bottom sediment in all areas. This indicates that bioaccumulation of selenium occurs in all areas. Bioaccumulation is greatest in the Gunnison, Middle Green, and Kendrick areas, where the largest amounts of selenium occur in water and in bottom sediment.

Table 4. Selenium concentrations in bird livers (all species) from reconnaissance study areas. (Units are micrograms per gram (ug/g) dry weight. Analytical reporting limit is 0.1 ug/g. NA = not available.)

Study Area	Abbreviated Name	Number of Samples	Range of Observed concentrations (ug/g)	Median (ug/g)	Percent of sampled with concentrations greater than	
					9 ug/g	30 ug/g
1	Klamath	15	2.8 - 16	4.2	13	0
2	Lower Colorado	0	-	-	-	-
3	Sacramento	52	1.5 - 11	3.7	1.9	0
4	Salton Sea	23	6.7 - 42	19	78	4.3
5	Tulare	10	26 - 120	> 30	100	NA
6	Gunnison	17	6.5 - 84	31	88	53
7	Arkansas River	78	0.32 - 56	16	69	14
8	Pine River	9	4.2 - 50	6.8	44	22
9	American Falls	10	0.80 - 42	8.0	40	20
10	Milk River	14	2.1 - 7.4	3.4	0	0
11	Sun River	15	2.3 - 46	25	80	33
12	Stillwater	239	1.0 - 48	6.9	38	7.1
13	Middle Rio Grande	24	0.85 - 9.1	3.7	4.2	0
14	Malheur	15	3.9 - 36	14	80	6.7
15	Angostura	0	-	-	-	-
16	Bell Fourche	8	6.5 - 29	12	50	0
17	Lower Rio Grande	0	-	-	-	-
18	Green River	17	2.0 - 43	7.1	35	12
19	Kendrick	12	13 - 170	30	100	58
20	Riverton	32	1.3 - 35	9.0	51	2.9

Selenium in Bird Livers

Analytical results of selenium in livers from all waterfowl collected at sampling sites in 17 reconnaissance study areas are presented in Table 4. Study areas in Table 4 are keyed by number to Figure 1 and all values represent selenium in micrograms per gram dry weight. Samples were not collected from the Lower Colorado, Angostura, and Lower Rio Grande areas. Results from all species from which livers were collected and analyzed, including ducks, shorebirds, raptors, and others, are combined in the data from each area. Analyses of livers from both adult and juvenile birds are included in Table 4. It is understood that there may be species-to-species differences in selenium uptake and that this artificial grouping may interfere with interpretation of the data. Analytical results were provided by Fish and Wildlife Service laboratories or their contract laboratories.

Livers from a total of 590 adult and juvenile birds collected from the 17 areas were analyzed for total selenium concentrations. Ranges of observed selenium concentrations and median values are compared to a level of 9 ug/g dry weight, which is the lower concentration of a range of 9 - 41 ug/g associated with adverse reproductive effects in mallards, including reduced egg laying and survival of chicks, according to Heinz and others (1987). Ranges and medians also are compared to a level of 30 ug/g dry weight above which embryonic deformities in birds are likely to occur (Skorupa and others, 1990).

Selenium concentrations in bird livers ranged from <0.32 ug/g dry weight in the liver of a coot from the Middle Arkansas River Basin to 170 ug/g dry weight in the liver of an avocet from the Kendrick Reclamation Project Area. Selenium concentrations were less than 9 ug/g in livers of all birds collected from the Milk River area. The selenium concentration (9.1 ug/g) in the liver of one bird from the Middle Rio Grande area exceeded 9 ug/g. Median selenium concentrations were less than 9 ug/g for these areas as well as for the Klamath, Sacramento, Pine River, American Falls, Stillwater, Middle Green, and Riverton areas. Median selenium concentrations exceeded 9 ug/g for 7 areas and were 30 ug/g or greater for the Tulare, Gunnison and Kendrick areas. Selenium concentrations in bird livers exceeded 30 ug/g in approximately 10 percent of all birds from all areas and exceeded 9 ug/g in approximately 46 percent of all birds. Deformed birds were found in the Tulare, Sun River, Stillwater, Middle Green, and Kendrick areas but the cause of the deformities in the birds at the Stillwater area may be a trace constituent other than selenium.

Some birds collected at 16 of the 17 sites accumulated selenium in their livers in potentially harmful quantities (> 9 ug/g). This occurred even in areas where selenium concentrations in other sampled media generally were low. This shows that selenium is readily bioaccumulated. Because mostly adult birds were collected, there is no way to know for certain whether the selenium in the liver was obtained at nearby sites, or from sites in other areas long distances away. However, the sampling programs were set up such that only adult birds thought to have arrived in the areas several weeks earlier were collected.

SOURCES OF SELENIUM

Cretaceous-age marine shales probably are the original sources for selenium in 16 of the 20 areas studied. This may be a direct or indirect relationship. For example, the Cretaceous-age Cody Shale underlies part of the Kendrick area and some soils formed directly on the shale. Selenium accumulating plants are found in the area. Large concentrations of selenium, presumably leached from the soil, were found both in water and bottom sediment samples from the area and in whole fish and livers of some of the birds collected from the area. Conversely, the Salton Sea area is an example of Cretaceous-age shales as an indirect source of selenium. No selenium sources occur in the vicinity of the Salton Sea area, but small amounts of selenium are contained in irrigation water diverted to the All-American Canal from the Colorado River. Selenium in the Colorado River is from Cretaceous-age deposits located in the Colorado River Basin upstream of the All American Canal diversion. Evaporative concentration of the irrigation water is the mechanism responsible for elevated selenium concentrations in water, bottom sediment and biota in the Salton Sea area.

Permian-age deposits, lacustrine deposits, and Cenozoic-age volcanic deposits may be sources for extremely limited amounts of selenium in the other four areas.

GENERAL OBSERVATIONS

Several observations based on data from all 20 areas are summarized below:

- 1) In areas where large concentrations of selenium in water were found, concentrations were not widely distributed over the area, but were found principally in drainwater, ground water, ponds, or wetlands.
- 2) Elevated selenium concentrations in bottom sediment generally tend to correspond with elevated selenium concentrations in water.
- 3) All species of fish sampled tend to accumulate selenium in their body tissues.
- 4) Comparisons of median selenium concentrations in water and in fish tissue, and in bottom sediment and fish tissue indicate that bioaccumulation of selenium occurs in all areas.
- 5) The normal ratio of median bird liver selenium concentration to bottom sediment selenium concentration appears to be in the 7:1 to 31:1 range.
- 6) Cretaceous-age marine shales are the principal sources of selenium in 16 of the 20 areas studied.
- 7) The potential for irrigation-induced water quality problems is enhanced in areas where closed drainage basins or sinks occur. Evaporative concentration of selenium may occur in these and other areas.
- 8) Climatic conditions, including variations in rainfall and streamflow, may affect the potential for irrigation-induced water quality problems from selenium and other trace constituent concentrations.

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