THE POTENTIAL FOR HEAVY METAL MIGRATION FROM SEDIMENTS OF LAKE COEUR D'ALENE INTO THE RATHDRUM PRAIRIE AQUIFER, KOOTENAI COUNTY, IDAHO

Susan A. Wyman

May, 1993

Idaho Water Resources Research Institute
Leland L. Mink, Ph.D., Director

Research Technical Completion Report

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ABSTRACT

The purpose of this project was to determine the potential for migration of heavy metals of Lake Coeur d'Alene into the Spokane Valley/Rathdrum Prairie Aquifer, as a result of changing lake chemistry caused by eutrophication. The upper sediment layers in Lake Coeur d'Alene are enriched in heavy metals and the lake appears to be becoming more eutrophic.

The geologic history of the region contributes to the understanding of the hydrogeology of the study area. The coarse-grained glacial outwash aquifer is bounded below by fine-grained sediments of the Latah formation, and bounded laterally by Precambrian sediments and metasediments. A conceptual model for surface water/groundwater interaction reveals that the cross sectional area of the aquifer increases from the northern end of Lake Coeur d'Alene farther into the aquifer. This could account for the steep hydraulic gradient from the lake to the aquifer. The steep gradient could also be a result of fine sediments which have infiltrated the glacial outwash and have decreased the hydraulic conductivity of the aquifer, adjacent to the lake. Evidence for the infiltration of fine material exists in grain size analyses and unpublished reports.

Lake Coeur d'Alene is dimictic and oligotrophic to eutrophic. Oxygen enrichment in the epilimnion and depletion in the hypolimnion are well-documented phenomena in eutrophic lakes. Dissolved oxygen concentrations as low as 52% were measured by the USGS northeast of Blue Point near Harrison in September, 1991. Anoxic, reducing conditions in the hypolimnion during summer stratification of the water column may cause Mn and Fe mobilization from sediments. Dissolved heavy metals in the hypolimnion are likely to coprecipitate with Mn oxyhydroxides (and to a lesser extent iron hydroxides) when the metals encounter more oxygenated water.

Seismic profiles of the lake bottom indicate that fine, laminated sediments cover the central portions of the lake and thin out near the lake margins. These sediments contain elevated metals concentrations in both particulate form and in sediment pore water. The concentration gradient of metals in pore waters probably contributes to the upward migration of metals and the development of an enriched band of Fe, Mn and other trace metals in the sediment column. The band of Fe and Mn may reduce the concentration of trace metals in the water column (Sigg, 1987).

The bulk of the water which moves from the lake into the aquifer during the summer "low flow" period leaves Lake Coeur d'Alene as underflow. The area through which most water moves is probably within 300 feet (90 m) of the shore, where fine, laminated lake bottom sediments are lacking. This zone is probably well oxygenated for most of the year.

Analyses from four monitoring wells at the surface water-groundwater interface reveal that metal concentrations are elevated in groundwater. Concentrations of Fe and Mn exceeded EPA SMCLs in all four wells. Three wells exceeded EPA MCLs for selenium. Well AIP-2 exceeded EPA MCLs for As, Cd and Pb.

Clay samples from the well were highly enriched in As, Co and Cu, but only slightly above average background concentrations in Fe, Mn, Zn, U, and Th. The concentrations of Pb, Ni, Sr, V, and Cr in clays were slightly below average background concentrations. Metal migration into the aquifer does not appear to be attenuated by ionic adsorption onto clay materials.

Eutrophication may have positive benefits for metal removal from the water column, as algae and Mn adsorb and precipitate trace metals. This benefit may be offset by the reducing conditions and elevated pH which result from aphotic biological activity in the hypolimnion.

ACKNOWLEDGEMENTS

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1.0 INTRODUCTION

1.1 Purpose/Problem Statement

Lake Coeur d'Alene and the Spokane River contribute approximately 30% of the total recharge to the Spokane/Rathdrum Prairie Aquifer (Painter, 1991(b)). Sediments in the recharge zone contain elevated levels of Ag, Cd, Co, Hg, Sb, and Zn. These heavy metals (and the metalloid, As) may represent a threat to drinking water in the "sole source" aquifer. Changes in surficial water chemistry, due to the eutrophication of Lake Coeur d'Alene, may affect the stability of metals contained in sediments. The purpose of this study was to evaluate the potential for the migration of heavy metals from Lake Coeur d'Alene sediments into the Rathdrum Prairie Aquifer.

1.2 Objectives

The specific objectives of this study were to:

1. Identify drinking water supplies most likely to be affected by the Spokane River and/or Lake Coeur d'Alene.
2. Identify all NPDES (National Pollutant Discharge Elimination System) sources to surface water in the study area.
4. Conduct a comprehensive literature search for technical papers on subsurface heavy metal migration, emphasizing both laboratory column studies and research in mining areas with heavy metal contamination.
5. Conduct a literature search for information regarding Lake Coeur d'Alene and Spokane River sediments, the Spokane River/Rathdrum Prairie Aquifer hydraulic characteristics, local geology and water chemistry data.
6. Develop a conceptual model for surface water/groundwater interaction in the Lake Coeur d'Alene/Spokane River study area.
7. Identify possible changes in lake chemistry, based on existing and available limnological studies.
8. Evaluate potential effects of changes in lake chemistry on heavy metal migration.
9. Verify the aforementioned predictions by sampling and analyzing groundwater proximal to the northern shore of Lake Coeur d'Alene.
10. Identify specific areas, if any, for further study.

1.3 Description of the Study Area

1.3.1 Location

The Spokane Valley/Rathdrum Prairie Aquifer occupies 408 square miles in Spokane County, Washington, and Kootenai and Bonner Counties, Idaho (Figure 1). The 283 square mile portion of the

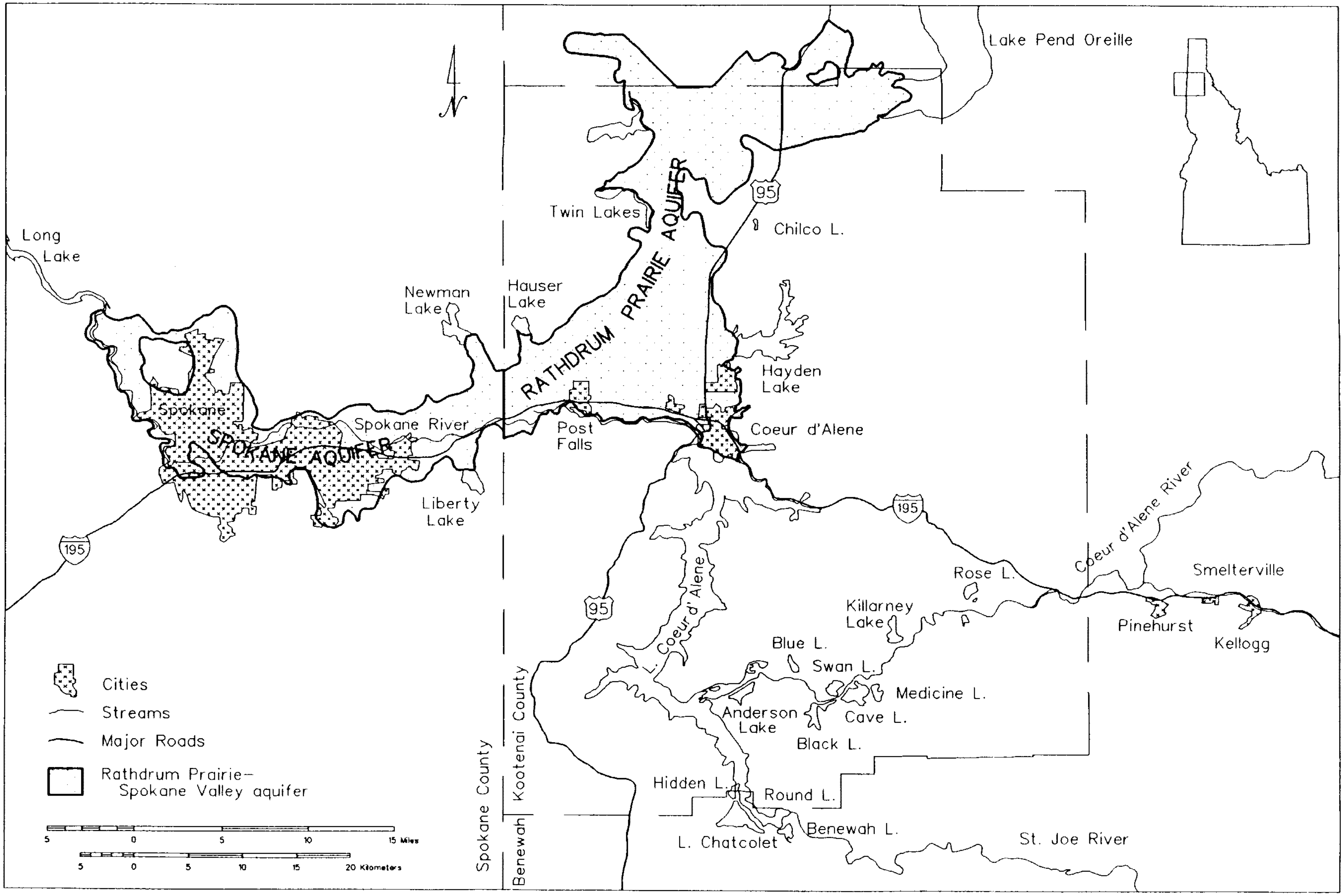


Figure 1. Location of the Rathdrum Prairie-Spokane Valley aquifer.

aquifer in Idaho is known as the Rathdrum Prairie Aquifer. The five to 17 mile-wide, valley-fill aquifer extends south from the outlet of Lake Pend Orielle to the outlet of Lake Coeur d'Alene and westward to the Washington/Idaho state line. The Spokane Valley Aquifer extends west to the mouth of Hangman Creek at Long Lake, west of Spokane, Washington.

The Rathdrum Prairie Aquifer occupies a glacially scoured trough (and fluvially eroded valley) between Mount Spokane to the north, the Mica Peak uplands to the south, and the Coeur d'Alene Mountains to the east (Figure 2). The elevation of Rathdrum Prairie surface decreases from 2360 feet (719.3 m) in the northern Rathdrum Prairie to 2120 feet (646.2 m) near the state line. The irregular relief of the gravel surface is due to the abandoned channels of streams which traversed the valley during the late Pleistocene epoch (McKinness, 1988).

The flat to rolling topography has no established surface drainage. Instead, tributary lakes and streams drain into the porous aquifer material. The Spokane River is the only continuous surface stream in the Rathdrum Prairie and Spokane Valley. The Spokane River, the surface outlet for Lake Coeur d'Alene, flows east to west along the southern margin of the Rathdrum Prairie, in places perched well above the water table aquifer.

Lake Coeur d'Alene lies within a naturally dammed river valley. The lake is approximately 210 feet (64 meters) deep and covers approximately 50 square miles (130 km^2). The St. Joe River flows into the southern end of Lake Coeur d'Alene from the east. The Coeur d'Alene River flows westward from its headwaters on the Montana/Idaho border to the central portion of Lake Coeur d'Alene. Together these two rivers provide 94% of the inflow to the lake.

This study focuses on the zone of recharge into the Rathdrum Prairie Aquifer at the northern end of Lake Coeur d'Alene and the nine mile (1.4 km) stretch of the Spokane River from the outlet of Lake Coeur d'Alene to Post Falls (Figure 3). At land surface, 2130 feet (650 meters) above sea level, the boundary between the lake and the aquifer spans approximately four miles, from the southern edge of the Spokane River to Tubbs Hill and from the north east edge of Tubbs Hill to the base of Potlatch Hill.

1.3.2 Climate

The climate of the area is strongly seasonal. Warm, sunny weather usually prevails from June through August, giving way to rainy weather in the fall and spring. Most of the precipitation in the area occurs as snow during the winter months.

Coeur d'Alene receives an average of 25.79 inches (65.5 cm) of precipitation annually. Fifty one percent of the annual precipitation occurs in the months of November, December, January and February (Figure 4). Only 19% of the annual precipitation is received during June, July, August and September (NOAA, 1982).

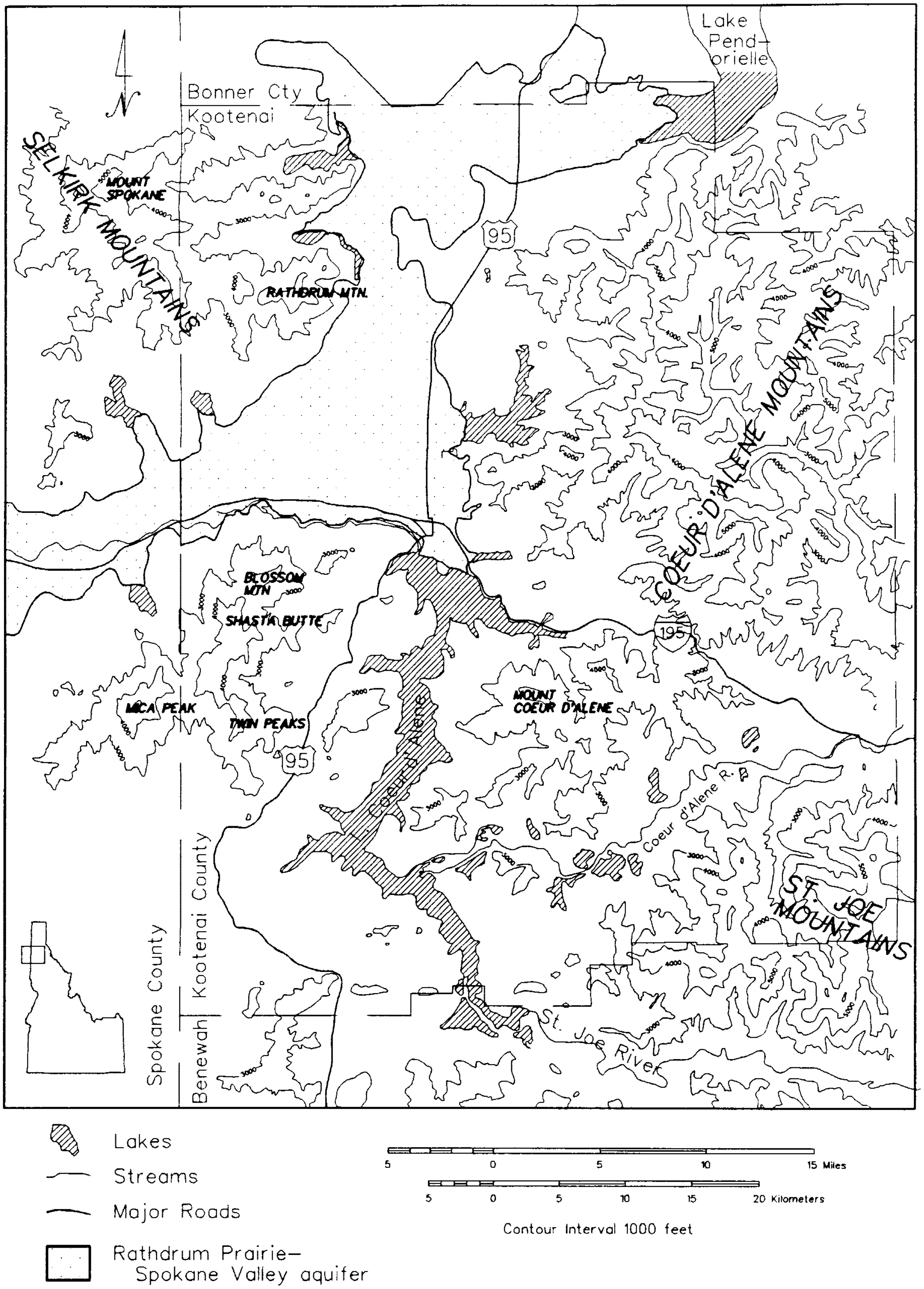


Figure 2. Topography of the southeastern Rathdrum Prairie aquifer and adjacent areas.

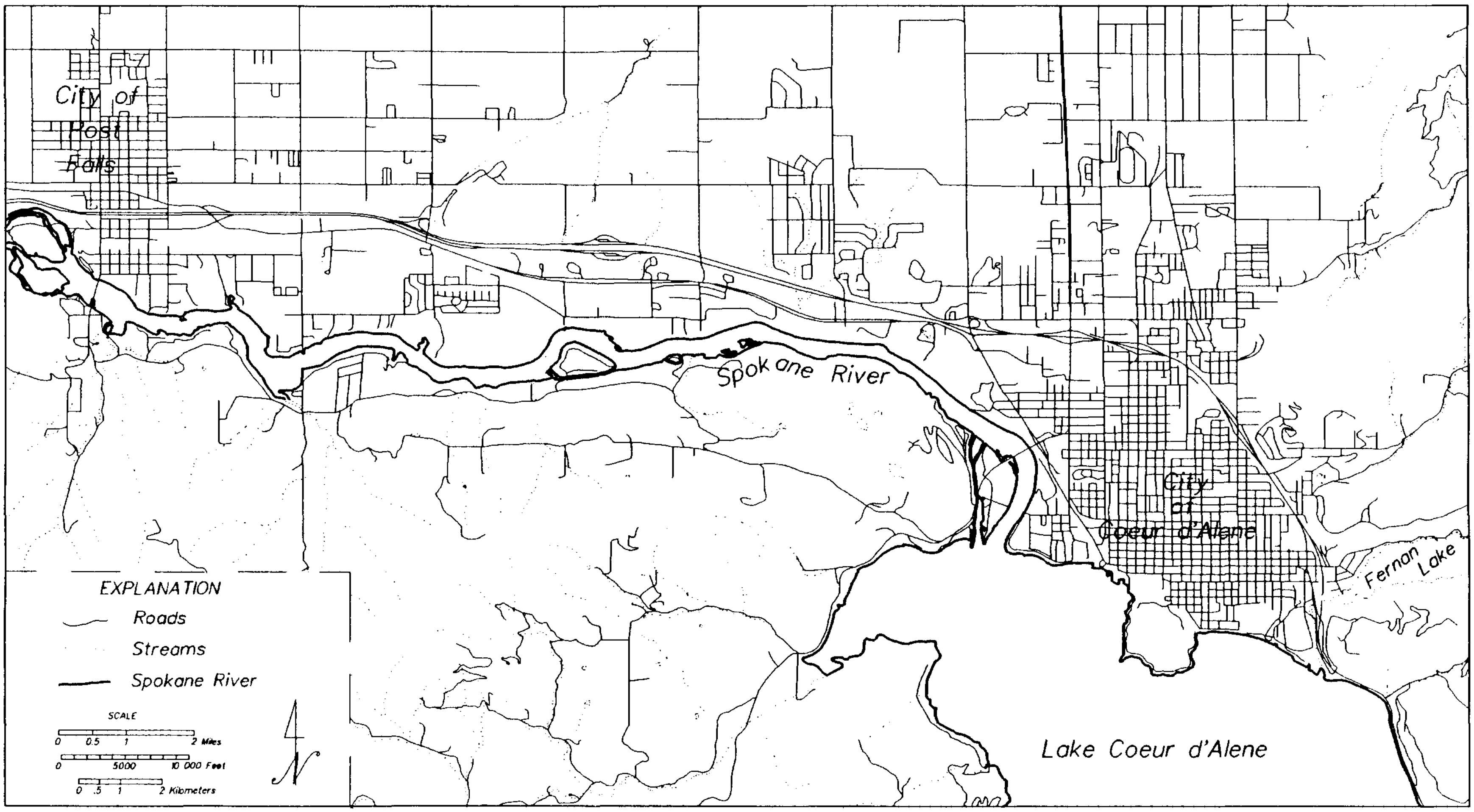


Figure 3. The study area includes the northern margin of Lake Coeurd'Alene and the nine mile reach of the Spokane River from the lake outlet to Post Falls Dam.

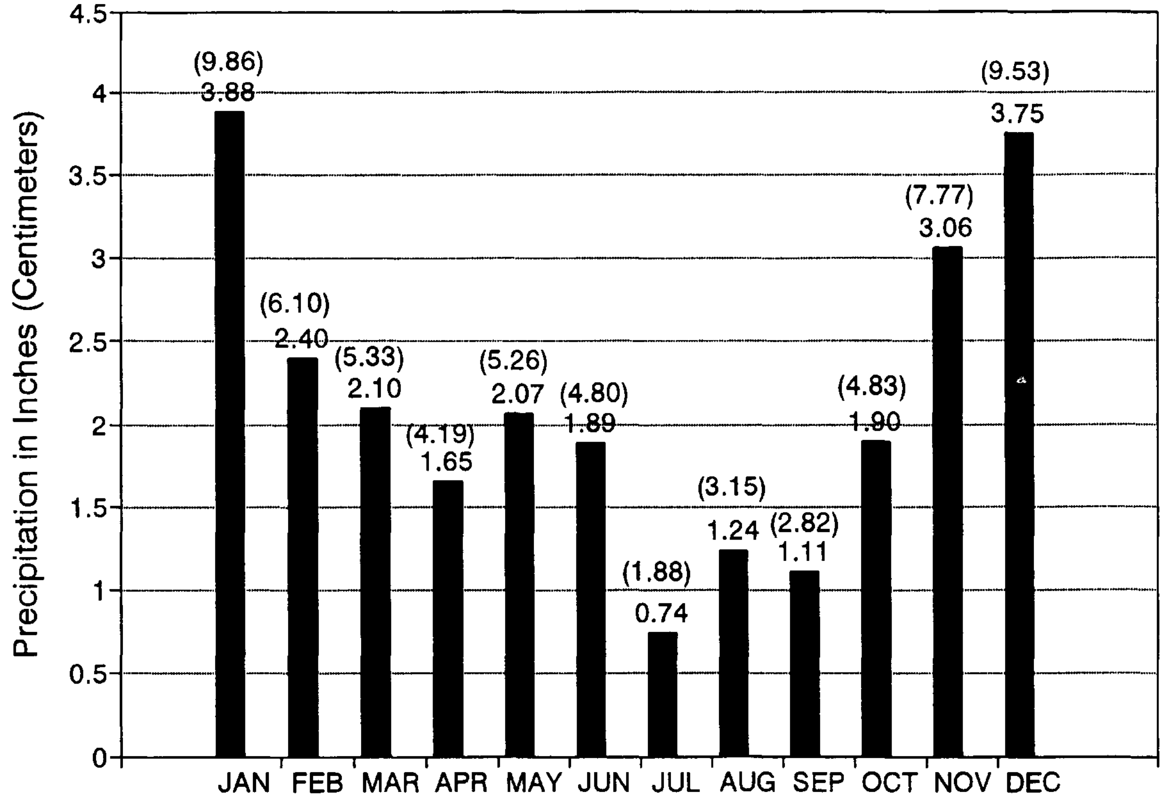


Figure 4. Monthly mean normal precipitation in Coeur d'Alene, Idaho, 1951-1980, in inches and centimeters.

The normal high temperature is 34.6°F (1.4°C) in January, 86.0°F (30.0°C) in July and 59.7°F (15.4°C) annually (Figure 5). Normal low temperatures range from 21.8°F (-5.7°C) in January to 52.4°F (11.3°C) in July, with an annual normal low of 36.8°F (2.7°C). Mean (average) normal temperatures are 28.2°F in January and 69.2°F in July. Average normal temperature is 48.3° F (9.06° C) annually.

1.3.3 Cultural Geography

Population

An estimated 62,600 persons reside in Kootenai County, Idaho. Most of the population is concentrated along the edge of the eastern and south central portion of the Rathdrum Prairie, in the cities of Hayden Lake, Dalton Gardens, Coeur d'Alene and Post Falls. The majority of the 337,000 people who reside in Spokane, Washington (State of Washington Population Trends, 1980) also live above the aquifer.

Kootenai County had greater than average population growth during the 1970's (University Research Center, BSU, 1985). The rate of population growth is expected to be slower than average from 1980 to the year 2000. The number of residents is expected to grow from an estimated 62,600 in 1990 to

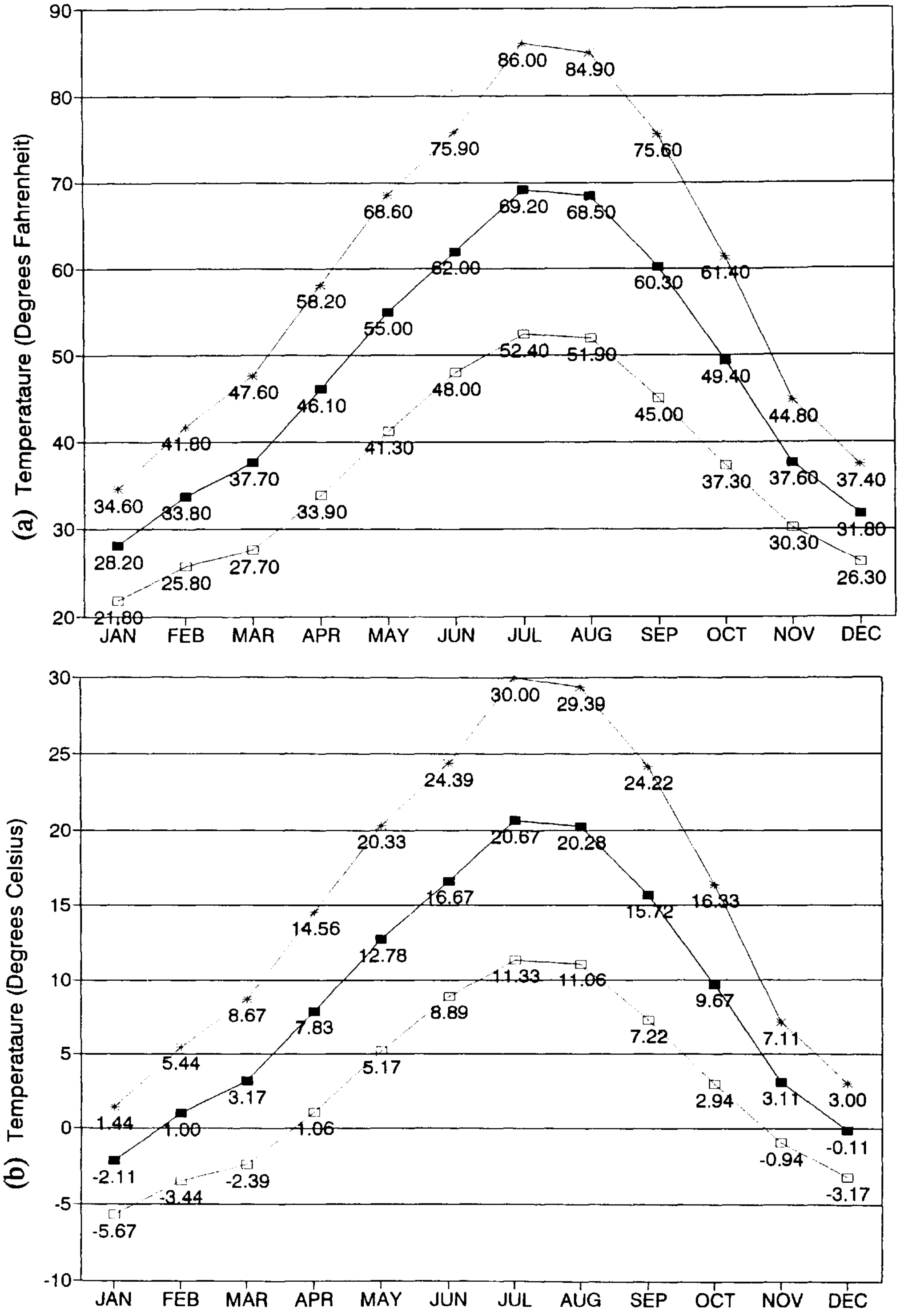


Figure 5. Monthly normal low, mean and high temperatures in Coeur d'Alene, Idaho, 1951-1980, presented in (a) degrees Fahrenheit and (b) degrees Celsius.

64,200 by 1995 and 71,400 by the year 2010.

Increased population leads to greater environmental pressures. As more houses are built along the shores of Lake Coeur d'Alene, both the number of septic tanks and the volume of nutrients (particularly nitrates) supplied to the lake will increase. [The Panhandle Health District is currently conducting a study to determine the number of sewered homes and septic systems adjacent to Lake Coeur d'Alene, for use in predictive models of eutrophication.] The consumption of groundwater for drinking water and the potential for chemical contamination of the aquifer are expected to increase with the predicted increase in population.

Groundwater and Surface Water Uses

The Spokane Valley/Rathdrum Prairie Aquifer supplies water to the cities of Spokane, Otis Orchards, Hayden Lake, Rathdrum, Spirit Lake, Coeur d'Alene and Post Falls. Large quantities of water are withdrawn for irrigation, industrial, municipal and domestic uses. Approximately 46,400 (over 70%) of the residents of Kootenai County receive their domestic water from public water supply (PWS) systems which withdraw water from the Rathdrum Prairie Aquifer (Painter, 1991 (a)). Most of the remaining residents obtain water from private wells in the aquifer, although some wells are located in local granitic and basaltic aquifer systems.

Lake Coeur d'Alene is used for log transport and storage, as well as recreational activities such as boating, sightseeing, swimming and windsurfing. The Coeur d'Alene Tribe also uses the lake for ceremonial and spiritual activities. The Spokane River is used for boating, log transport and hydroelectric power generation.

Sole Source Aquifer Designation

The Spokane Valley-Rathdrum Prairie Aquifer was designated as a "sole source" aquifer by the US Environmental Protection Agency in 1978, in accordance with Public Law 93-523, the 1974 Federal Safe Drinking Water Act. During May, 1977, through June, 1978, the Spokane County Water Quality Management Program (208 Program) conducted a comprehensive investigation of the aquifer in Washington. A "cause and effect" report was published and several groups petitioned the U.S. Environmental Protection Agency for "sole source" designation. The U.S. Geological Survey prepared a report on the Spokane-Rathdrum Aquifer and submitted it to the U.S. EPA for "sole source" consideration. The aquifer was declared a "sole source" of water supply for the greater Spokane and Coeur d'Alene metropolitan areas.

Mining History

Mining activities in the Coeur d'Alene area began in 1884, after A.J. Pritchard reportedly discovered gold on Pritchard Creek, a tributary of the North Fork of the Coeur d' Alene River (Day, 1963). N.S. Kellogg discovered lead/silver deposits on Milo Creek and the South Fork of the Coeur d'Alene River in August, 1885. The Bunker Hill and Sullivan mines were in operation by April, 1886 (Stoll, 1932). Active mine production has been maintained in the district since 1885.

In the early years of mining, the ore was concentrated by a gravity separation process known as jigging. The rock was crushed and placed in a "jig"--a box with a screen at the top. The "jig" was filled with water and a plunger was moved up and down to separate the heavy from the light grains. The lightest grains migrated to the top of the mass and were discarded as waste. Because of the inefficiency of the process, the waste, known as jig tailings, had very high concentrations of valuable metals. These tailings were discharged directly on the ground or into a nearby stream.

The selective flotation process replaced gravity separation method for metal recovery by 1916. The ore was ground to a fine pulp, mixed with water and xanthates (chemical flotation agents) and agitated. Bubbles rose to the surface to form a mineralized froth, which was skimmed off for further refinement. The fine (0.295-0.044 mm) waste material usually contained residual metals and was discharged into the river or on the ground.

The Coeur d'Alene River experienced severe suspended sediment problems as a result of the discharge of waste material until 1968 when the federal government required the installation of tailings settling ponds. Liquids, such as contaminated mine water at the Bunker Hill mine (and probably most other mines) were discharged directly into the river until a Central Impoundment Area (CIA) was constructed.

Much of the fine sediment introduced to the Coeur d'Alene river between 1916 and 1968 moved downstream and was deposited in the lateral lakes of the Coeur d'Alene River and in Lake Coeur d'Alene. The largest and heaviest fractions which reached Lake Coeur d'Alene settled out relatively close to the mouth of the Coeur d'Alene River. Very fine suspended sediment and dissolved metals were carried farther out into the lake and deposited.

1.3.4 Geologic Setting

Five general rock units comprise the boundaries and water-bearing portion of the southeastern Rathdrum Prairie Aquifer (Figure 6). The aquifer itself is composed of thick deposits of sand, gravel and silt. The aquifer is bounded below by the Latah Formation which is characterized by thick sequences of shale or clay with some sands and gravels (Pardee and Bryan, 1926). The Latah beds lie unconformably over pre-Tertiary sediments, metasediments and granitic rocks. Intercalated with the Latah formation, peripheral to the aquifer, lie Miocene age basalts of the Columbia River Basalt Group.

The pre-Tertiary age rocks of the Spokane Uplands and Mica Peak, north and south of the southern Rathdrum Prairie, respectively, have been mapped as both highly metamorphosed Precambrian sediments of the Belt Supergroup (Griggs, 1973; Harrison, *et al.*, 1972) and pre-Belt schists and gneisses

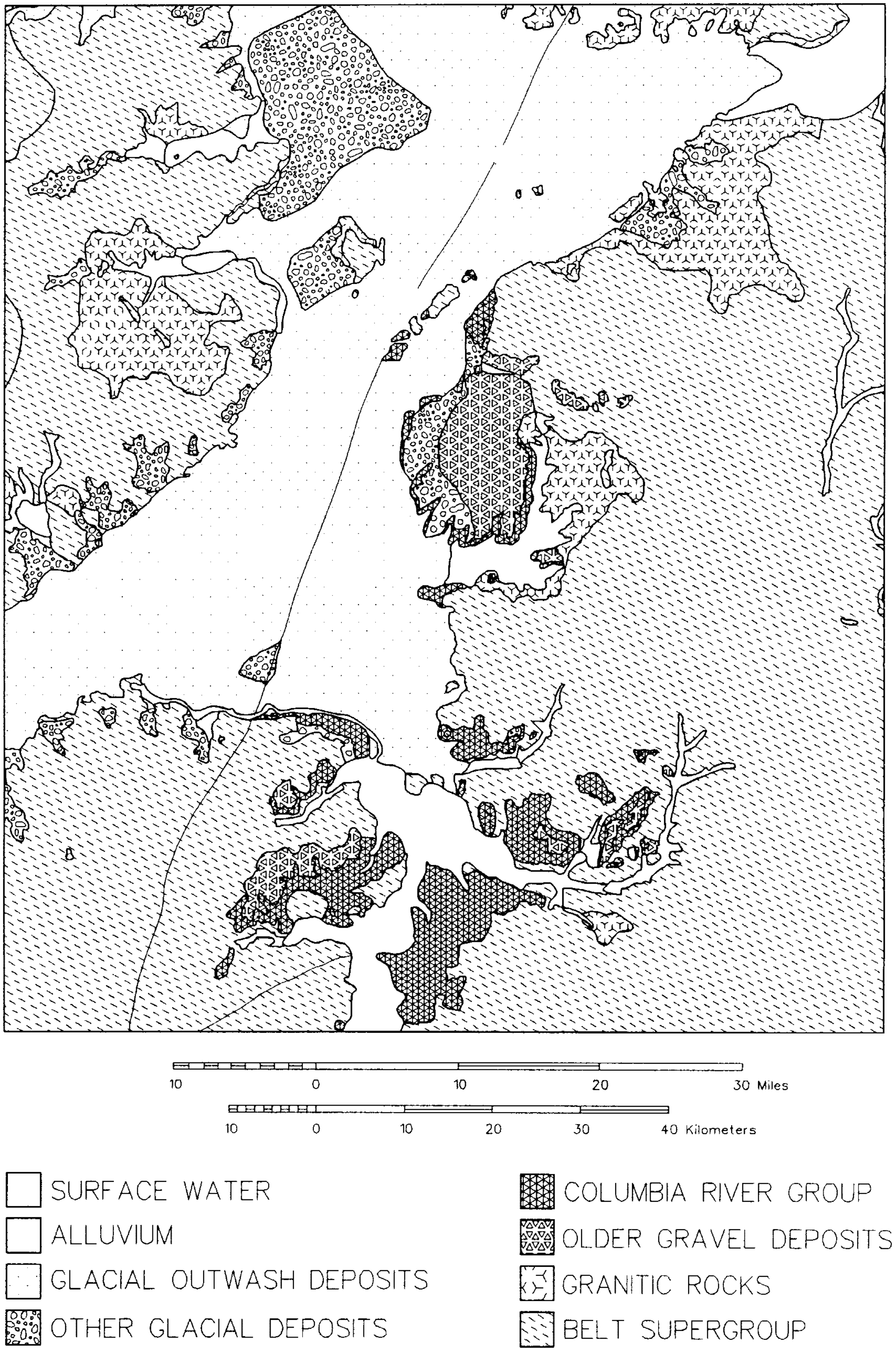


Figure 6. Geology of the southern Rathdrum Prairie.

(Cheney, 1980; Winston, *et al.*, 1989). Authors agree that the Coeur d'Alene Mountains, east of the Rathdrum Prairie, are primarily metasedimentary rocks of the Belt Supergroup, including the Prichard, Burke, Revett and St. Regis Formations (Anderson, 1940; Griggs, 1973; Harrison, *et al.*, 1972). Locally, all of these rocks have been intruded by granitic rocks of Cretaceous age. The pre-Tertiary and Cretaceous age rocks generally have very low permeabilities and act as an impervious basement which underlies the entire area.

Remnants of the Miocene-age lacustrine Latah Formation, Grande Ronde basalt and the Priest Rapids member of the Wanapum basalt can be found at the margins of the aquifer, along the Spokane River, north of Hayden Lake, and in wells in the western parts of the aquifer. Griggs (1973), McKinness (1988) and Swanson, *et al.*, (1979) mapped exposures of basalt and Latah Formation along the valley margins in the vicinity of the north end of Lake Coeur d'Alene (Figure 7).

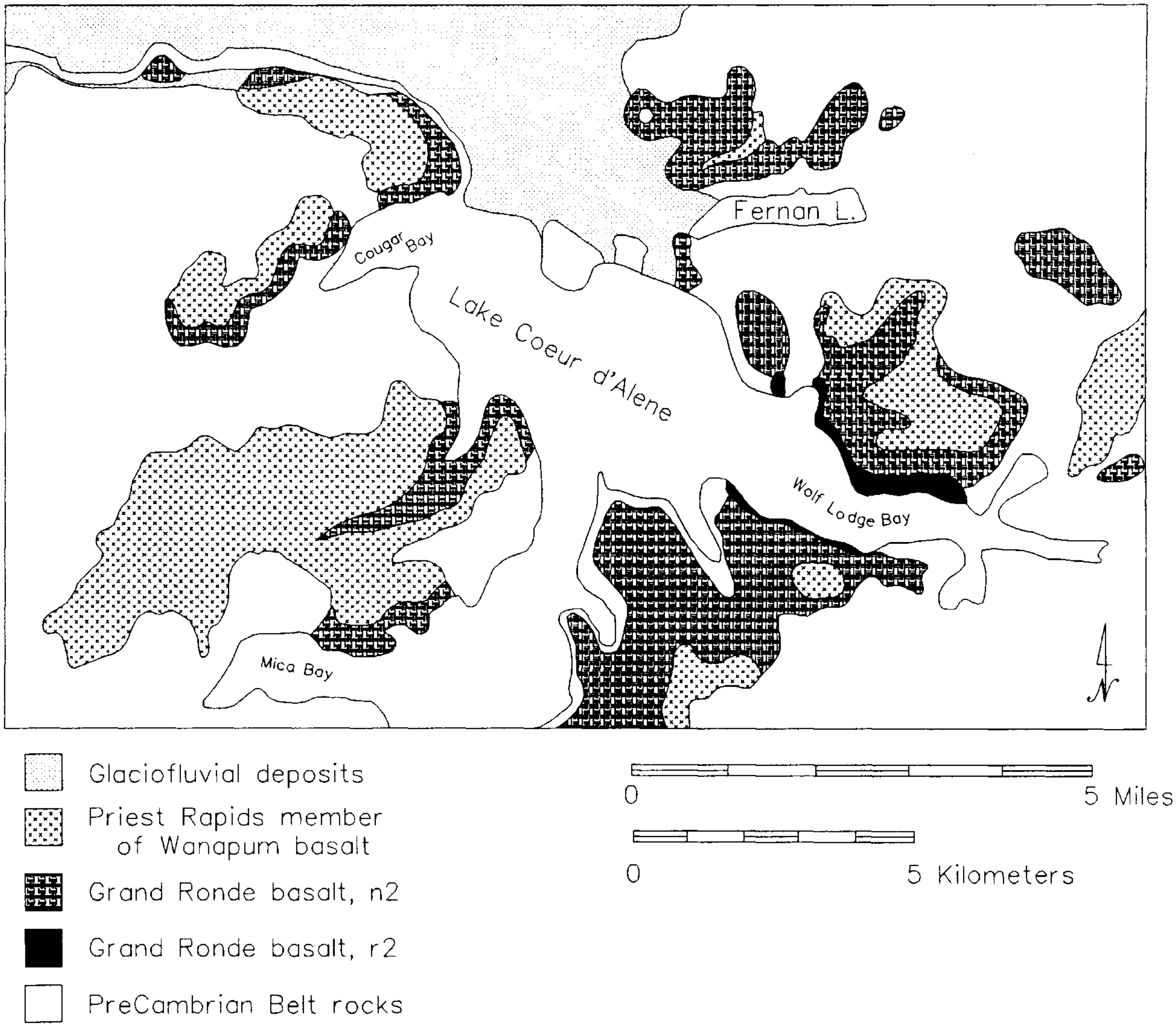


Figure 7. Basalt along the northern margins of Lake Coeur d'Alene (after Swanson, *el al.*, 1979).

The Purcell Trench exerts the dominant structural control. This trench forms a graben which developed during the Late Mesozoic and Early Cenozoic Eras as the Kaniksu Batholith cooled. The structure extends from 200 miles north of the Canadian border south to the Rathdrum Prairie. The major north-south trending valley between the Coeur d'Alene Mountains and the Mt. Spokane Uplands, in the northern Rathdrum Prairie, is the probable southern extension of the Purcell Trench (Harrison, *et al.*, 1972). Lake Pend Orielle occupies part of the Purcell trench, and some authors believe that the trench extends as far south as Lake Coeur d'Alene. Jehn (1988) asserts that the Purcell Trench extends southward to Coeur d'Alene and then curves westward toward Spokane. If so, the bulk of the Rathdrum Prairie Aquifer is contained by the Purcell Trench.

1.3.5 Geologic History

An understanding of the geologic history of the Coeur d'Alene region is vital to the formulation of a hydrogeologic conceptual model. Ancestral stream drainage patterns, geologic structure and lithology controlled the deposition of sediments in the past and therefore affect the occurrence and movement of ground water today.

The Belt Rocks and Cambrian Sediments

The oldest rocks in the study area are highly metamorphosed pre-Belt or Belt crystalline rocks. The sediments of the Belt Supergroup were deposited in a large, shallow marine basin, during the Precambrian Era, from 1,450 to 850 million years ago (Winston, *et al.*, 1989). Low grade regional metamorphism altered the thick sequences of sediments to quartzites, siltites and argillites, while intrusions of gabbroic-dioritic dikes and sills were emplaced during the Precambrian Era.

As much as 20,000 feet (6100 meters) of Belt sediments were eroded before the Paleozoic Era (Connors, 1976). During the Cambrian period, sandstones, limestones and shales were deposited on top of the Belt rocks by transgressive seas. Most of these sediments were removed during the long period of erosion since the end of the Cambrian period.

The remaining Belt rocks were intruded by granitic plutons which apparently originated from the Kaniksu Batholith (Weissenborn and Weis, 1976) which was emplaced during the Cretaceous period (Larsen, *et al.*, 1958). Faulting which accompanied the emplacement of the Kaniksu batholith produced the 280 mile long (448 km) Purcell Trench (Harrison, *et al.*, 1972).

Basalts and Sediments

A mature, deeply dissected, erosional surface had developed by early Miocene time. It is believed that the ridge crests and mountain tops had gently rounded forms (Molenar, 1988) and some rugged canyons were 2,000 feet (610 m) or more in depth (Connors, 1976). Newcomb (1953) interpreted seismic data to indicate that the Spokane Valley was v-shaped at this time.

Rivers flowed generally to the southwest in a well developed drainage system (Figure 8). A major drainage extended from the valley of Lake Pend Orielle to Spokane via the Rathdrum Prairie. The "Rathdrum River", ancestral to the Spokane River, drained the basins of what are now known as the Clark Fork River, Kalispell River, Priest River and Pend Orielle. The canyon of the Rathdrum River was deeply entrenched, perhaps 1000 feet (305 m) below present Rathdrum Prairie (Savage, 1965).

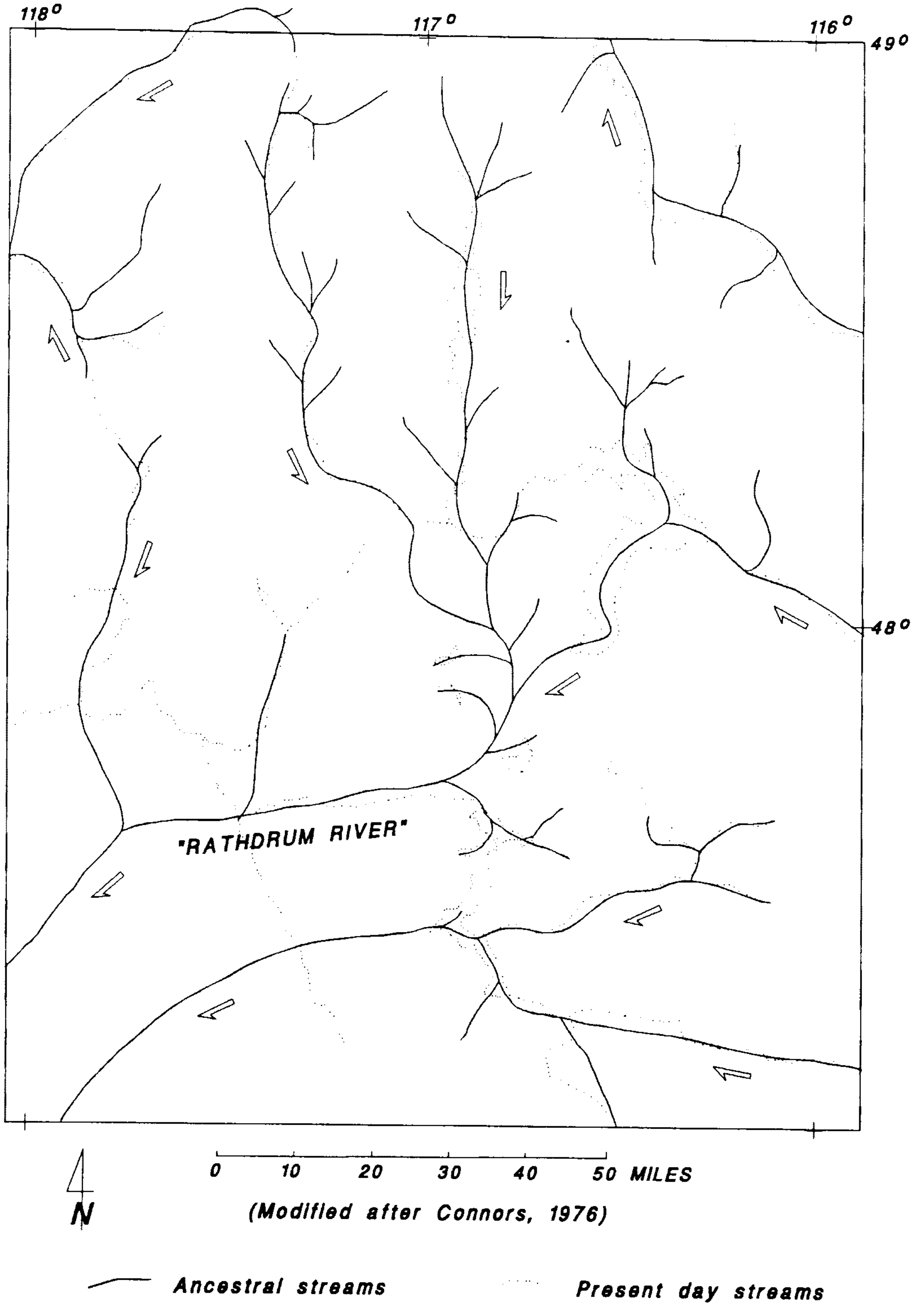
Basaltic lava flows encroached on the region from the southeast during the Miocene Period. The Rathdrum River and other streams were repeatedly blocked by lava dams as basalt flowed up-drainage into the Spokane Valley from the Columbia Plateau. Lakes formed in the deep valleys behind the basalt flows. Silts and clays, derived from basement rock, accumulated in these lakes to depths of up to 1500 feet (542.5 m) in the Spokane area (Pardee and Bryan, 1926; Knowlton, 1926). These sediments, known as Latah Formation, consist predominately of white, yellow, orange and brown lacustrine silt and clay beds which contain some fluvially deposited sand and gravel units (McKinness, 1988).

Basalt flows continued to accumulate progressively farther up-valley. Basalt and Latah sediments filled in most of the Rathdrum and Spokane Valleys to an elevation of at least 2400 feet (730 m) (Kiver and Stradling, 1989). Grande Ronde basalt (14.0 to 16.5 mybp [Meyers, Price, *et al.*, 1979]) covered the thousand feet of Latah beds in the vicinity of the present day outlet of Lake Coeur d'Alene. The basalt was then covered by additional Latah beds which were subsequently covered by another Grande Ronde Basalt flow. Approximately 40 feet (13 m) of Latah beds were deposited above the Grande Ronde flows in the study area, only to be covered by the olivine-rich "rim rock" basalt (Priest Rapids member of Wanapum basalt) just prior to 13.5 mya (Myers, Price, *et al.*, 1979).

The basalt and sediments were then excavated by stream erosion. The valley was cut more than 800 feet (244 m) in the Latah Creek (Washington) area, and perhaps 500 feet (152 m) in the vicinity of present day Lake Coeur d'Alene. Then another series of basalt flows almost filled up the valleys.

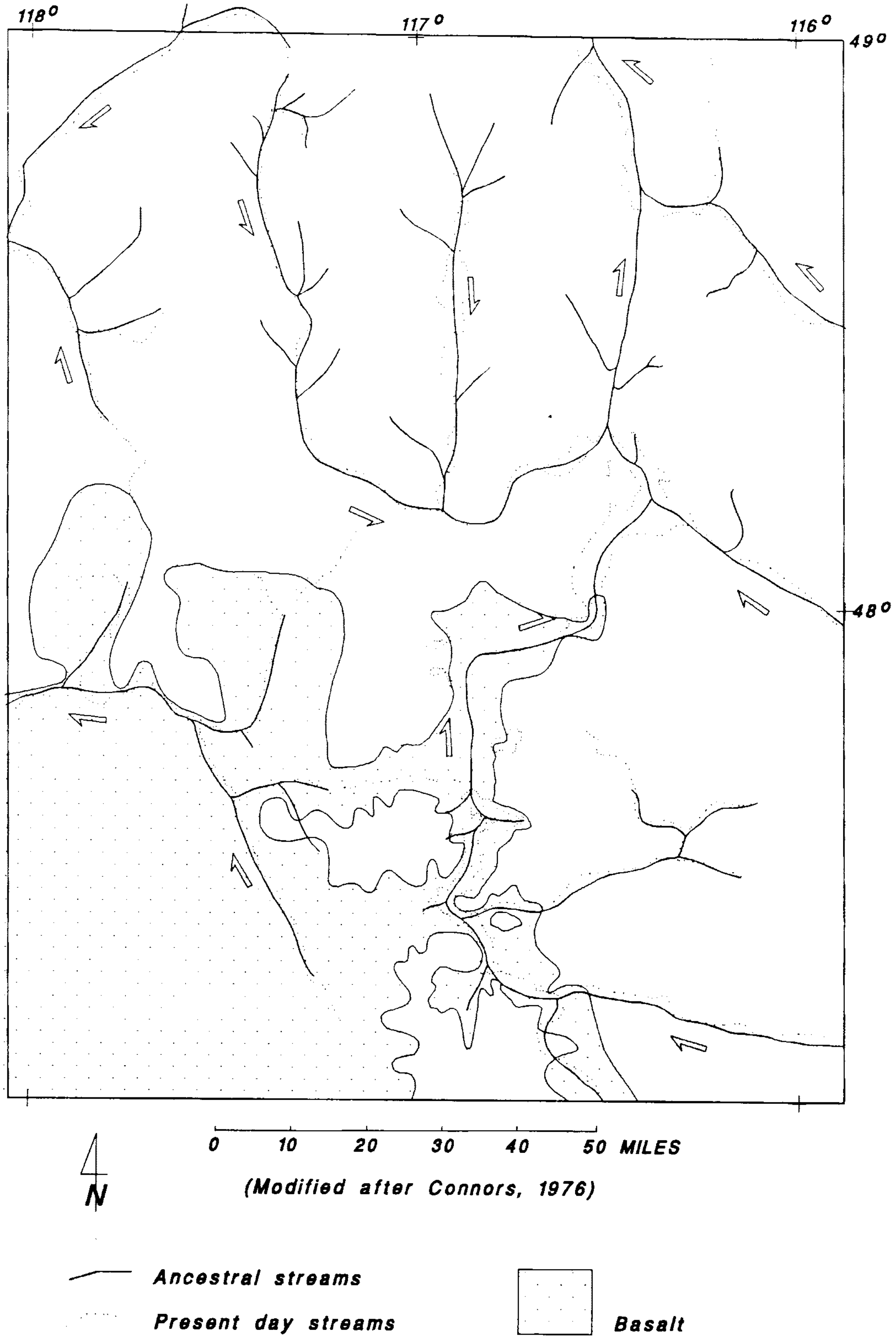
As lava accumulated to higher elevations, water continued to accumulate east of the basalt plateau in a plateau marginal lake. This lake eventually breached the low divide of the mountains to the north. The Rathdrum River established a new drainage route (Figure 9) along the margin of the basalts, cutting the valley which is now occupied by Lake Coeur d'Alene (Connors, 1976; Savage, 1965). The river flowed north along the Purcell Trench, through what is now Lake Pend Orielle, and west toward the Columbia River canyon.

The easily eroded Latah sediments were partially removed during the long period of slow downcutting and erosion, from the late Miocene through early Pleistocene periods. As much as 600 feet (183 m) of Latah sediments may have been removed (Anderson, 1927), except where protected by overlying basalt flows.



(Modified after Connors, 1976)

Figure 8. Early Miocene age drainage patterns: Rivers flowed generally to the southwest in a well developed drainage system (after Savage, 1965; Connors, 1976).



(Modified after Connors, 1976)

Figure 9. Late Pliocene age drainage patterns: The Rathdrum River was forced to flow north, along the margin of the basalts (after Connors, 1976).

Despite erosion, substantial thicknesses of Latah Formation still remain below the Rathdrum Prairie Aquifer. Newcomb (1953) estimated from seismic information that 800-900 feet (244-274 m) of these Miocene lake sediments still remain below the gravels of the Rathdrum/Spokane Aquifer at the Washington/Idaho state boundary. Similarly, about 1000 feet (305 m) of Latah Formation beds were discovered below an exposed basalt flow during the drilling of a deep well west of Hayden Lake (Anderson, 1940).

Glaciation

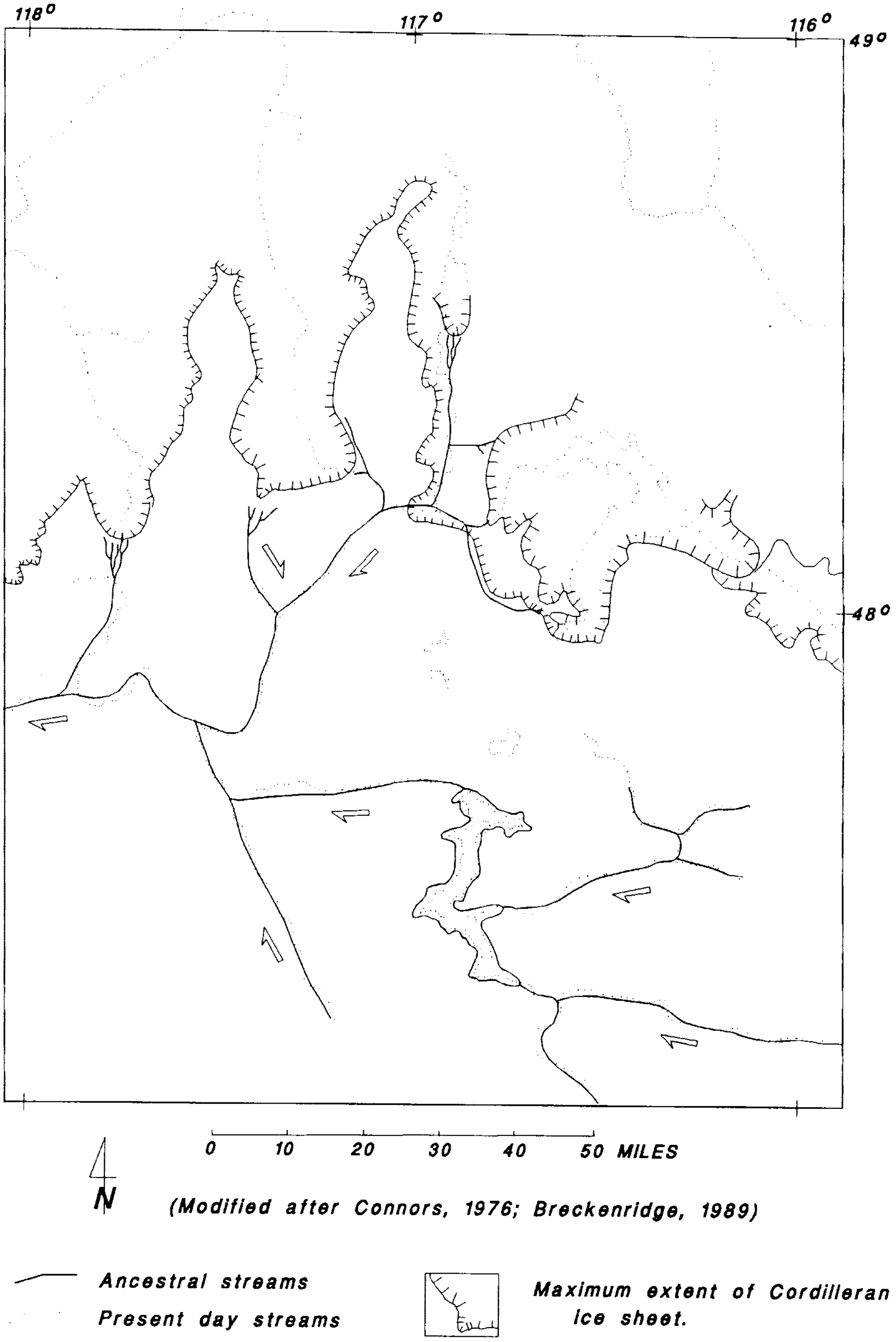
A glacial episode began at least 35,000 years ago, during Pleistocene time. Lobes of the Cordilleran ice sheet periodically advanced southward from Canada down the Purcell Trench and other north-south trending valleys. The estimated maximum extent of the ice sheet is shown in Figure 10. The Purcell Trench lobe is believed to have advanced as far south as the northern end of the Rathdrum Prairie in early Pinedale time. The glacier apparently terminated near Round Mountain, south of present-day Lake Pend Orielle.

Large quantities of sediment were carried beyond the glacier terminus by very heavily loaded, braided streams. These glacial outwash sediments accumulated rapidly, forming thick deposits of sand, gravel and silt in the Spokane/Rathdrum valley on top of the remaining basalts and Latah deposits.

The rapid and deep accumulation of glacial outwash blocked the tributary valleys to the "Rathdrum River". Streams which flowed down the tributary valleys dropped their sediment load when they encountered the temporary base level of the outwash sediments. The fine-grained sediments deposited by the tributary streams formed hydrogeologic barriers which sealed off tributary lakes. Many of these lakes persist today at the margin of the Rathdrum Prairie (e.g. Coeur d'Alene, Hayden, Liberty, and Spirit lakes).

The glacial outwash did not accumulate steadily, but rather catastrophically. During each major ice advance, an ice dam impounded waters of the Clark Fork River to create Glacial Lake Missoula. When the ice dam failed as much as 7.4×10^5 cubic feet per second (cfs) (2.1×10^7 m^3/sec) of water was released (Baker, 1973). The 2,000 feet (650 m) deep waters of Glacial Lake Missoula surged across ice in the Lake Pend Orielle basin and burst forth upon the outwash plain of the northern Rathdrum Prairie (Connors, 1976). Kiver and Stradling (1989) believe that the valley margin and valley center deposits are all flood produced. The Lakes contained in the tributary valleys along the Rathdrum/Spokane Valley are impounded by sand and gravel pendant and eddy bars.

Field evidence suggests that at least fifteen outburst floods occurred (Kiver and Stradling, 1989). Waitt (1980) inferred that at least 40 great floods occurred. Successions of 50-62 flood deposited beds are exposed in the Walla Walla valley, Washington. Elsewhere, 89 separate flood beds have been identified (Atwater, 1986).



(Modified after Connors, 1976; Breckenridge, 1989)

Figure 10. Late Wisconsin stage (Pleistocene) drainage patterns: Lobes of the Cordilleran ice sheet supplied meltwaters and outwash sediment to proglacial streams (after Connors, 1976; Breckenridge, 1989).

The average period between floods was 20-35 years, as evidenced by varves (Waitt and Atwater, 1989). Near the beginning of glacial Lake Missoula, the period between floods was 20 years. The period increased to about 50 years at glacial maximum. During the long deglaciation the period between flood events gradually decreased to 40, 30, 20 and less than 10 years (Atwater, 1986).

The last major flood episode may have occurred about 14,000 years ago. Atwater (1986) infers that the Missoula floods occurred between 15,550 (±450) and 13,350 (±550) ybp, based on varve count extrapolation from a radiocarbon date on a piece of wood. Various limits on the ice sheet and floods suggest that glacial Lake Missoula existed for 2,000-3,000 years (Atwater and Waitt, 1989).

During maximum flood stage, most of the water was channeled south and then west, along the Spokane/Rathdrum valley on its way to the Columbia River. Part of the overflow of Lake Missoula floodwaters moved south through the Lake Coeur d'Alene valley and out the Setters spillway, which connects Windy Bay and the Rock Creek drainage (Dort, 1960). Giant ripple marks in the seismic profile obtained by the USGS in 1991 (Figure 11) provide further evidence that water from at least the last major flood flowed up the Lake Coeur d'Alene valley and must have spilled out over Setters Pass (Breckenridge, 1993, verbal communication). Backwash deposits have been identified in the valley of the Coeur d'Alene River as far east as Wallace, Idaho (Dort, 1960).

The maximum elevation of outwash fill at the north end of Lake Coeur d'Alene must have been at least 2,500 feet (760 m) (Connors, 1976). The erosional waters of the Spokane Floods passed directly over the outwash barrier at the north end of the lake, reshaping the floor of the valley into megaripples and removing perhaps 370 feet (113 m) of glacial outwash and lake bottom sediments.

As the glaciers receded (Figure 12), the outbreaks of glacial floods became fewer. Eventually, the stream drainages took on the pattern seen today (Figure 13). The Spokane River was probably forced to flow along the south margin of the outwash plain, probably due to the gentle slope of the outwash surface towards the sides of the valley (Connors, 1976). Kiver and Stradling (1989) similarly state that a high bank of deposits hemmed in the Spokane River against the valley margin. The outwash level was considerably higher in the past, so when the river cut down through the outwash, it was superimposed onto granitic rocks at Post Falls and basalts at Spokane Falls.

Rathdrum Prairie today has no surface drainage. Instead, water from the valley marginal lakes and from surface streams drain directly into the permeable glacial sediments. The "Rathdrum River" has been replaced by one of the most productive aquifers in the United States.

1.4 Previous Investigations

Early studies of the Spokane River and Rathdrum Prairie Aquifer, in the 1950's and 1960's, focused primarily on water supply. Detailed investigations of recharge in the Coeur d'Alene/Spokane River area have either been largely ignored or have met with only moderate success due to the complexity

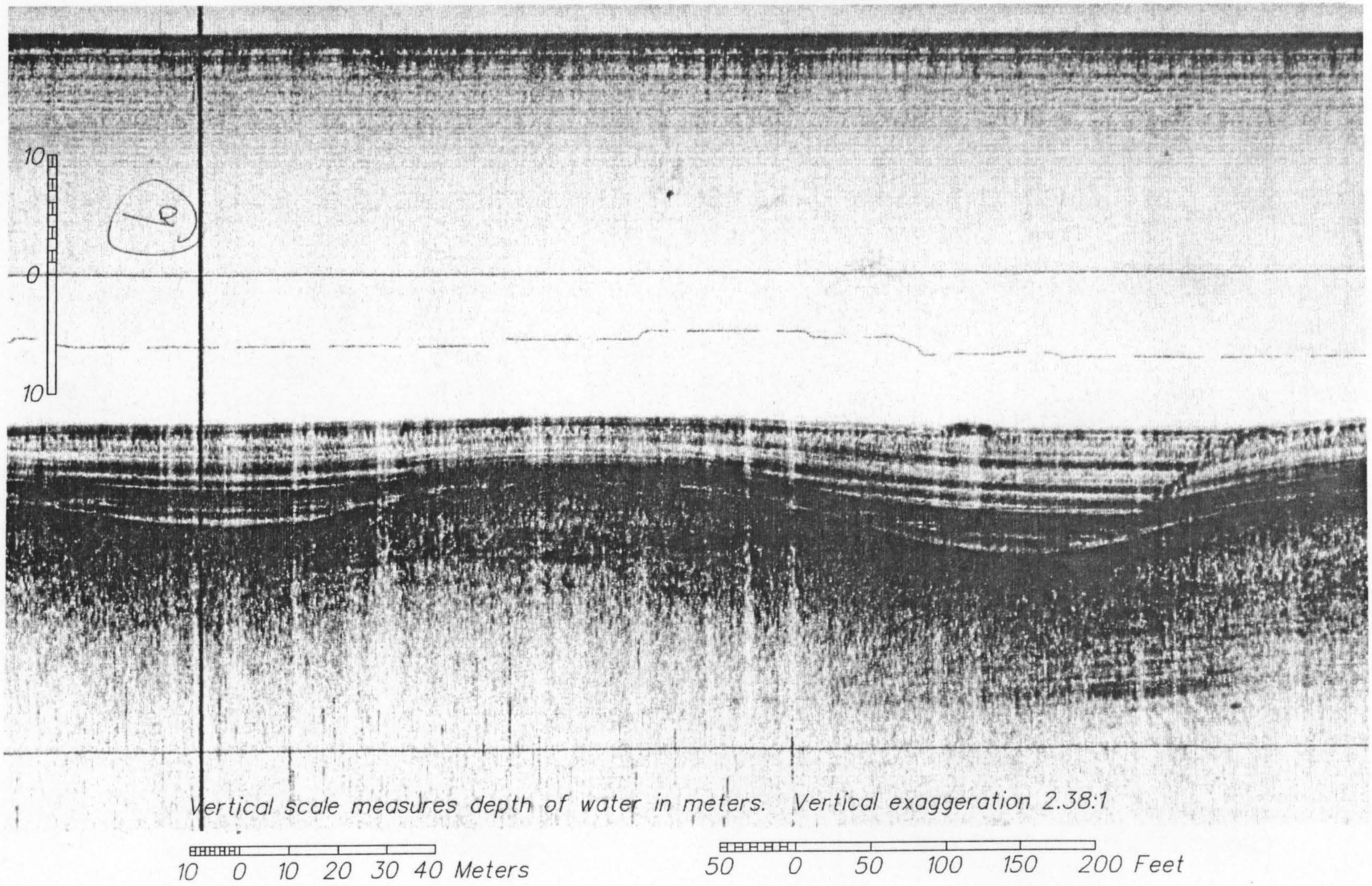
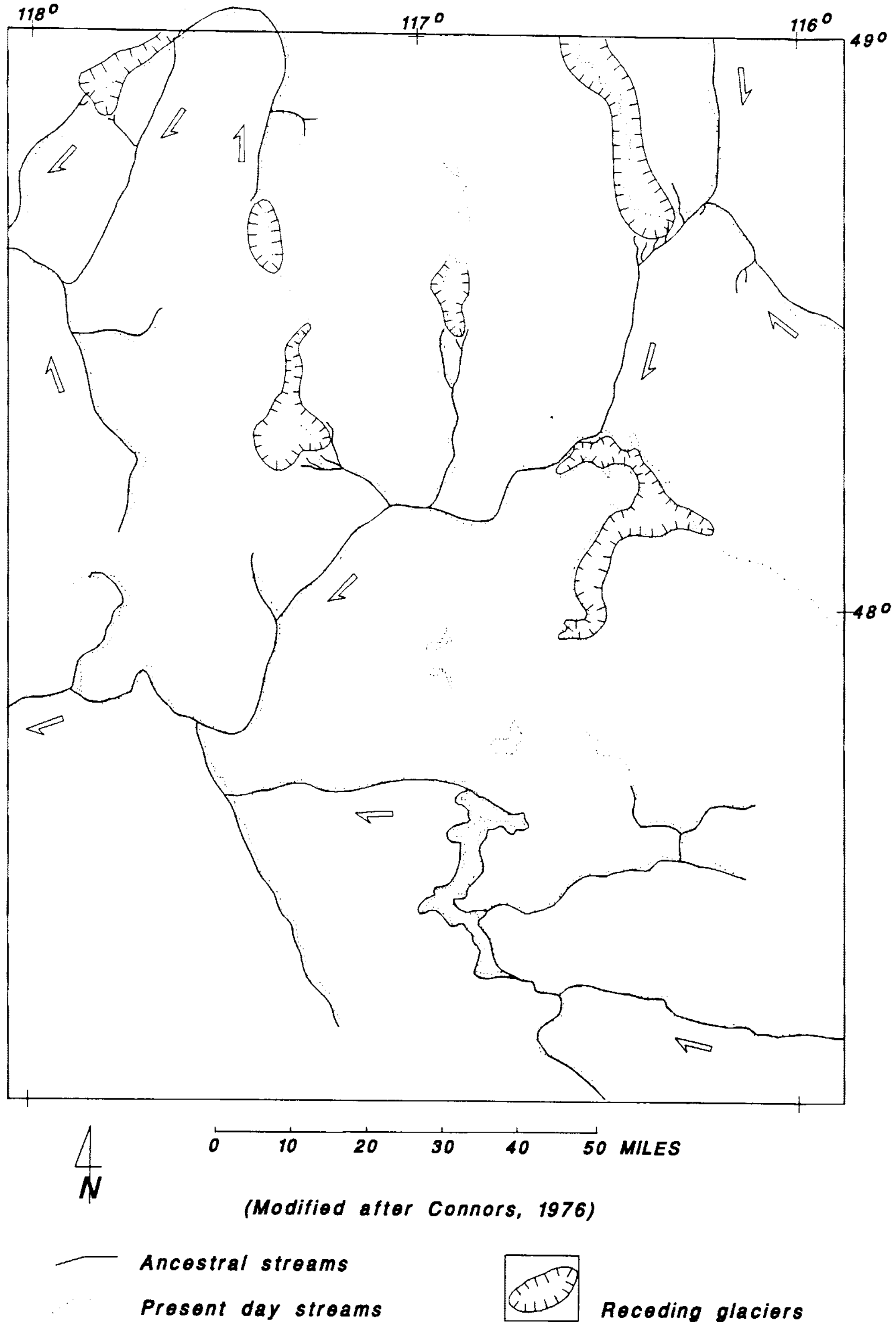


Figure 11. Giant ripple marks, seen in the seismic profile of the subsurface below Lake Coeur d'Alene, indicate that floodwaters flowed up the Lake Coeur d'Alene valley.



(Modified after Connors, 1976)

Figure 12. Late Pleistocene age drainage patterns: As the glaciers receded, drainage patterns became reestablished (after Connors, 1976).

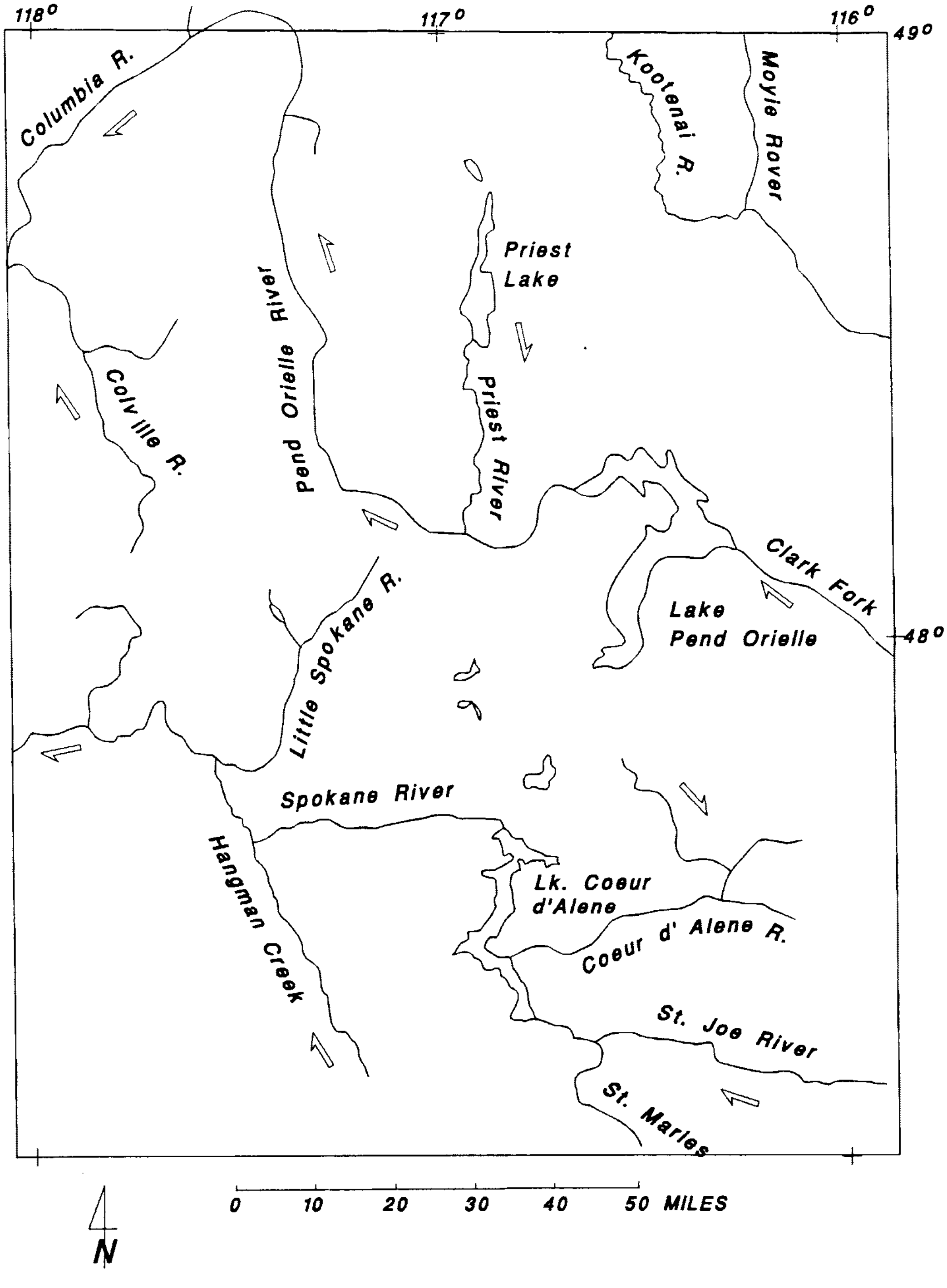


Figure 13. Late Holocene: Present day drainage patterns in eastern Washington, northern Idaho and western Montana.

of the system. Concern over the **quality** of surface water, particularly the influx of sediment and metals into the South Fork and main stem of the Coeur d'Alene River, have been expressed for many decades. However, investigations into the quality of Lake Coeur d'Alene and the Spokane River did not begin until the early 1970's. Water quality of the Rathdrum Prairie Aquifer has become a concern only relatively recently.

1.4.1 Spokane River System Studies

Piper and LaRocque, 1944

Piper and LaRocque described the relationship between the Spokane River and the adjacent aquifer. They recognized that the Spokane River is a losing stream from the outlet of Lake Coeur d'Alene to approximately Otis Orchards and a gaining stream beyond that.

Anderson, 1951

Anderson, with the U.S. Bureau of Reclamation, estimated that the quantity of recharge into the Rathdrum Prairie Aquifer from the Spokane River, between Lake Coeur d'Alene and Post Falls, was more than 300 cubic feet per second (cfs) (10.6 m^3/sec). He evaluated the aquifer material and reported that coarser gravels and boulders, in center of prairie, grade into finer sands and silts near the prairie margins.

Rorabaugh and Simons, 1966

A study of artificial recharge to the Rathdrum Prairie Aquifer from the Spokane River was conducted. The researchers determined that groundwater flow to the river varies with the height of the water table.

Sagstad, 1977

Sagstad conducted field work in summer of 1975. He recorded water levels in wells adjacent to the Spokane River, near Coeur d'Alene and Post Falls, and analyzed well water for sodium (Na), calcium (Ca), magnesium (Mg), iron (Fe), and zinc (Zn).

The study determined (estimated) that the hydraulic conductivity of the aquifer is 10,000 gal/day/ft^2 (1400 ft/day; 0.5 cm/s) and that fine grained sediments largely control the magnitude of recharge through the channel bottom. Sagstad attempted to determine the hydraulic conductivity of the stream bottom sediments by (1) analyzing constant head injection tests conducted by Idaho Department of Highways and (2) conducting a variable head test.

Sagstad's study determined that the rate of groundwater recharge from Lake Coeur d'Alene and the Spokane River (between Lake Coeur d'Alene and Post Falls) is 225 cfs (8 m^3/s). No statistically significant difference (at $r=0.05$) was observed between water chemistry (Na, Ca, Mg) in the Spokane River and in the aquifer adjacent to the river.

The observed concentrations of Mg and Ca increased significantly away from the Spokane River and Na increased only slightly. Calcium was recognized as the dominant cation. Concentrations of Zn in groundwater were generally below 0.01 mg/l. Water in 62 of 82 wells sampled contained less than 0.05 mg/l Zn. Thirteen wells had Zn concentrations greater than 0.20 mg/l. A local anomaly was observed in wells on Harbor Island, where Zn averaged 0.5 mg/l. Sagstad concluded that "although zinc is a common constituent of the Spokane River, it is not found in the ground water" (Sagstad, 1978, p.82).

Funk, Rabe and Filby, 1983

Funk, Rabe amd Filby found that the concentrations of copper (Cu), nickel (Ni), cadmium (Cd), lead (Pb) and mercury (Hg) at ten sampling stations in the Spokane River, between the Washington-Idaho state line and Hangman Creek below Spokane, were relatively low. During the 1982 study, Cu, Cd, and Pb concentrations were less than 1 μg/l most of the time. Nickel concentrations were most often less that 5 μg/l. Mercury concentrations were most often less than 5 μg/l but did reach 70 μg/l at one station in one sampling event.

Unlike other metals measured, the level of Zn in the upper Spokane River was high. The Zn concentrations ranged from 5 to 225 μg/l, most of which were in a filterable fraction. Dr. Funk recognized a correlation between flow volume and Zn concentrations in the river. The Zn concentrations were highest during January through June, corresponding to the higher flows during that time of year. As the flow of water decreased, the Zn concentrations were two to three times less than those of the early winter (high flow) months of 1979 and 1980.

In the same study, Cu concentrations ranged from <1 to 8 μg/l. Nickel concentrations ranged from <5 to 22 μg/l, Cd ranged from <1 to 7 μg/l and Pb from <1 to 8 μg/l.

Yearsley, 1980

In 1978 the US Environmental Protection Agency collected data in order to estimate the impact of waste discharge on dissolved oxygen in the Spokane River under summer low-flow conditions. The study included field measurements of nutrient levels in the receiving waters, algal assays and a reconnaissance survey of aquatic plants. Yearsley and other EPA personnel measured the temperature, nitrogen, phosphorous, dissolved oxygen (DO), total organic carbon (TOC), biological oxygen demand (BOD), and water clarity of the stretch of the river from Coeur d'Alene to Post Falls.

Yearsley reported that DO concentrations and saturation levels were nearly uniform longitudinally and vertically in December 1978, when the degree of saturation ranged from 80.8-89.6%. During periods of reduced stream flow and elevated water temperature, DO levels generally exceeded saturation at water surface but were always less than saturation at the bottom of the stream channel. At shallower stations the level of DO saturation at the bottom of the river was ≥ 84.8%. In deep downstream stations DO concentrations as low as 33.0% were measured. The concentrations of DO were lower in August than in July, even though water temperatures had dropped.

During summer low flow water had a long residence time and relatively high temperature. In 1978, the minimum DO at Ford Rock was 2.9 mg/l in July and 0.5 mg/l in August. Minimum DO at Post Falls was found to be 2.8 mg/l in July and 0.9 mg/l in August. By September, river flows were rising, water temperatures were dropping, and DO levels improved substantially.

Generally, a high pH corresponded to high DO and a low pH was equated to a low DO concentration. The pH ranged from a low of 6.3 in the deep water at Ford Rock to a high of 7.6 in surface water near the Lake Coeur d'Alene outlet.

Based in part on Secchi disk transparencies of 10-20 feet, Yearsley called the Spokane River to Post Falls oligotrophic to mesotrophic. He determined that the morphology of the channel bottom has substantial impact upon water quality during low flow and that dissolved oxygen decreases with depth and with distance downstream. Yearsley also reported that the evaluation of algal assays was complicated by the presence of substances which inhibited algal growth.

Seitz and Jones, 1981

The 1980-1981 study by Seitz and Jones was designed to assess the quality of water entering the Spokane River from Lake Coeur d'Alene, to document any changes in water quality between the lake outlet and Post Falls dam and to characterize the flow and channel geometry of the river. Water samples were collected monthly and tested for temperature, dissolved oxygen, specific conductance, pH, and discharge during the period from March 1980 through January 1981. The researchers also determined water depth, width, velocity and discharge at eight locations during June, August and November, 1980.

The concentrations of dissolved oxygen were generally greater than 6 mg/l, but in deeper sections of the river, DO concentrations of 3 mg/l or less were observed. DO concentrations ranged from 9.2-10.2 mg/l in June, 7.7-8.8 mg/l in August and 9.5-10.4 mg/l in November, 1980. Temperatures throughout the study area ranged from 55-59°F (13.0-15.0°C) during June, 64-70°F (18.0-21.0°C) during August, and 50-52°F (10.0-11.0°C) during November.

The pH values ranged from 7.4-8.0 in June, 7.3-8.1 in August and 7.7-8.8 in November. The pH did not appear to follow a pattern downstream, perhaps because the measurements were made in a composite sample obtained from three vertical sections at each location. Specific conductance was relatively consistent in the water throughout the reach and changed very little during the three sampling periods. Measurements of specific conductance ranged from 51-56 μmho/cm in June, 56-63 μmho/cm in August and 65-68 μmho/cm in November.

Metal concentrations (Cd, Cu, Cr, Fe, Pb, Hg, and Zn) in water at the lake outlet and below Post Falls dam were relatively low. Idaho instream water-quality standards were not exceeded.

Yearsley, 1982

Yearsley examined the nutrient and heavy metals budget in the Spokane River between Post Falls and Hangman Creek from August, 1979 to February, 1981. The high concentrations of heavy metals in the waters were attributed to metals processing industries on the South Fork of the Coeur d'Alene River. The study also noted that the Spokane Industrial Park and influent groundwater were important sources of Cu. Based on mass inventories of Cd, Cu, Fe, Hg, Pb, and Zn, Yearsley hypothesized that metals generally are deposited in the river at low flow and scoured out at high flows, with no net gain or loss occuring during average flows. Zinc data did not fit the proposed hypothesis at high flow. Iron data supported the hypothesis during average conditions and high flow but not during low flow conditions. The uncertainties in the estimates of average loadings made it difficult to identify all sources and sinks for metals in this stretch of the Spokane River.

Yearsley and Duncan, 1989

Yearsley and Duncan conducted a field study of water quality in the Spokane River between the outlet of Lake Coeur d'Alene and Post Falls Dam during August, 1988, to assess water quality during a period of low flow and elevated water temperature and to develop a dissolved oxygen budget of this reach of the river. Water quality concerns included dissolved oxygen, heavy metals toxicity and nutrient loading.

The study revealed that average temperatures of the Spokane River ranged from 70.5-73°F (21.4-22.9°C) during August 15-18, 1988. The water temperature was uniform in segments whose depth was less than 23 feet (7 m). A thermocline existed from 23 feet (7 m) to the bottom at three stations where depth exceeded 23 feet (7 m). Surface water temperature was 66°F (19°C) between May 25-June 25, 1988.

Yearsley and Duncan observed a consistent increase in DO from morning to afternoon in areas where the river is shallow and well-mixed from top to bottom. Three stations in deeper water (at river mile 103.1, 102.2 and at Post Falls Dam) showed the diurnal increase in DO only in top five meters and had extremely low DO values at depth. On August 18, DO concentrations at river mile 103.1 were 8-8.5 mg/l above thermocline, decreasing to 0 at a depth of 43- 56 ft (13-17 m). The deeper stations also exhibited less diurnal variation in DO than did the shallow stations.

The average pH increased downstream from the outlet of Lake Coeur d'Alene. Water leaving lake had a mean pH of approximately 6.05, and a minimum of 5.95. The mean pH downstream was around 6.3.

The average totals of phosphorous were below detection (0.01 mg/l) at the outlet of the lake, and increased to 0.055 mg/l at the first river sampling station downstream of the sewage treatment plant. Phosphorous concentrations decreased consistently downstream after that. Table 1 summarizes the results of EPA sampling for heavy metals in the upper Spokane River during 1988.

Station	River Mile	As μg/ℓ	Cr-total μg/ℓ	Cd μg/ℓ	Cu μg/ℓ	Fe μg/ℓ	Hg μg/ℓ	Pb μg/ℓ	Zn μg/ℓ
CdA STP	108.6	1.53	3.47	0.70		234.5	0.11	5.3	46.5
1	111.1	0.50	0.56	0.57	3.0	21.7	0.32	1.3	68.3
2	110.4	0.57	1.13	0.50	4.7	24.7	0.15	2.	64.7
4	106.5	0.63	1.00	0.30	3.0	33.3	0.19	1.7	55.3
5	104.4	0.60	1.20	0.63	3.2	47.3	0.21	1.3	55.7
8	102.2	0.57	0.93	0.23	4.2	30.0	0.11	1.3	45.3
MinDL	---	0.5	0.5	0.1	0.1	7	0.08	1	5

Table 1. Concentration of metals in waters of the Spokane River, 1988. Arsenic and mercury are reported as total; other constituents are "total recoverable".

1.4.2 Lake Coeur d'Alene Studies

Maxfield and Wai, 1971

Two sediment samples in the Coeur d'Alene River delta were investigated for heavy metals content. Lead levels were 4148 ppm and 3700 ppm. Cadmium values were 8.0 and 43 ppm. Zinc levels were 3800 and 3680 ppm. Common background ranges for soils were given: Pb 2-200 ppm, Cd 0.01-0.7 ppm and Zn 10-300 ppm.

Parker, 1972

Parker evaluated the algae production and nutrient enrichment in Lake Coeur d'Alene between July, 1971 and November, 1971. Measurements of specific conductance, DO, temperataure, Secchi disk transparency, nitrates, phospates, inorganic carbon, pH and alkalinity were collected. Parker called the southern end of Lake Coeur d'Alene meso-eutrophic, the middle portion of lake mesotrophic, and the northern end of the lake oligotrophic, based on nutrient levels, plankton (algae and diatom) community structures, primary productivity, Secchi transparency and carbon fixation rates. Parker also determined that the concentrations of phosphate, nitrate, alkalinity and productivity were higher in the middle and southern portions of the lake than in the north.

Funk, Rabe and Filby, 1973

Funk, Rabe and Filby published the results of an investigation into the biological effects of metallic and organic pollution in the Coeur d'Alene/Spokane River drainage system in 1973. They measured temperature, Secchi transparency, depth, alkalinity, DO, and conductivity of the water at various sampling stations in Lake Coeur d'Alene and the Spokane River. Water samples were analyzed for phosphorous, sulfate, sulfide, nitrogen, BOD, hardness and iron. Water samples, sediments, and fish tissues were analyzed for Fe, Co, Se, Hg, Cr, Rb, Cs, Th, Sb, Co, Zn, Sc, and Eu.

Thermal stratification was observed in Lake Coeur d'Alene from late June until mid-October. In October, the lake overturned, producing homothermous conditions. In the spring, it was noted, shallower waters at south end of the lake warm earlier. Temperatures appeared to remain relatively uniform for deep water stations during most of the year.

Secchi disc transparencies in the early 1970's ranged from 7-15 feet (2-4.5 m) and were lowest at the southern end of the lake. Transparency did not severely limit biological production. The depth of the euphotic zone was approximately 33 feet (10 m), as determined by photometer readings.

No stations in the lake system were found to be devoid of dissolved oxygen. The lowest DO recorded was 2-4 mg/l in Chatcolet and <4.0 mg/l in the hypolimnion in the vicinity of Conkling Park south to the Hidden Lake area in late summer.

The average NO_3-N content of Lake Coeur d'Alene was 0.177 mg/l, well below the world average of 0.30 mg/l for fresh water. The PO_4 content of the lake was 0.01 mg/l, compared to a world average of 0.01-0.03 mg/l. The southern portion of Lake Coeur d'Alene, however, contained twenty-five times the world average PO_4, probably due to its shallow depths.

The researchers looked for metals in upper 3 cm (1.2 in) of lake sediments. Sediments were analyzed for Zn, Fe, and Sb by neutron activation, and for Zn, Cu, Mg by atomic absorption spectroscopy. Zinc concentrations were 0.45-0.73% in sediments north of Harrison, but less in Carlin Bay, and no Zn was detected to the south. Concentrations of Pb and Zn decreased in sediments north of Coeur d'Alene River delta. Funk calculated sedimentation rates of 0.86-0.28 cm/yr in the lake. Shifts in diatom population was observed in sediment cores where metal enrichment occurred, probably due to metal toxicity and increased turbidity.

The water quality of the Spokane River was, for the most part, good to excellent except for metals content. The study showed that metals were being concentrated by the algae and other aquatic plants and passed on to aquatic insects and fish. Relatively large quantities of metallic elements were found in the tissues of aquatic insects and fishes. It was believed that metals were in relatively innocuous forms because fish were swimming in "waters containing as much or more than that quantity to injure them under laboratory conditions" (Funk, Rabe and Filby, 1973, p.132).

Maxfield, et al., 1974

Core samples were collected in the Coeur d'Alene River delta and were analyzed for Sb, Zn, Pb, Mn, Cu, Cd, Ag, and Hg. The sediments were mostly fine silt. The nature of the sediments seemed to be related to the metals content in different layers of the core samples.

Parker and Rabe, 1978

Four regions of different trophic status were delineated, based on nitrate, phosphate, phytoplankton abundance and the rate of primary productivity in Lake Coeur d'Alene. The average phosphate concentrations in the northern region of the lake averaged 0.036 mg/l and ranged from 0.006 to 0.09 mg/l. Phosphate concentrations in the southern region were higher, averagingd 0.12 mg/l and ranging from 0.015 to 0.48 mg/l. The highest phosphate concentrations were seen in Lake Chatcolet, at the southern end of Lake Coeur d'Alene.

Molnau and Kessler, 1985

Molnau sampled lake bottom and water samples in Kidd Island Bay in August, 1985. Six transects with six sampling points each were analyzed. Core samples of the bottom sediment were analyzed for bulk density, nitrate content, and particle size distribution. Water quality samples were analyzed for NO_3 content as well as Pb, Zn and Hg. The nitrate content of sediment samples ranged from 0.5 ppm on the east side of the peninsula to 3.7 ppm on the east side of the bay. A study of lakes in Wisconsin, cited by Wetzel (1983), reported a nitrate content of bottom sediments of 0.3 ppm in eutrophic lakes. Mercury and Pb in Lake Coeur d'Alene water samples were below detection limits of 0.04 mg/l. Nitrate in waters ranged from less than 0.01 mg/l to 0.09 mg/l. (The EPA has established a limit of 10 ppm for domestic water supply. Limnological research has indicated nitrate levels of 0.5 mg/l to 1.5 mg/l in circulating water generally leads to eutrophication problems.) Zinc levels ranged from 0.01 to 0.11 ppm. Molnau and Kessler reported 'no major problems' with Pb, NO_3, Zn or Hg within the bay.

Wai and Mok, 1985

Wai and Mok studied the sediments in the main stem of the Coeur d'Alene River and in the delta where the river enters Lake Coeur d'Alene. The occurrence of As and Sb and the leachability of As, Sb, Zn, Cu, Cd, Pb, Ni, Fe and Mn were examined. An accumulation of As and Sb on the surface sediments was observed in the delta area.

The researchers determined that the leaching of As and Sb from the sediments along the main stem depends on the pH of the water and on the Fe and Mn content of the sediments. The amount of As and Sb leached was high in acidic or basic solutions. The releases of As and Sb from the sediments appear to be associated with the free iron oxides and manganese oxides in the sediments.

Significant amounts of Zn, Fe and Mn were also released during the laboratory leachability studies, but Cu, Cd, Pb and Ni were much less leachable. According to this study, interaction of water with the existing sediments is likely to be a major factor controlling the water quality of the Coeur d'Alene River.

Harenberg, et al., 1991

The U.S. Geological Survey, Water Resources Division, conducted extensive studies of the water quality in Lake Coeur d'Alene and the lateral lakes of the Coeur d'Alene River from 1990-1992. Lake characteristics such as Secchi transparency, incident light, pH, temperature, dissolved oxygen and specific conductance were recorded at various depths and locations. Water samples from selected sites were analyzed for nitrogen, phosphorous, and chlorophyll (phytoplankton). Composite samples from the euphotic zone at several sites were also analyzed for As, Cd, Cu, Hg and Zn. Selected samples from Lake Coeur d'Alene underwent a complete analysis for pH, specific conductance, hardness, Ca, Mg, Na, K, carbonate alkalinity, sulfate (SO_4), chloride (Cl), fluoride (F), silica (SiO_2), TDS, N, P, As, Cd, Pb, Hg, Zn and phytoplankton. Part of the sampling results have been published in the 1991 USGS Water-Data Report and are summarized and evaluated later in this report. The USGS report and model for eutrophication of Lake Coeur d'Alene is in preparation.

Horowitz, Elrick and Cook, 1992

The U.S. Geological Survey, under contract to the Idaho Division of Environmental Quality, conducted a three year study of surface water and sediment heavy metal concentrations. A comprehensive study of metal concentrations in 172 surficial (upper 2 cm) bottom sediment samples and seven deeper cores was conducted in 1991-92. The researchers determined the bulk metal concentrations, concentrations of metals per size fraction, and phase associations. Research continues on pore water chemistry of sediments and phase relationships. The preliminary results of this study are described later in this report.

1.4.3 Rathdrum Prairie Aquifer Studies

Piper and Huff, 1943

Piper and Huff measured water levels in a series of wells and made estimates of the hydraulic gradient in different parts of the aquifer. Hayden Lake, Lake Coeur d'Alene and Lake Pend Orielle were identified as major sources of recharge to the aquifer. The estimated total discharge to rivers and springs from the aquifer was 900 cfs (25.5 m^3/s).

Nace and Fader, 1951

Fader measured water levels in wells bimonthly from January, 1949 to December, 1950. As part of a U.S. Geological Survey/U.S. Bureau of Reclamation joint study, well logs and water levels were used to assess the hydrology of the aquifer.

Frink, 1962, 1964

Frink evaluated the conclusions of Anderson (1951) related to recharge. Lake Pend Oreille was determined to be only a minor source of recharge. The report concluded that at least 600 cfs (17 m^3/s) of recharge occurred east of Post Falls and another 150 cfs (4.3 m^3/s) of recharge occurred between Post Falls and the state line. Frink also published water table and specific capacity maps of the Rathdrum Prairie Aquifer.

Pluhowski and Thomas, 1968

Pluhowski and Thomas conducted a water balance study of the Rathdrum Prairie Aquifer. They estimated that the underflow from the aquifer to the Spokane River, in the reach between Otis Orchards and Long Lake Washington, averages 1,000 cfs (28 m^3/s). Principal recharge sources include direct infiltration, seepage from lakes along the perimeter of the aquifer, infiltration of surface waters which originate in the surrounding highlands, and seepage from the Spokane River. A detailed water budget analysis of Lake Coeur d'Alene showed that 250 cfs (7 m^3/s) of water moves from Lake Coeur d'Alene and the Spokane River into the aquifer.

Hammond, 1974

A detailed geophysical (gravity) survey was made by the USGS to calculate the thickness of alluvium in the west, middle and Chilco channels. The study provided new information on the thickness and configuration of fill, ruled out the middle channel as a conduit for groundwater, and determined that most water flows through west channel. Hammond used an aquifer thickness of 1,000 feet in the west channel and a hydraulic conductivity (K) of 90,000 gal/day/ft^2 (12,700 ft/day; 1.8 cm/s). He reported that the width of the water-bearing zone in the Chilco channel is about 5,000 feet (1500 m). The hydraulic gradient is 0.0095 ft/ft ($\approx$50 feet/mile; 9.5 m/km), transmissivity is 630,000 g/day/ft (84,200 ft^2/day; 906 cm^2/s), and hydraulic conductivity is 9400 g/day/ft^2 (1260 ft/day; 4.4 x 10^{-1} cm/s). Hammond also determined that the thickness of glacial outwash near Round Mountain is approximately 1500 feet (457 m).

Drost and Seitz, 1978

Drost and Seitz prepared a comprehensive report on the Spokane Valley-Rathdrum Prairie Aquifer in response to a petition to the US EPA for "sole source" aquifer designation for the aquifer. The report described the hydrologic characteristics, patterns of water use and disposal, quality of water in the aquifer, and alternative water sources.

Drost and Seitz tabulated data on groundwater quality from the files of federal, state and local agencies, from previous studies of the aquifer and from private laboratories. The data summary tables indicate that groundwater from wells northwest of Coeur d'Alene exceeded the standards for NO_3, Fe and

Mn at least once. (The 1975 standard for NO_3 was 10 mg/l and the 1977 Secondary Maximum Contaminant Levels for Fe and Mg were 0.3 mg/l and 0.05 mg/l, respectively.) Groundwater was also analyzed for Cl, F, TDS, pH, As, barium (Ba), Cd, Cr, Cu, Pb, Hg, and Zn, in addition to organic constituents. The data did not indicate elevated levels of these constituents in groundwater near Coeur d'Alene.

Surface water quality at selected sites near the aquifer were also reported. Four sample stations were located in the Coeur d'Alene recharge area: (1) on Lake Coeur d'Alene, west of Tubbs Hill, south of the city park, (2) on the Spokane River, 1/8 mile northeast of Blackwell Island, (3) near Black Bay on the Spokane River, one mile west of Harbor Island and (4) south of Post Falls, 1/4 mile east of the dam. Water quality at these sites, from Funk (1973) and the Idaho Department of Health and Welfare (IDHW), was good. Site 1 exceeded pH standards once in seventy sampling events and nitrate standards in one of 120 samples. Sites 2-4 did not exceed standards for Fe, Mn, Cl, Fl, NO_3, TDS, pH, color, turbidity, As, Cd, Cr, Cu, Pb, Hg or Zn.

From July, 1973 to September 1975, samples from Lake Coeur d'Alene across from Half Round Bay were analyzed for Fe, Mn, NO_3, Pb, Hg, Zn, Cu, Cd and As. All metal concentrations were below drinking water standards, except Hg, which exceeded standards in two of 21 samples, and Cd, which exceeded standards in one of 21 samples. Tests of surface water at the outlet of Lake Coeur d'Alene between 1973 and 1975 reveal that the drinking water standard was exceeded once in six sampling events for Fe, one of 24 times for Cd, and two of 25 times for Pb. Drinking water standards for Zn, Cu, Hg, F, NO_3 and As were not exceeded. Samples from Echo Bay off Lake Coeur d'Alene to the north exceeded the drinking water standard for Fe in one of nine samples, and Hg in one of 24 samples between July, 1973 and May, 1975.

Bolke and Vaccaro, 1979

Groundwater data were collected from March 1977 to May 1978 in the Spokane Valley for the purpose of developing a computer simulation of flow and mass transport in the Spokane Aquifer. Data collected included an inventory of wells and springs, water level data and chemical analyses from selected wells and springs.

Parliman, Seitz and Jones, 1980

The U.S. Geological Survey collected water samples as part of a reconnaissance study of 116 wells in northern Idaho from July 1977 to May 1978. The fifty-five wells in the Rathdrum Prairie Aquifer included domestic/private, commercial/private and municipal water supplies. The samples were analyzed for specific conductance, pH, water temperature, coliform, fecal coliform, hardness, Ca, Mg, Na, K, HCO_3, CO_3, $CaCO_3$ (alkalinity), SO_4, F, TDS, $NO_2 + NO_3$, P, Fe, Cl, and SiO_2. Groundwater samples from the Rathdrum Prairie Aquifer were not analyzed for heavy metals.

The report also summarized the geologic and hydrologic character of northern Idaho aquifers. Yields from wells completed in the thick glacial deposits of the Rathdrum Prairie range from 5-3,000 gal/min (0.3-189.3 l/sec). Leakage from adjacent lakes and tributaries and direct precipitation provide most of the recharge to the aquifer.

Parliman, Seitz and Jones concluded that the geologic environment probably has the greatest effect on water quality in northern Idaho. Changes in population, urban and industrial development, irrigation, crop treatment mining and recreation were identified as potential factors influencing future groundwater quality.

Jehn, 1988

Paul Jehn, of the Idaho Department of Health and Welfare Division of Environmental Quality, summarized the geology, hydrology, climate, soils, land and water use, groundwater quality, and potential contamination sources of the Rathdrum Prairie Aquifer in 1988. The report states that the total dissolved solids in groundwater range from 42-220 mg/l with a median of 152 mg/l, which makes the groundwater suitable for all uses. Minor amounts of volatile organic compounds are present in the aquifer. Elevated nitrate concentrations have been recognized and are primarily caused by septic system drainage into the porous aquifer. Jehn also reported that Pb, Hg, Zn, As and Cd concentrations are below the detection limit in the aquifer, proximal to Lake Coeur d'Alene and the Spokane River.

Painter, 1991 (a)

Brian Painter, of the Idaho Department of Health and Welfare, Division of Environmental Quality (DEQ) prepared a groundwater quality status report. The current monitoring program on the Rathdrum Prairie Aquifer, water quality trends, historical contamination events and potential contamination sources were identified. Recommendations for the protection of groundwater were also given. Painter also reported that "past analyses for heavy metals have shown that these constituents are not likely to be significant contaminants in the aquifer unless releases are made from an industrial point source into the groundwater" (Painter, 1991 (a), p. 16).

2.0 METHODS AND MATERIALS

2.1 Literature Search and Background Investigation

The GeoRef and Selected Water Resources Abstracts data bases were utilized in an extensive literature search for technical papers on (1) heavy metal cycling in sediments and surface water, (2) changes in redox potential and pH in lakes as a result of eutrophication, (3) subsurface heavy metal migration and (4) case studies of regional mining areas with heavy metal contamination. Publications were evaluated in light of their significance and applicability to Lake Coeur d'Alene and the Rathdrum Prairie Aquifer. Articles and books which were identified by data base searches and deemed applicable to this study were obtained from library stacks and through interlibrary loans.

Information regarding Lake Coeur d'Alene and Spokane River sediments, the Spokane River/Rathdrum Prairie Aquifer hydraulic characteristics, local geology and water chemistry data was obtained from the University of Idaho (UI) library stacks, government documents collections, Idaho DEQ, U.S. EPA Region 10 library, Washington Water Power, the Hagadone Hospitality Corporation, and the Idaho Department of Transportation. Personal communication regarding aquifer characteristics was conducted with several engineering firms, Idaho Department of Transportation personnel, Coeur d'Alene city employees and others.

Data on stream flow, pertinent to the study, were obtained from the U.S. Geological Survey. Database records for USGS gaging stations on Carlin Creek, Plummer Creek and Fighting Creek, which discharge directly into Lake Coeur, d'Alene were obtained for water years 1990 and 1991. Stream gage data for Wolf Lodge Creek was obtained for December, 1986 to September 1992. Information regarding daily water levels and monthly averages in Lake Coeur d' Alene were available from 1904 to September, 1992. Stream flow records for the South Fork of the Coeur d'Alene (1911-1912, 1920-1972, 1987-1992) and the St. Joe River at St. Maries (Oct. 1959 to Sept. 1992) were also acquired. The surface water outflow from Lake Coeur d'Alene was read from records of the gaging station at Post Falls dam, from 1901 to 1992.

2.2 Investigation of Geology/Lithology

2.2.1 Grain Size Analysis

Two 3-inch boreholes were augured by hand at two stations on the shores of the Spokane River and Lake Coeur d'Alene (Figure 14). Borehole A was augured on September 19, 1992 to a depth of 9.12 feet (2.80 meters). Borehole B was augured on September 20 to a depth of 11.5 feet (3.52 meters). Continuous samples of the alluvium were collected, with about a 95% recovery. Thirty seven samples were collected from borehole A, in 3-4 inch (8-10 cm) intervals until progress was impeded (presumably) by a cobble or boulder.

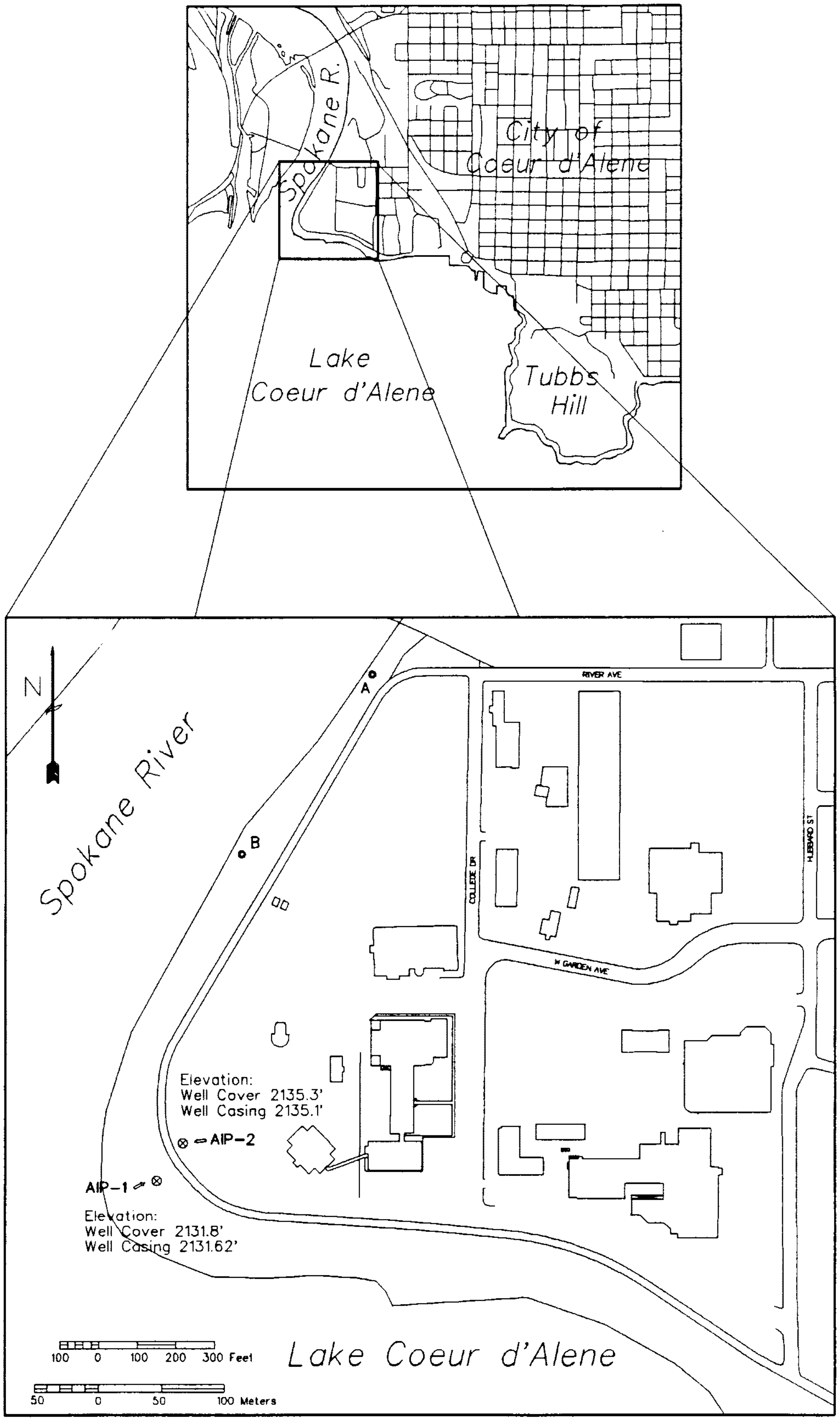


Figure 14. Location of hand-augured boreholes, A and B, and monitoring wells AIP-1 and AIP-2.

Samples from borehole B were collected in 3-4 inch (8-10 cm) intervals and analyzed for grain size. Each of the 49 samples was air-dried in the lab for 5-10 days. Most samples were passed through a Tyler sample splitter two times to obtain a 350-450 gram fraction. Each sample was dry-sieved for 17 minutes in a Forney sieve shaker through a stack of 4.75 mm, 4.0 mm (-2ϕ), 2.0 mm (-1ϕ), 1.0 mm (0ϕ), 0.42 mm ($\approx 1\phi$), 0.24 mm ($\approx 2\phi$), 0.124 mm (3ϕ), and 0.63 mm (4ϕ) sieves. Each fraction was weighed on an electronic balance with a precision of 0.1 gram. Data were plotted on probability paper and analyzed according to Folk and Ward (1957) for mean grain size, sorting and skewness. The results of the grain size analysis are tabulated in Appendix I and are discussed in Section 3.1.1.

2.2.2 Geologic Cross Sections

Geologic cross sections were constructed for two locations. Logs of wells in the study area were obtained from the Idaho Department of Water Resources and used to determine the lithology at depth. Appendix II summarizes the data extracted from these logs. Information from the literature, including descriptions of seismic surveys and well drilling in Spokane County, was used to estimate thickness of the Latah Formation and Quaternary alluvium. Two possible interpretations of the subsurface stratigraphy were developed for each cross section.

2.2.3 Seismic Reflection Analysis

Seismic scrolls from a 1991 USGS seismic reflection survey of Lake Coeur d'Alene were utilized to determine the morphology of the lake bottom and the thickness of fine, laminated, lake bottom sediments. The latitude and longitude coordinates from each station along 25 transects were imported into AutoCAD and projected into State Plane Coordinates. The seismic station locations were registered to a 1:100,000 scale USGS topographic map in order to determine horizontal distances. These data were interpreted in light of the movement of surface water into the adjacent aquifer.

2.3 Investigation of Groundwater

2.3.1 Water Table Configuration

Water level elevations from the U.S. Geological Survey Water Resources Division records (1978 data set), along with water level elevations measured by Sagstad in 1975, were contoured to create a map of the water table. The data are included in Appendix III. Information from water levels in the two shallow monitoring well on the North Idaho College campus and three monitoring wells on the Hagadone Hospitality Corporation golf course were factored into the conceptual model for the hydraulic gradient at the surface water/groundwater interface, although the water levels were not given strict interpretation due to the temporal variability in measurements.

2.3.2 Monitoring Well Construction

Two shallow monitoring wells were installed in the surface water/groundwater interface, on the beach and campus grounds at North Idaho College (Figure 14). Well locations and elevatons were surveyed by students in the North Idaho College drafting technology program. The first well, AIP-1 (Aquifer Interface Project, well #1), is located on the NIC Beach point at land surface elevation 2131.8 feet (649.8 m). The second well (AIP-2) is located near the NIC dike, just off the cedar-lined jogging trail in the Fort Sherman Park area at land surface elevation 2135.3 feet (650.8 m).

The boreholes were drilled on September 30 and October 1, 1992, with a SIMCO 2000, trailer-mounted, hollow stem auger rig. Sample recovery with the split spoon sampler was unsuccessful, so continuous samples from a definitive depth could not be obtained.

Borehole AIP-1 was augered to a depth of 22.58 feet (6.88 m). The casing settled during installation, giving a casing depth of 24.25 feet (7.39 m) below land surface. This depth was reduced to 24 feet (7.32 m) as a result of well repair in November. Well AIP-2 extends 31.23 feet (9.52 m) into the subsurface.

The monitoring wells are cased with 2-inch, flush-threaded, PVC pipe and capped with a 2-inch, locking, watertight cap. Well AIP-1 has a glue-on PVC cap on the bottom, a 5-foot section of 10-slot PVC, and 19 feet of blank casing to the surface (Figure 15 [a]). The annulus around the screen is filled with 30-mesh silica sand to 18 feet (5.49 m) below land surface and fine sand to 17 feet (5.18 m) below land surface. The borehole was backfilled with bentonite chips to about 1.5 feet (0.46 m) below land surface, where a concrete plug was set to house a 7-inch diameter, aluminum, vaulted, flush-mounted well cover. Well AIP-2 has a threaded PVC cap on the bottom, 5 feet of 10-slot PVC screen and 26 feet of blank casing (Figure 15 [b]). A natural sand and gravel pack surrounds the well screen, because of borehole caving. Bentonite seals the casing from 23 feet up to 3 feet (7.0 - 0.9 m) below land surface. A 7-inch diameter, flush-mounted well cover is set in concrete at the surface.

The wells were developed with a stainless steel 2-inch diameter, 5-foot long bailer. Approximately 60 well volumes were removed from AIP-2; 20 well volumes from AIP-1. Turbidity is a continuing problem in both wells. Water level elevations were measured in both wells in the early fall of 1992. Well AIP-1, closest to the surface water, went dry after October 17, in response to planned drawdown of Lake Coeur d'Alene by the Washington Water Power Corporation. Water level elevations were taken weekly in well AIP-2 throughout the fall, winter and early spring and are included in Appendix IV.

2.3.3 Sample Collection and Analysis

Groundwater samples were collected from well AIP-2 in December, 1992, and January, 1993. Three well volumes were purged from the well with a stainless steel bailer. Temperature and pH were

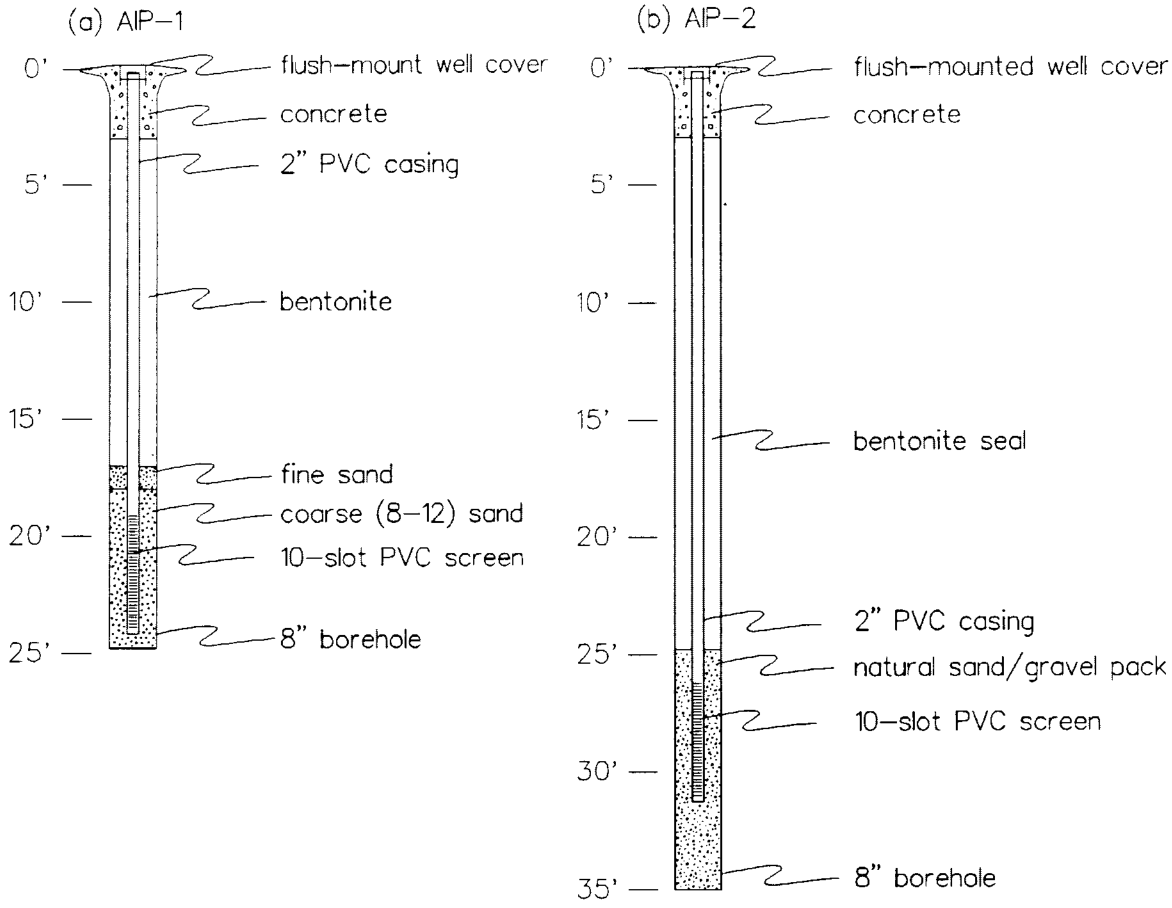


Figure 15. Well construction schematic for (a) monitoring well AIP-1 and (b) monitoring well AIP-2.

read at the site. The samples were collected and filtered through a 0.45μm filter in the field. Each sample was acidified with 6-8 drops of ultra-pure (J.T. Baker Ultrex II, trace metal analysis grade) nitric acid. One duplicate and one blank (Millipore-filtered) sample were included. Samples were shipped to Acme Analytical Laboratories and analyzed for Mo, Cu, Pb, Zn, Ag, Co, Ni, Mn, Fe, As, Sr, Cd, V, Ca, P, Li, Cr, Mg, Ti, B, Al, Na K, Ce, Be, and Si by Ultrasonic Nebulizer Inductively-Coupled Plasmometry (ICP).

A sample of the clay filtrate from well AIP-2 was oven-dried for 18 hours, disaggregated and sent to the laboratory. The sample was digested with 3 ml HCl, HNO_3, H_2O at 95°C for one hour and diluted to 10 ml with water. The leach is partial for Mn, Fe, Sr, Ca, P, La, Cr, Mg, Ba, Ti, B, W and limited for Na, K and Al. One duplicate sample of the clay filtrate was run. The results of these analyses are presented in Section 5.2.2, Section 6.3, and Tables 8 and 9.

3.0 HYDROGEOLOGIC SETTING

3.1 Hydrogeology

3.1.1 Lithology

The Rathdrum Prairie Aquifer is composed of stratified glacial outwash. Most authors assert that the sediments are poorly- to moderately-well-sorted, well-rounded clasts, of granitic and metamorphic origin. Hammond (1974) determined that the alluvial fill of the lowlands is derived predominantly from bedrock of nearby highlands, according to driller's logs and cuttings obtained from wells.

The aquifer is said to consist of primarily fine to coarse, relatively clean sand and gravel with some beds of cobbles and boulders and a few scattered clay lenses (Drost and Seitz, 1978; Esvelt, 1978). The sand and gravel are relatively free of fine sand and silt except in the uppermost 3 to 5 feet (0.9-1.5 m) (Esvelt, 1978).

The aquifer material at the interface between Lake Coeur d'Alene and the aquifer is different from that described above, according to the results of field studies performed as part of this project. The sediments in borehole B (Figure 14), an 11-foot (3.52-meter) deep hand-augered borehole on the banks of the Spokane River, were very poorly sorted (Appendix I). Clasts ranged from clay-size to cobble-size (7 cm, observed). The median grain size, for each depth interval below the soil zone, ranged from -0.17ϕ to -2.72ϕ (1.13-6.58 mm) and the mean grain size ranged from -0.50ϕ to -2.88ϕ (1.42-7.38 mm). The variability in grain size and sorting (Figure 16) reflects the heterogeneity of the glaciofluvial deposits adjacent to Lake Coeur d'Alene.

The clay contained in these samples appears to be a coating around and between the coarser sand and gravel particles, rather than distinct beds or laminae. Any sedimentary structures which may have been present, however, were demolished by the soil auger. A similar sediment, described as "sand, gravel and fine brown silt" was identified from a borehole by a consultant to the State of Idaho Department of Transportation in 1966, while planning the construction of Highway 95 over the Spokane River. From thirteen feet (4.3 m) below the river bed to the bottom of the borehole (almost 45 feet [15 m] below the river bottom), the fine silts and brown clays were mixed with the coarser aquifer materials (State of Idaho Department of Highways [Transportation], 1966).

The poorly sorted, mixed clay and gravel sediments in this area could have been formed by the transport of fine lacustrine sediments from the lake bed into the coarser aquifer material. This process may have occurred in several stages. First, fine-grained sands, silts and clays collected on the bed of the tributary lake during the Pleistocene. These lake bed sediments built up in the tributary valley while glacial outwash accumulated in the Rathdrum Valley proper. Second, the fine lake sediments were probably removed during the repeated outbursts of flood waters from glacial Lake Missoula. Hammond (1974) states that it is likely that catastrophic floods may have removed some of the fines from preexisting tills and outwash deposits. The waters of the last major glacial flood are known to have flowed south

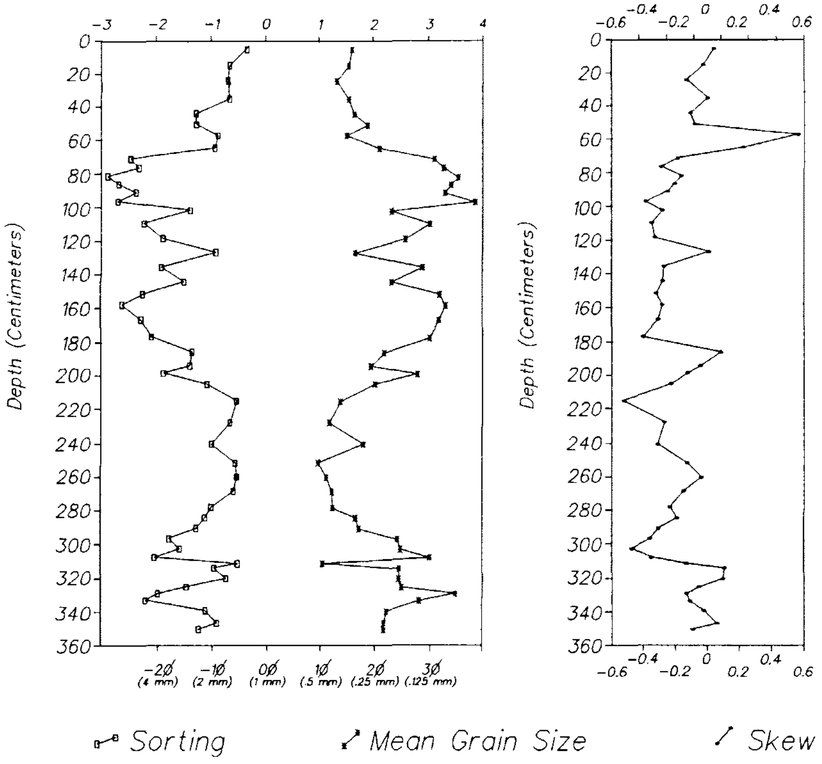


Figure 16. Mean grain size and sorting of sediments with depth, from borehole B. (See also Appendix I.)

through the valley of Lake Coeur d'Alene. The flood waters resorted and redeposited the coarse material under the present day lake bed, as evidenced by seismic profiles (shown in Figure 11).

Finally, more silts and clays were carried into the lake valley by the St. Joe River and Coeur d'Alene Rivers and several small creeks. In the absence of a lake bottom "seal", A portion of these sediments were carried through the coarse, porous glacial deposits. Eventually, the fine sediments plugged the pore spaces and the lake bottom regained its seal. The present day lake bottom sediments were deposited less than 14,000 years ago, after the last catastrophic flood.

3.1.2 Hydraulic Conductivity and Transmissivity

The mixture of coarse and fine sediments in the aquifer near the northern end of the lake impede the ability of the sediment to transmit water. The conductivity of the aquifer is determined by the size and shape of pore spaces in the sediments and the degree of interconnection of pores. The hydraulic conductivity at the surface water/groundwater interface is probably several orders of magnitude less than in the central portion of the aquifer.

The Rathdrum Prairie Aquifer is known for its exceptionally high transmissivities. Drost and Seitz (1978) reported that the estimated transmissivity of the Rathdrum Prairie Aquifer in the Coeur d'Alene area is 6.7 x 10^5 ft^2/day (4.3 x 10^4 m^3/day) (Figure 17). Transmissivities are slightly higher (1.3

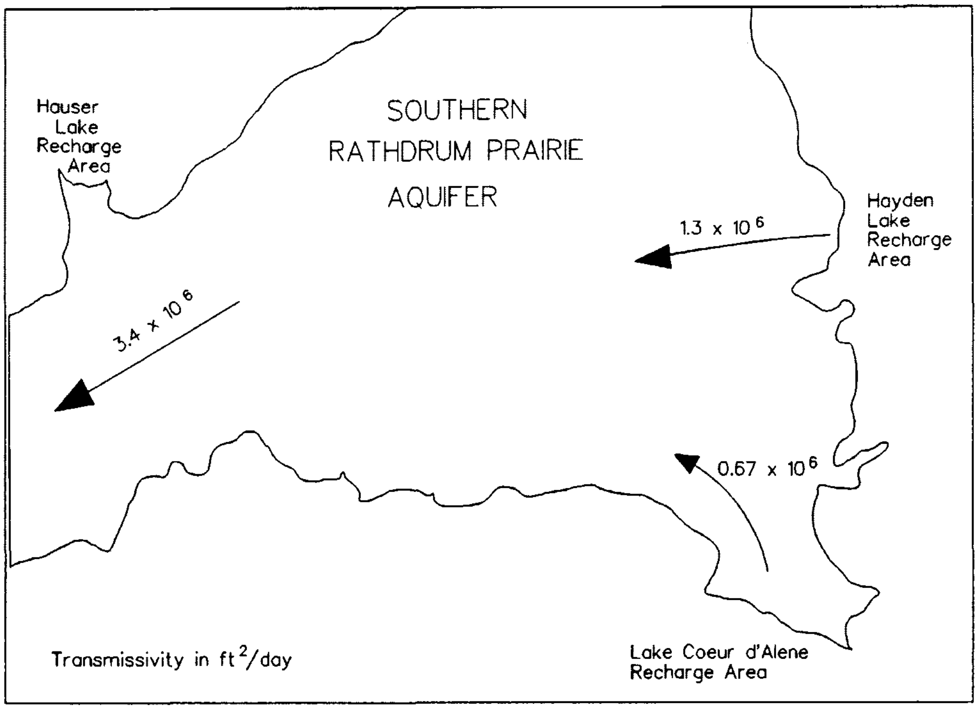


Figure 17. Generalized transmissivity map of the southern Rathdrum Prairie Aquifer, based on estimated or calculated flow rates and observed hydraulic gradients (Drost and Seitz, 1978).

x 10^6 ft^2/day, 1.2 x 10^5 m^3/day) several miles north of Coeur d'Alene at Hayden Lake. The estimated transmissivity increases to 3.4 x 10^6 ft^2/day (3.4 x 10^5 m^3/day) west of Post Falls. The average transmissivity ranges from 0.13 to 11 million ft^2/day (1.2 x 10^4 - 1.02 x 10^6 m^3/day) over the entire Spokane/Rathdrum aquifer and from 0.27-11 million ft^2/day (2.5 x 10^4 - 1.02 x 10^6 m^3/day) in the Idaho portion. Transmissivity, based upon pumping tests, is about 1.3 x 10^7 ft^2/day (1.2 x 10^6 m^3/day) near the Idaho/Washington state line (Jehn, 1988; Hammond, 1974). This figure is higher than the averages reported by Drost and Seitz.

Sagstad (1977) used specific capacity data from historic well production tests from four wells near Coeur d'Alene and 20 wells near Post Falls to estimate transmissivity and hydraulic conductivity. He applied the Theis (1935) method to transform specific capacity (the ratio of pump discharge to drawdown) to transmissivity. Based on an assumed saturated thickness of 175 feet, the estimates of hydraulic conductivity ranged from 240 ft/day to 896 ft/day (0.08 - 0.32 cm/s) in Coeur d'Alene and 254 to 2,141 ft/day (0.09 - 0.76 cm/s) in Post Falls. (These figures equate to transmissivities of 42,000 to 156,800 ft^2/day (3,900 - 1,450 m^2/day) and 44,450 to 374,700 ft^2/day (4,100 - 34,800 m^2/day), about one order of magnitude lower than that reported by Drost and Seitz for the Coeur d'Alene and Post Falls areas). The Post Falls area was believed to have greater hydraulic conductivities (and transmissivities) due to the greater percentage of gravels, pebbles and coarse sands than in the Coeur d'Alene area.

3.1.3 Aquifer Thickness

The thickness of the Spokane/Rathdrum Prairie Aquifer is not well established. Most wells do not penetrate deeper than 50-60 feet (15-18 m) into the aquifer, because sufficient quantities of water are easily available at relatively shallow depths. The only wells that penetrate the entire thickness of the aquifer do so near the margins.

The aquifer is generally thickest in the northern area and thins to the south and southwest. Near the Idaho/Washington state line, a seismic survey by Newcomb (1953) indicated that the glacial alluvium is 340-376 feet thick (104-115 m), of which 255 feet (78 m) is saturated. The northern portion of the aquifer, near Athol, Idaho, reportedly contains 1,400 feet (427 m) of quaternary sediments, which may be entirely glacial outwash deposits (Hammond, 1974).

A test hole, drilled in 1963 in the Hillyard Trough (north of Spokane, between the Mt. Spokane highlands and Fivemile Prairie), revealed about 780 feet (237 m) of unconsolidated material, according to Drost and Seitz (1978). Seismic interpretation of the same area showed 150 feet (46 m) of unsaturated alluvium and 160 feet (49 m) of saturated alluvial aquifer. The remaining 470 feet (143 m) were impermeable sediments of the Latah Formation.

The Latah Formation may be all or partly absent beneath the Spokane Valley and westward, because basalt flowed in from the west and cooled as Latah beds were deposited in the east. Seismic surveys in the Spokane area indicate that the depth to bedrock (basalt) is 400-700 feet (120-210 m) (Esvelt, 1978).

The Latah Formation does exist in the Idaho portion of the aquifer. Newcomb (1953) suggests that 800-900 feet (244 - 274 m) of Miocene fill (Latah Formation) still remains beneath the Quaternary flood gravels. West of Hayden Lake, Anderson (1940) reported 1,000 feet (305 m) of Latah Formation below a layer of basalt exposed at land surface.

Wells in the vicinity of Coeur d'Alene also confirm the presence of Latah Formation beneath 270-310 feet (82-94 m) of glacial outwash. One well penetrated clean sand and gravel down to 269 feet (82 m) where basalt (probably late, valley-fill basalt) was reached. A well owned by the City of Coeur d'Alene was drilled through 340 feet (103.6 m) of sand and gravel followed by 15 feet (4.6 m) of blue, sandy clay (probably Latah deposits). A U. S. Forest Service well penetrated 309 feet (94 m) of mostly sand and gravel without reaching the Latah Formation at NW¼, NW¼, Sec. 3, T50N, R4W.

Figure 18 gives the location of two geologic cross sections across the surface water/groundwater interface zone. Cross section A-A' extends from Blackwell Hill to Potlatch Hill; line B-B' extends from Blackwell Hill to Best Hill. The cross sections are based on well logs in the area (Appendix I), surface topography, and existing reports. Two versions of each cross section were constructed (Figures 19 and 20). One version illustrates a fairly smooth erosional surface along both the basement rock/Latah contact and the Latah/glaciofluvial outwash contact. The second illustrates a possible irregular erosional surface.

The total cross-sectional area of the glaciofluvial deposits along line A-A' is 2,363,000 ft^2 (219,500 m^2) for the first (smooth) profile and 2,914,000 ft^2 (270,700 m^2) for the second (irregular) profile. The saturated aquifer thickness along A-A' is estimated to be 1,761,000 ft^2 (163,600 m^2) and 2,312,000 ft^2 (214,800 m^2). Cross section B is constructed farther away from the lake outlet, across a deeper portion of the ancestral valley. Therefore the total cross-sectional area is larger: 3,220,000 ft^2 (299,100 m^2)for the first (smooth) cross section and 3,444,000 ft^2 (320,000 m^2) for the second (irregular) profile. The corresponding saturated cross-sectional areas are 2,790,000 ft^2 (259,200 m^2) and 2,656,000 ft^2 (246,800 m^2).

3.1.4 Water Table/Hydraulic Gradient

The water table slopes from Hoodoo valley and Lake Pend Orielle southward to the Rathdrum/Coeur d'Alene area and south-southwest toward Spokane. The maximum height of the water table in the Rathdrum Aquifer is approximately 2180 feet (664.5 m) above mean sea level in the northern

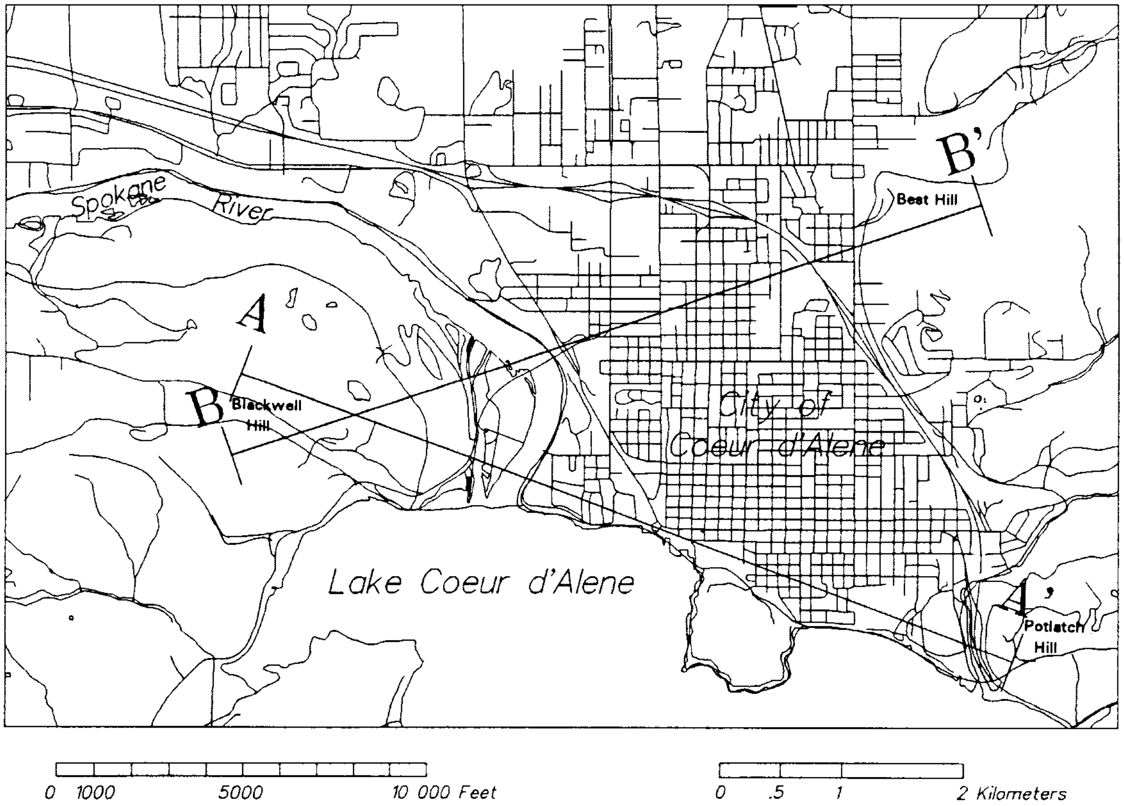


Figure 18. Location of geologic cross sections.

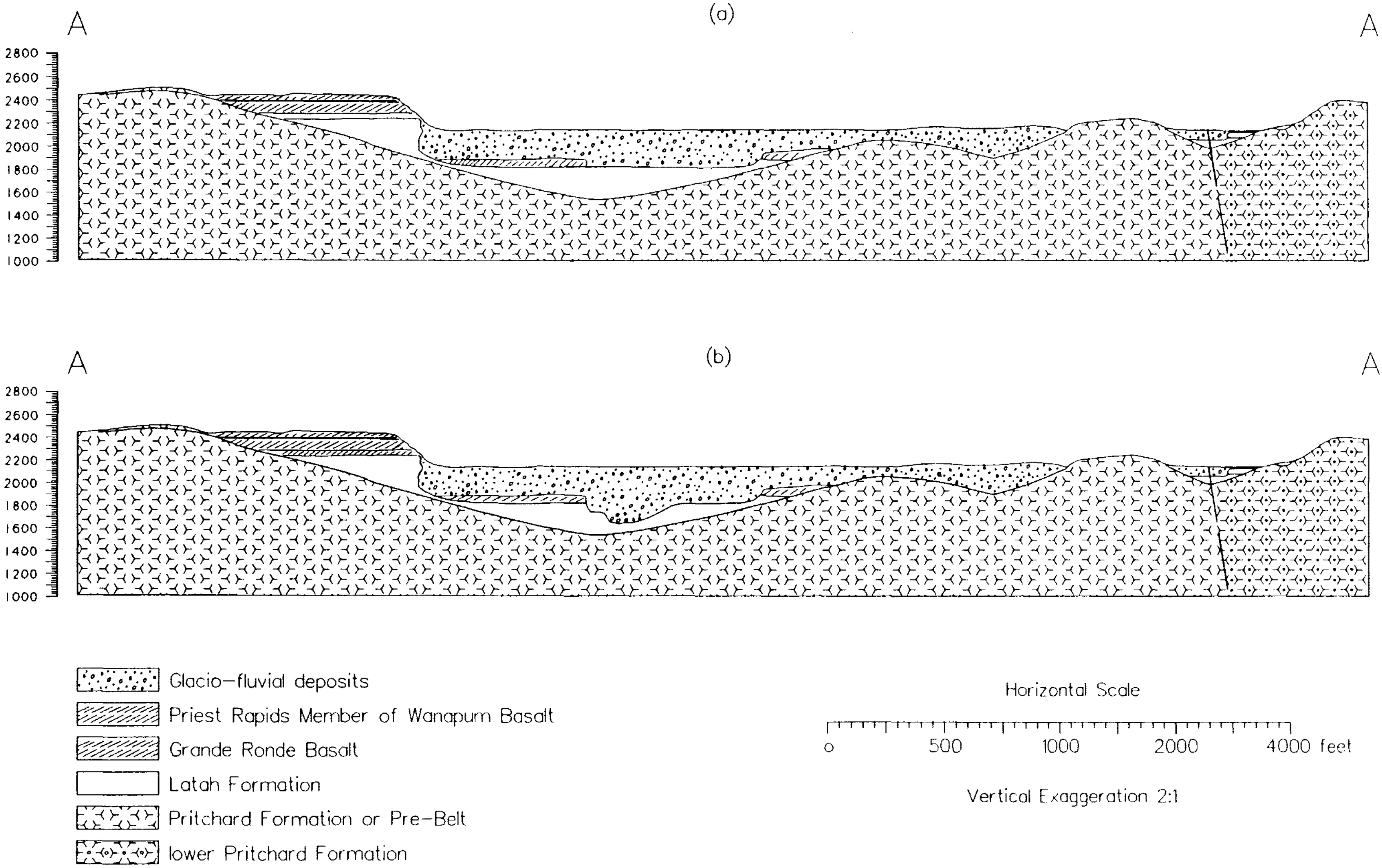


Figure 19. Geologic cross section from Blackwell Hill to Potlatch Hill showing (a) smooth erosional surfaces and (b) irregular erosional contacts.

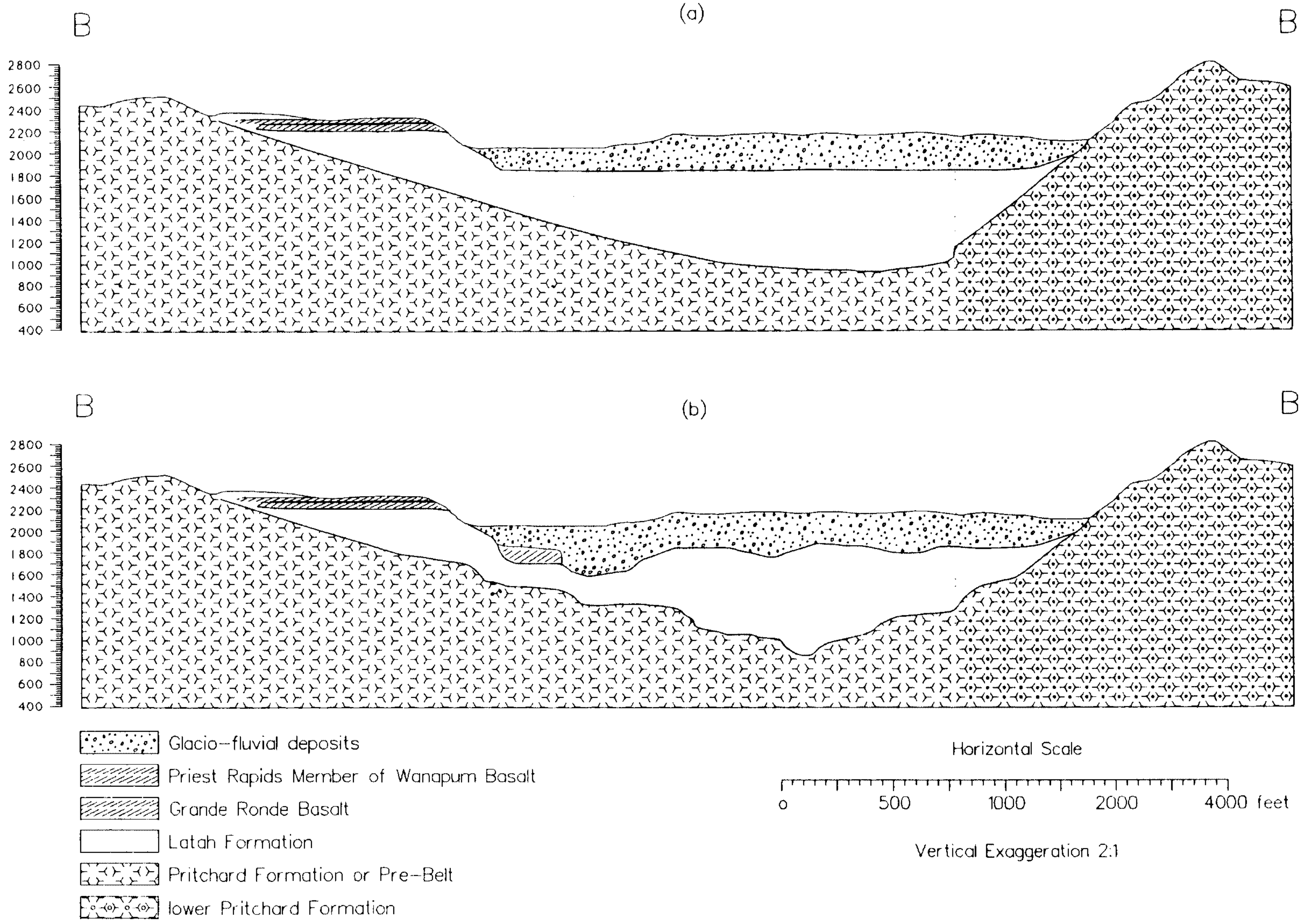


Figure 20. Geologic cross sections from Blackwell Hill to Best Hill showing (a) smooth erosional surfaces and (b) irregular erosional contacts.

part of the aquifer in Idaho. The water table slopes downward to an elevation of about 1970 feet (600 m) at the Idaho/Washington state line. From there, the water table declines to a minimum elevation of approximately 1540 feet (469.4 m) near Nine Mile Falls, Washington. Depths from land surface to the water table range from a maximum of about 400 feet (122 m) in the northern reaches of the aquifer to about 153 feet (46 m) in the vicinity of the state line (Jehn, 1988) and to about 40 feet (12 m) near the eastern Spokane city limits (Esvelt, 1978).

The average hydraulic gradient is steepest in the northern portions of the aquifer, where the water table slopes 20 feet/mile (0.0038 ft/ft; 3.8 m/km). From Round Mountain to the southern end of the Hillyard Trough, the slope of the water table ranges from 2 to 10 feet/mile (0.0038-0.0019 ft/ft; 0.38-1.9 m/km). The hydraulic gradient is extremely steep (60 ft/mi; 0.011 ft/ft; 11.4 m/km) in the Hillyard Trough (Drost and Seitz, 1978).

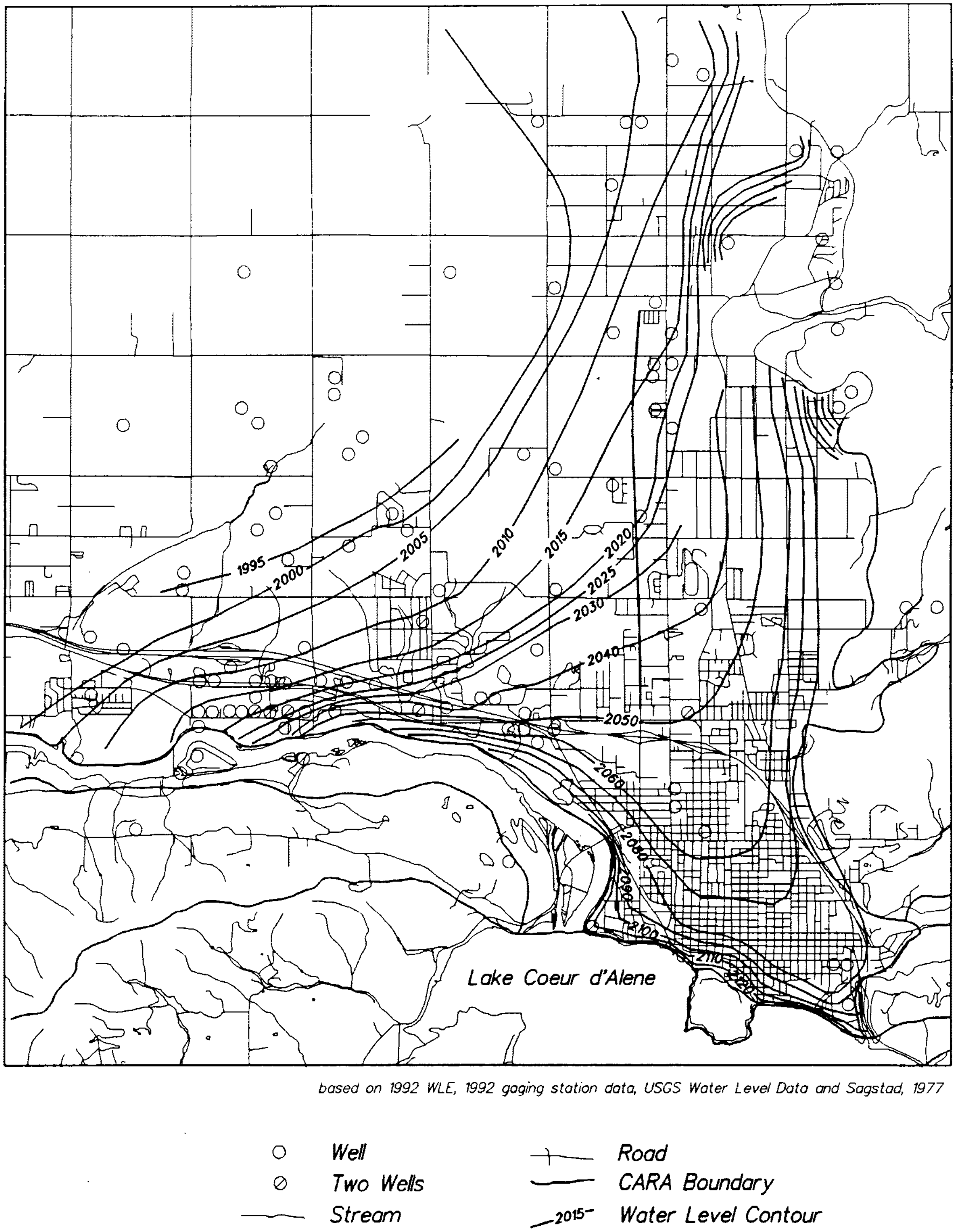
Figure 21 illustrates that the hydraulic gradient is extremely high in the vicinity of Lake Coeur d'Alene. Water level elevations drop 360 feet/mile (0.068 ft/ft; 68 m/km) or more adjacent to the lake. The lake level elevation in October, 1989, averaged 2127.4 feet (648.43 m) above mean sea level. A short distance (1,400 and 2,320 feet) from the lake shore, water levels in monitoring wells were measured at 2,095 and 2,071 feet, respectively. This steep hydraulic gradient (2.4%, 122 ft/mi, 24 m/km) reflects the low hydraulic conductivities of sediments in this area, relative to the rest of the aquifer.

Jehn (1988) reported that, in general, water level fluctuations are less than 30 inches (76 cm) per year in most areas of the Rathdrum Prairie Aquifer. However, Drost and Seitz (1978) reported that the water table of the Spokane Valley-Rathdrum Prairie Aquifer usually fluctuates 5-10 feet (1.5-3 m) and generally less than 15 feet (5 m) during the year. The greatest fluctuations are observed in wells near the Spokane River, in response to changing stages of the river (Drost and Seitz, 1978).

The water levels in two monitoring wells adjacent to Lake Coeur d'Alene were recorded in the fall of 1992 and spring of 1993 as part of this study, and are summarized in Appendix IV. Water levels dropped drastically as a result of planned drawdown of Lake Coeur d'Alene by the Washington Water Power Company. The water level in AIP-1 fell from 18.75 feet (5.72 m) below land surface on October 7, 1992 to 21.45 feet (6.538 m) on October 17. The well was dry by November 4. The water level in AIP-2 fell from 2112.2 feet (643.8 m) above sea level on November 7, 1992 to 2104.6 feet (641.48 m) on December 16, 1992. The well was essentially dry in January, 1993, and recovered in March.

3.1.5 Recharge Sources

Lake Coeur d'Alene and the Spokane River contribute approximately 30% of the recharge to the Rathdrum Prairie Aquifer. Pluhowski and Thomas (1968) performed a detailed water budget analysis from which they concluded that seepage from the lake and the reach of the Spokane River above Post



based on 1992 WLE, 1992 gaging station data, USGS Water Level Data and Sagstad, 1977

Figure 21. Water level elevations in the Rathdrum Prairie Aquifer near Lake Coeur d'Alene.

Rainfall infiltration	33.2%	250.0 cfs
Lake Coeur d'Alene/Spokane River	30.6%	230.0 cfs
Blanchard Area	8.3%	62.2 cfs
Lake Pend Orielle	6.6%	50.0 cfs
Chilco Channel	5.4%	40.6 cfs
Hayden Lake	5.0%	37.8 cfs
Twin Lakes	3.3%	25.0 cfs
Spirit Lake	3.0%	22.3 cfs
Bayview/Kelso	2.0%	14.8 cfs
Hauser Lake	1.1%	8.2 cfs
Hidden Valley	1.0%	7.3 cfs
Canfield	0.6%	4.6 cfs

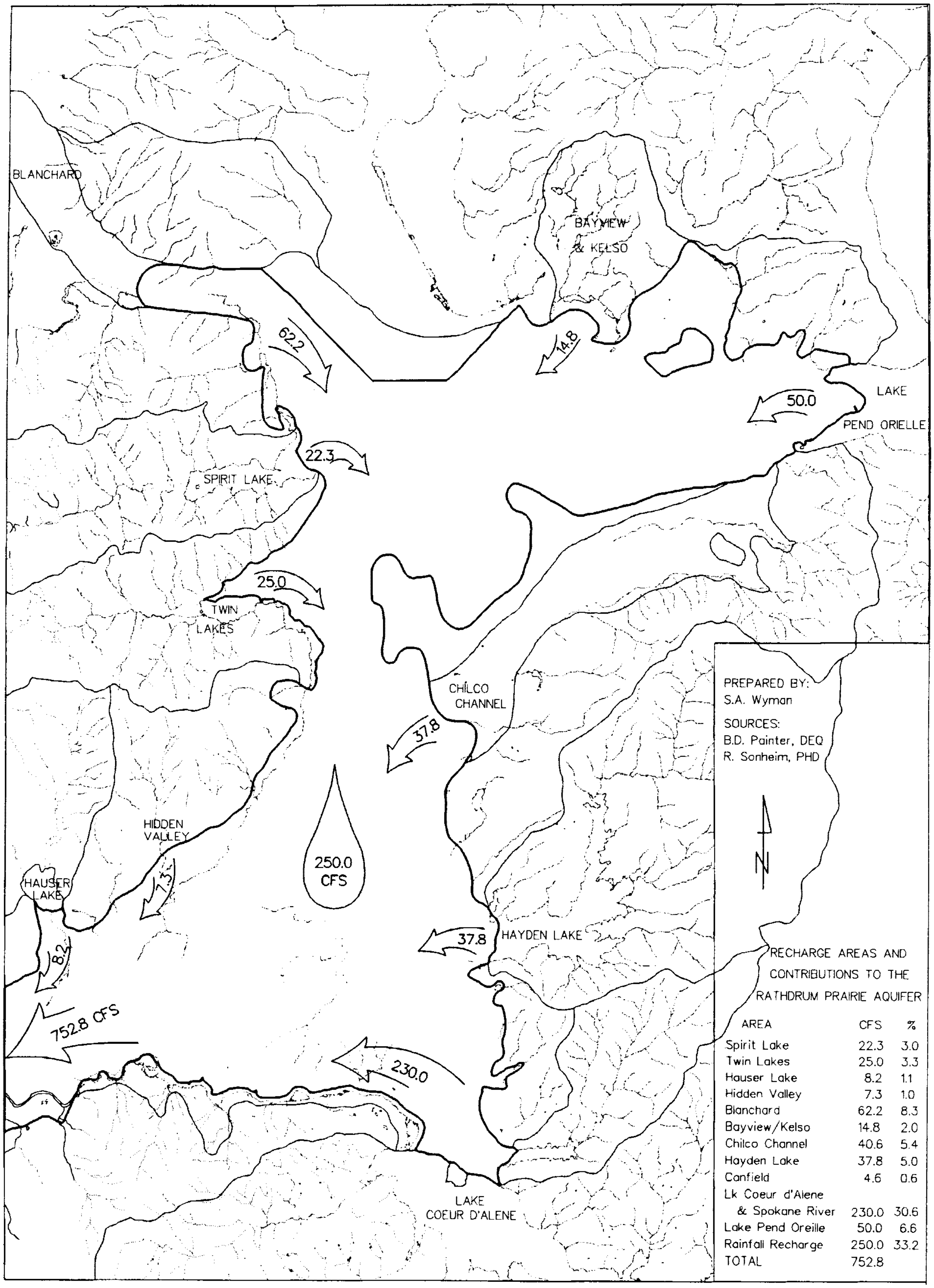
Table 2. An estimate of recharge to the Rathdrum Prairie Aquifer in Idaho from all sources, prepared by Brian D. Painter, 1991 (b).

Falls is about 250 cfs. Painter (1991 [b]) initially placed this amount at 230 cfs for the purpose of modelling the aquifer system. His estimates of recharge to the aquifer from all sources in Idaho are presented in Figure 22 and in Table 2.

Sagstad (1977) estimated the flow from Lake Coeur d'Alene and the Spokane River by first calculating total recharge using the Darcy equation, second estimating that 75% of annual precipitation enters the aquifer and, third, subtracting precipitation from total groundwater flow (obtained first) to arrive at an estimate of 225 cfs. He believed that this estimate was probably low.

Other investigators calculated higher estimates for recharge to the aquifer from Lake Coeur d'Alene and Spokane River above Post Falls. In 1951, Anderson estimated the recharge rate at 300 cfs. Frink (1964) also arrived at a 300 cfs recharge rate. Drost and Seitz (1978) estimated that the recharge from Lake Coeur d'Alene is 250 cfs, plus an additional 15 cfs from the reach of the Spokane River from the outlet of Lake Coeur d'Alene to one mile below Post Falls.

Separating the Spokane River fraction of recharge from that which exits Lake Coeur d'Alene as underflow into the aquifer has proven to be difficult. Attempts by USGS to quantify seepage losses within the nine-mile reach of the river have been largely unsuccessful because of the low velocities in the backwater area and the resultant difficulty in obtaining accurate discharge measurements. Patmont, *et al.*, (1985) assumed that no water was transferred from the Spokane River to the aquifer. He stated that "some seepage loss in this region is thought to be likely, on the basis of aquifer characteristics, but has



AREA	CFS	%
Spirit Lake	22.3	3.0
Twin Lakes	25.0	3.3
Hauser Lake	8.2	1.1
Hidden Valley	7.3	1.0
Blanchard	62.2	8.3
Bayview/Kelso	14.8	2.0
Chilco Channel	40.6	5.4
Hayden Lake	37.8	5.0
Canfield	4.6	0.6
Lk Coeur d'Alene & Spokane River	230.0	30.6
Lake Pend Oreille	50.0	6.6
Rainfall Recharge	250.0	33.2
TOTAL	752.8	

Figure 22. An estimate of recharge to the Rathdrum Prairie Aquifer from all sources (from Painter, 1991 [b]).

proven difficult to measure" (Patmont, *et al.*, 1985, pg. 8). Seitz and Jones (1981) reported no measurable gain or loss of discharge during two low-flow surveys.

Though difficult to measure, water does seep from the Spokane River into the Rathdrum Prairie Aquifer over the 18.7 mile reach from the outlet of Lake Coeur d'Alene to just above Otis Orchards, Washington. Where the water level elevation in the river is above the water table, the river feeds the aquifer. The entire river upstream of approximately river mile 88 (Sullivan Road) is situated above the aquifer (Esvelt, 1978; Bolke and Vacarro, 1981). The exact length of this influent reach may vary temporally due to changes in precipitation, outflow from the Post Falls dam, and possibly groundwater withdrawal.

The fine-grained river bottom sediments in some places form a seal which prevents the flow of water from the river to the aquifer, in spite of the local hydraulic gradient. Supporting evidence for the perched nature of the Spokane River includes reports by personnel of the Idaho Department of Transportation. During construction of the bridge over the Spokane River at the state line in 1970, the sediment seal in the river bottom was punctured and water drained out of the river and down into the underlying aquifer (Larry Wolf, P.E., 1992, State of Idaho Transportation Department, personal communication).

Prior to construction of the same project, twelve test holes were bored in the river bottom. The deepest borehole stopped at about elevation 1950 feet (594.4 m), nearly 65 feet (19.8 m) below the deepest part of the river channel. The log of borings indicates that no static water table was encountered.

It is difficult to state with certainty where the river becomes perched and how much water drains from the perched river into the aquifer. Records from seven boreholes in the river bottom (at Highway 95 crossing in Coeur d'Alene) indicate that the river bottom sediments are coarser and more poorly sorted there than 30 feet downstream (State of Idaho Department of Highways [Transportation], 1966). The mixture of sand and fine gravel on the river bottom at Coeur d'Alene may allow some seepage. The gravelly silty sand and silty sandy gravel at Post Falls and at the State Line may be sufficient to prevent any significant water loss from the river.

The nine-mile reach of the river from Coeur d'Alene to Post Falls is considered, in this report, to be consistently influent. The portion of recharge due to the river is not separated from the underflow and direct recharge flow from Lake Coeur d'Alene, although the Lake Coeur d'Alene fraction must be significantly greater than the Spokane River fraction.

3.2 Surface Streams

3.2.1 Surface Inflow to Lake Coeur d'Alene

The Coeur d'Alene and St. Joe rivers supply almost 94% ($\approx 1.29 \times 10^9$ ft^2/yr; $\approx 4.73 \times 10^9$ m^3/yr) of the surface water inflow to Lake Coeur d'Alene. The lake also receives input from Wolf Lodge

Creek, Plummer Creek, Fighting Creek, Carlin Creek and least 40 other minor streams. The volumetric input is highest in the late spring and early summer, after snowmelt in the mountains. Daily stream flows for six streams are illustrated in Figures 23 and 24.

The headwaters of the Coeur d'Alene River originate in the Bitterroot Range on the Idaho/Montana border. The Coeur d'Alene drainage basin is approximately 1,500 square miles (3,830 km^2) and includes the historic mining district commonly referred to as the "Silver Valley," within the South Fork drainage. The Coeur d'Alene River enters the central portion of the lake from the east.

The headwaters of St. Joe river also originate along the Idaho/Montana border. The St. Joe River drains a 1,750 square mile (4,480 km^2) watershed and discharges into the southern end of the lake from the east. The water is free from heavy metal contamination, but is a source of sediment, nitrate and phosphorous loading to the lake (Woods, 1992, personal communication).

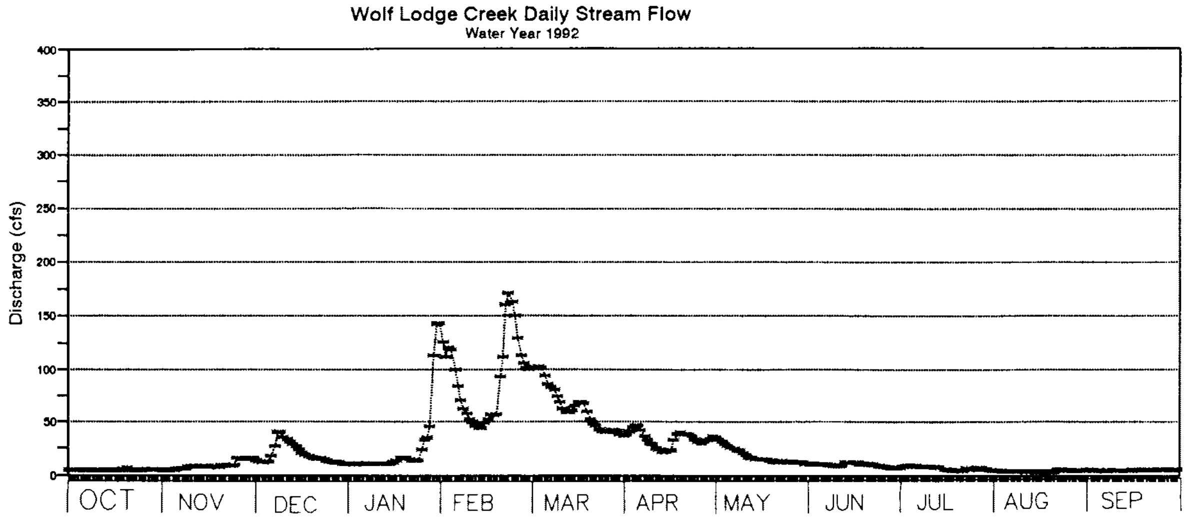
3.2.2 Surface Outflow

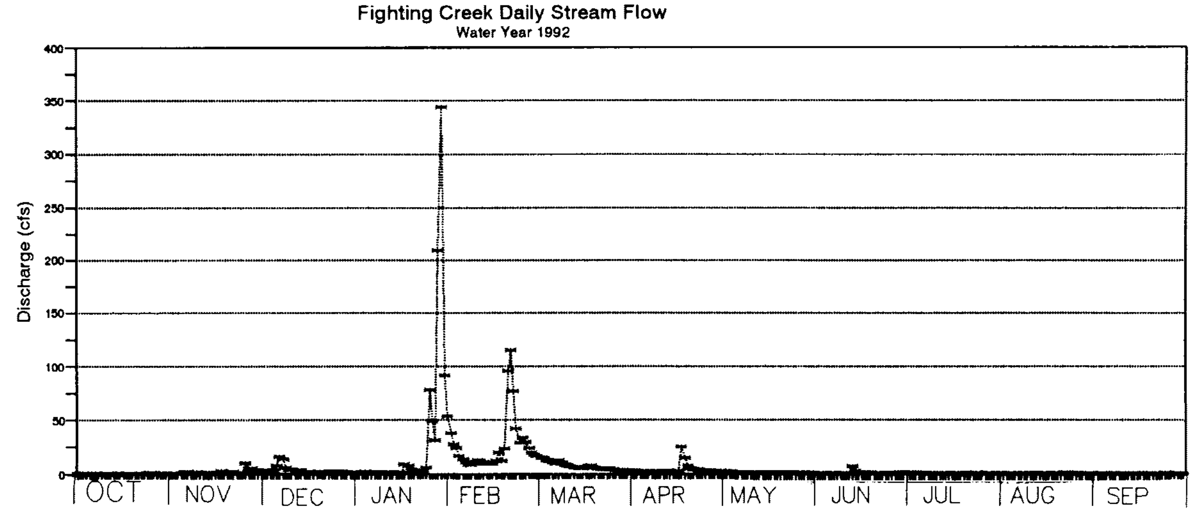
The Spokane River is the only surface outlet of Lake Coeur d'Alene and is also distinguished as the only continuous surface stream on the Rathdrum Prairie. The discharge of the Spokane River, measured at Post Falls Dam over calendar year 1991, was 2,564,017 cubic feet (72,605 m^3). Three minor streams feed into the Spokane River between the outlet of Lake Coeur d'Alene and the USGS gaging station at Post Falls. The Rathdrum Canal and Old Farm Canal have historically diverted water from the river, but are presently not in operation.

The Spokane River is essentially an extension of Lake Coeur d'Alene during much of the year. The water, impounded by Post Falls Dam, is maintained at a normal summer elevation of 2128 feet (648.3 m). According to the Washington Water Power (WWP) Company's current operating plan, drawdown of the lake and river begins in mid September. The water is slowly lowered to approximately 2122 feet (646.8 m) by January, then allowed to recede at its natural rate of outflow. From January until the end of spring snowmelt and runoff, the Spokane River acts as a free flowing stream. WWP then resumes control of the water levels for the remainder of the year.

Channel configurations at seven locations along the river (Figure 25) were determined by Seitz and Jones, of the U.S. Geological Survey, in 1981. The Spokane River is generally shallow, warm and well oxygenated (Yearsley, 1980; Seitz and Jones, 1981). However, deep pools which exist near Ford Rock and above Post Falls dam may contain cooler, oxygen deficient water during the summer months (Yearsley, 1980; Seitz and Jones, 1981; Yearsley and Duncan, 1989).

Daily discharge rates and monthly volumetric totals for 1991 are shown in Figure 26. The median discharge at the lake outlet, from 71 years of record (1913-1983), is 2,900 cfs, with 90% of the recorded flow rates between 1,500 and 6,420 cfs. The flow rate of the river at Post Falls is slightly less: 2,730 cfs with 90% between 1,340 and 6,280 cfs. Losses to the Rathdrum Canal (river mile 106.6, from


Wolf Lodge Creek Daily Stream Flow
Water Year 1992


Fighting Creek Daily Stream Flow
Water Year 1992

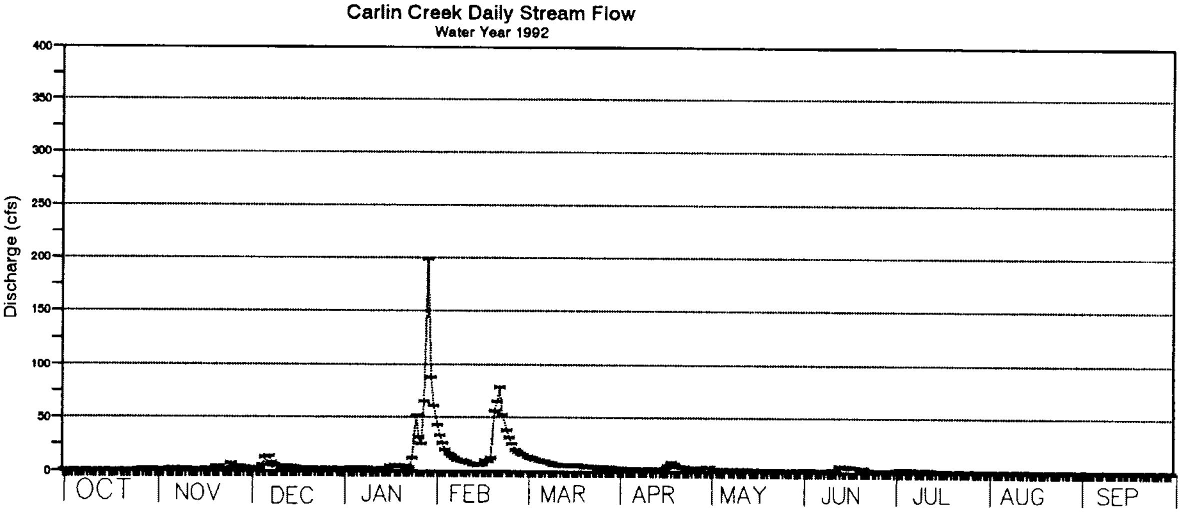
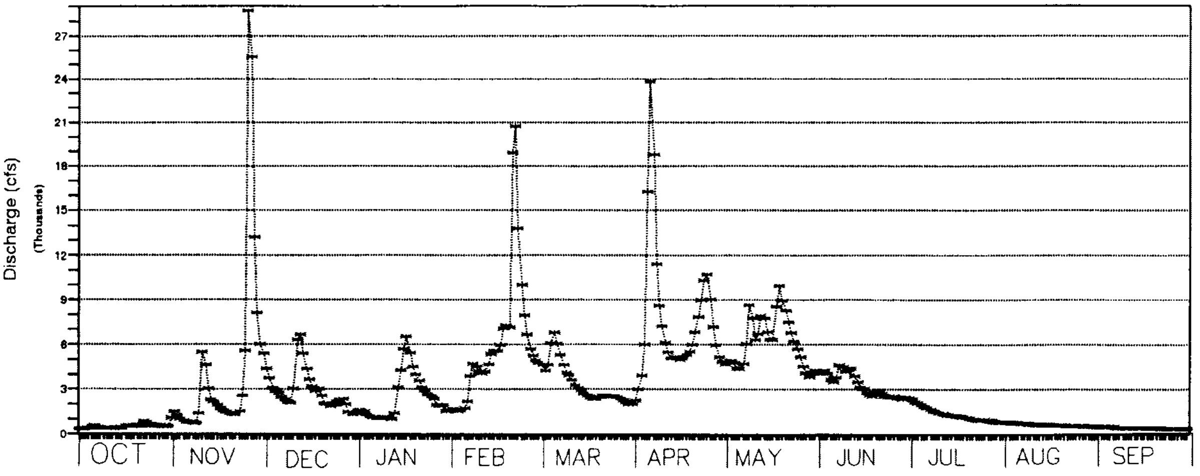
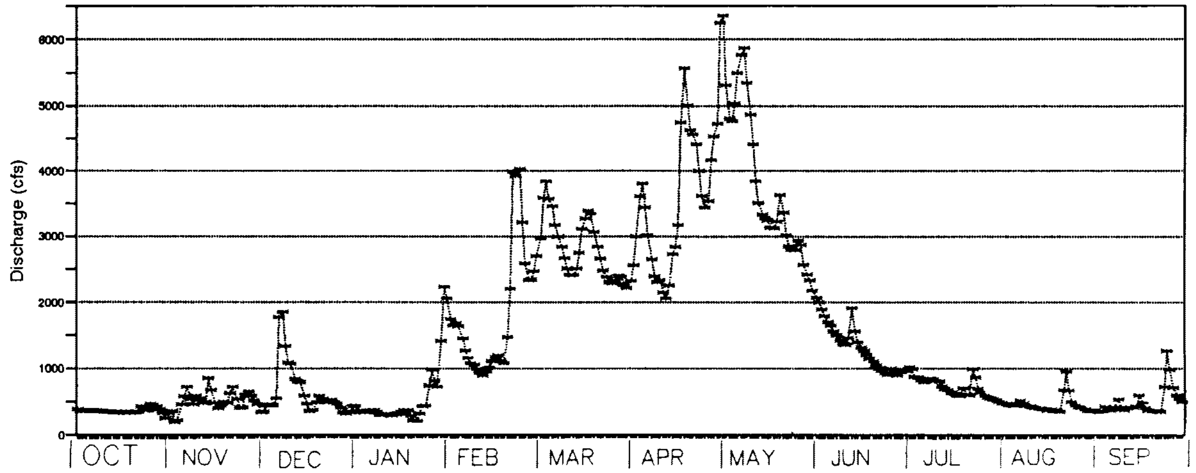

Carlin Creek Daily Stream Flow
Water Year 1992

Figure 23. Daily stream flow for Wolf Lodge Creek (at Wolf Lodge), Fighting Creek and Carlin Creek measured in 1991.

Coeur d'Alene River Daily Stream Flow
Water Year 1992



St. Joe River Daily Stream Flow
Water Year 1992



Plummer Creek Daily Stream Flow
Water Year 1992

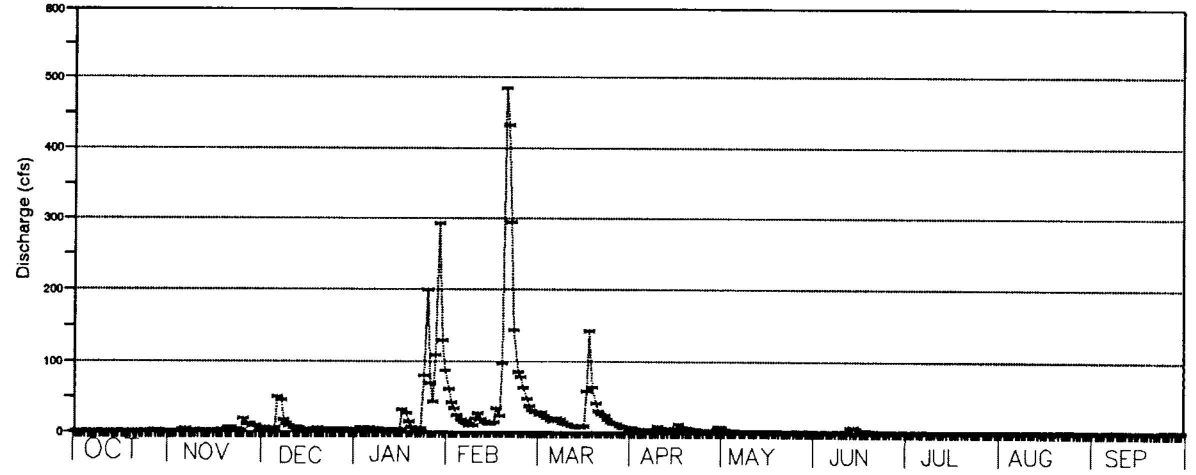


Figure 24. Daily stream flow for the Coeur d'Alene River (at Cataldo), the St. Joe River (at St. Maries) and Plummer Creek, measured in 1991.

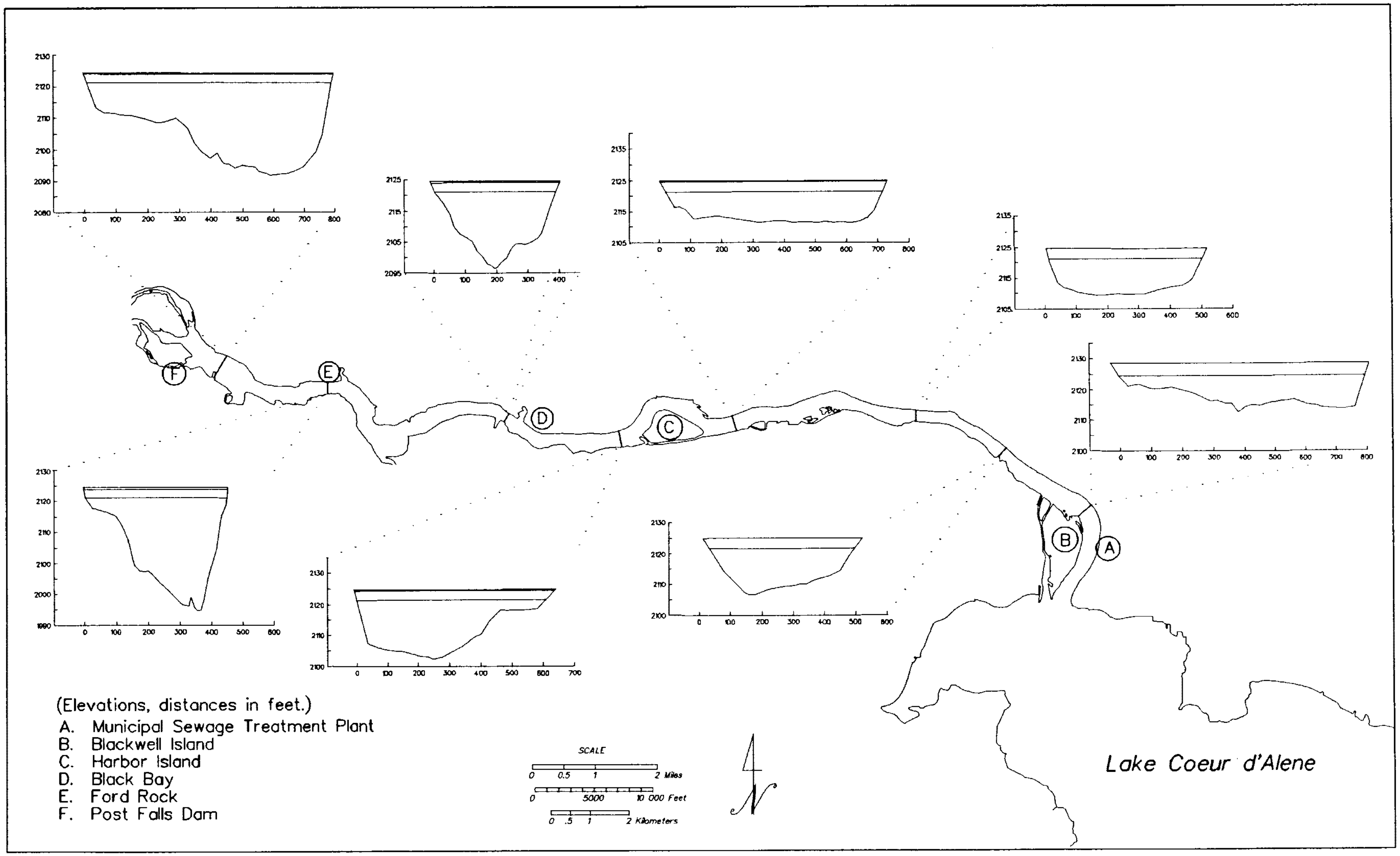


Figure 25. Channel configurations at seven locations along the Spokane River, as determined by Seitz and Jones (1981).

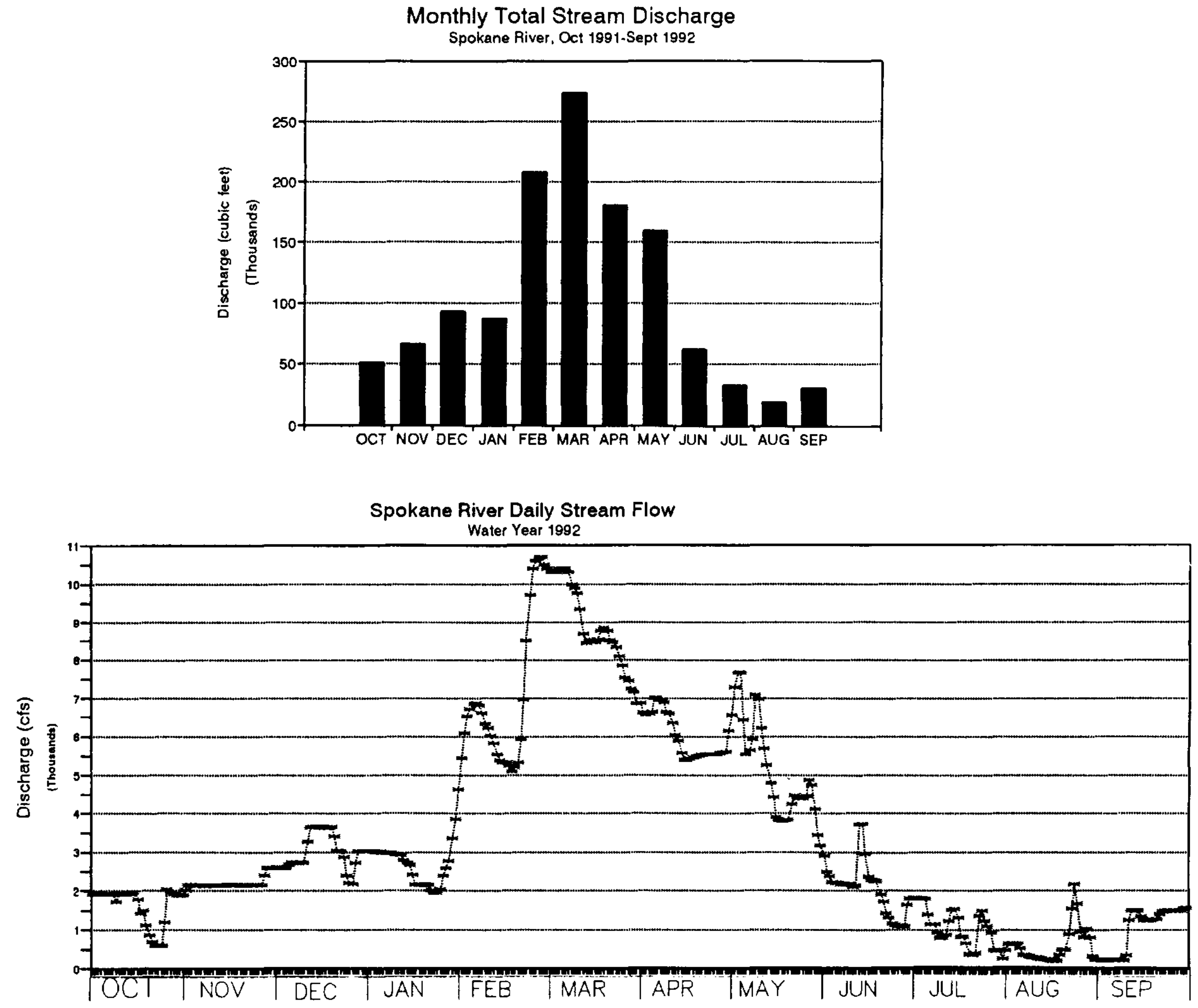


Figure 26. Hydrographs of (a) daily discharge and (b) monthly volumetric totals for the Spokane River below Post Falls Dam, 1991. (Data from USGS stream gage records.)

1966 to 1983) and the Old Farm Canal (river mile 101.7, 1913-1966) do not account for the difference in flow.

Patmont, *et al.*, (1985) also studied the reach of the Spokane River, from the outlet of Lake Coeur d'Alene (river mile 111.7) to the Post Falls Dam (river mile 102.1). The estimated discharge from Lake Coeur d'Alene averaged 1,470 cfs during nine low flow days in August, 1984. Meanwhile, average discharge at Post Falls was 1,440 cfs. Again, the difference in flow must be due, in part, to leakage from the river to the aquifer. However, in constructing a model for phosphorous attenuation in the Spokane River, Patmont chose to neglect seepage in that stretch of the river because the volume was too difficult to quantify.

The recorded outflow and recurrence interval (given in parentheses) from Lake Coeur d'Alene is 2,900 cfs (1:2 years), 2070 cfs (1:5 years), and 1650 cfs (1:10 years). The twenty year low flow

(1:20) is 1500 cfs. Patmont, *et al.*, (1985) concluded that a 20-year low-flow condition for the groundwater exchanges of the Spokane River does not necessarily coincide with the 20-year low flow at the outlet of Lake Coeur d'Alene. The velocity of the Spokane River was studied during a 20-year low-flow period in August of 1984. Researchers determined that the travel time of a parcel of water, from Lake Coeur d' Alene to Post Falls, ranged from 2 to 7 days and averaged 4.1 days. The average river velocity was only O.14 ft/sec (4.3 cm/sec) (Patmont, *et al.*, 1985).

Spokane River Sediments

The Spokane River is noted for its lack of fine sediments and its "armored" surface. Funk, in 1973, was unable to obtain a sample of Spokane River bottom sediments. Similarly, in 1991 Horowitz failed to collect sediments from the upper Spokane River because of the armored river bottom. Fine-grained, metal-laden sediments are unlikely to be deposited on the tightly packed, coarse gravels which make up the river bed throughout its shallow reaches. Yearsley (1982) reported that heavy metals are probably deposited in the river at low flow and scoured out at high flows. Very few sediments accumulate in the Spokane River channel, however, because the river carries very little suspended sediment at low flow. Most of the fine particles carried in by the Coeur d'Alene river are probably deposited in the lake before the water exits via the Spokane River. Several deep reaches of the Spokane River are probably less scoured by the current and may be zones of accumulation of fine sediments.

3.2.3 NPDES Sources

The US Environmental Protection Agency regulates discharges to surface waters under the National Pollutant Discharge Elimination System (NPDES). Very few direct discharges to the Spokane River and Lake Coeur d'Alene are permitted. The cities of Coeur d'Alene and Post Falls discharge effluent from municipal sewage treatment plants directly to the Spokane River.

The effluent from the Post Falls sewage treatment plant (STP) is regulated and monitored for effluent quantity, biochemical oxygen demand (BOD), total suspended solids (TSS), fecal coliform bacteria, total residual chlorine, pH, and visible contaminants. Monitoring requirements are also in effect for nitrogen and phosphorous. The effluent limits from the Coeur d'Alene STP include those listed for Post Falls as well as ammonia (nitrogen). Phosphorous removal and dissolved oxygen monitoring are also required.

No direct sources are permitted to discharge pollutants to Lake Coeur d'Alene under the NPDES. The city of Harrison operates a municipal sewage treatment plant which receives domestic wastewater from municipal and commercial source, treats and disinfects and discharges into Anderson slough. The slough discharges into Anderson Lake, which flows into the Coeur d'Alene River approximately one mile upstream from the mouth. Limitations are in effect for monthly average discharge, pH (6.0-9.0), floating solids or foam, BOD, TSS, fecal coliform bacteria and residual chlorine.

Property owners on Kidd Island Bay were permitted to discharge effluent from February, 1976 through December 31, 1980. This permit is no longer in effect.

The Idaho Division of Environmental Quality administers a total maximum daily load (TMDL) process, by which point source and nonpoint source pollutants are evaluated. The process involves (1) the determination of the pollutant level which a stream can dilute or process without harm to the beneficial uses of the water, (2) comparing the "safe pollutant load" to the current load of the stream to determine the amount of load reduction required and (3) allocating the load reductions to both point and nonpoint sources (Harvey, 1991). The TMDL process has been completed for the Coeur d'Alene River.

3.3 Hydrology and Limnology of Lake Coeur d' Alene

The sediments of Lake Coeur d'Alene are enriched in heavy metals. An influx of nutrients, namely nitrate and phosphate, is affecting lake chemistry. As dissolved oxygen in the lake water decreases, metals may be liberated from sediments into the water column and may potentially migrate into the adjacent aquifer. In order to evaluate the impact of changing lake conditions, it is necessary to examine the total system, including lake morphology, the nature of the bottom sediments and the process of eutrophication.

3.3.1 Lake Characteristics

Morphology

Lake Coeur d'Alene occupies a naturally dammed river valley. The north-trending lake is approximately 23 miles (37 km) long and contains 3.4 x 10^{10} cubic feet (9.6 x 10^{8} m^3) of water. The average width increases from about 3/4 mile (1.2 km) in the southern reaches to about 1.5 miles (2.4 km) in the central and northern areas. The depth generally increases to the north also. The depth of water exceeds 175 feet (53 m) north and northeast of Arrow Point. Water depth exceeds 165 feet (50 m) west of Echo Bay and exceeds 197 feet (60 m) in the vicinity of Driftwood Point and Mica Bay. Other deep pockets of water in the lake occur west of Tubbs Hill, east of Carlin Bay, west of Rockford Bay and near Powderhorn Bay.

The water level of the lake increased with the construction of Post Falls Dam in 1901. However, the depth of the lake has decreased in some areas, in part due to the accumulation of rock flour carried in by the Coeur d'Alene River from upstream mining operations. Funk (1973) reported that the estimated maximum silt buildup in Cottonwood Bay (across from the Coeur d'Alene River delta) was 12 feet (3.6 m). Runoff from farming and timber harvest areas also contributes to siltation of the lake.

The U. S. Geological Survey conducted a seismic reflection survey of the lake bottom during the summer of 1991. The researchers made 25 transects of the lake and employed global positioning technology to fix the locations at 6 to 19 stations along each transect. The maximum depth of water recorded at a station was 209 feet (63.7 meters) on Transect 7, Station 3A, 47° 35' 28" N, 116° 48' 24" W (southeast of Harrison). Figure 27 gives the location of stations and depths from three transects of the northern area of the lake.

Lake Sediments

Several significant characteristics of the lake bottom can be recognized in the seismic profiles. The lake bottom consists of laminated, silt- to clay-sized sediments deposited over coarser sands, gravels and boulders. The contact between fine and coarse material shows up distinctly in the seismic profile of the subsurface below Lake Coeur d'Alene (Figure 28).

The fine-grained sediments of Lake Coeur d'Alene probably have a hydraulic conductivity on the order of 3×10^{-9} ft/day (1×10^{-12} cm/s) (Stephen Burchett, Budinger & Assoc., verbal communication). Seismic profiles of the northern lake bottom indicate that the maximum thickness of fine sediments is greater than 67 feet (20.4 meters).

The fine sediments thin out approximately 400 feet (121 m) from the shoreline of the lake, under 122 feet (37.4 m) of water (Figure 28). The lake bottom sediment consists of coarse sand and gravel deposits from there to the shore. The hydraulic conductivity of this material is much greater than that of the fine sediments. Although the seismic profile in Figure 29 was taken off of Stevens Point, this type of shoreline exists elsewhere along the lake where the slope of the bank is shallow. The aquifer recharge zone contains two general types of shorelines: (1) a gradational shoreline, in which the fines thin out, exposing the coarse aquifer material near the shore, and (2) a steep shoreline in which fine sediments abruptly contact the crystalline basement rock of Tubbs Hill (Figure 30.)

The Coeur d'Alene River has supplied massive amounts of sediment to the lake, facilitated by the availability of fine-grained sediment in the Coeur d'Alene River valley. Marcy (1979) found that sediments in Smelterville Flats were primarily less than 0.2 mm in size, with as much as 90% by weight consisting of particles 0.075 mm or smaller. The river current carried fine sediments far out into the lake during the early to middle period of active mining. After 1968, the percentage of the material transported in the dissolved form by the Coeur d'Alene River probably increased, although silt- and clay-sized particles continue to be transported from stream banks down to the lake. These transport processes and the sediment source account for the extremely fine-grained nature (mostly $<63 \mu m$) of tailings in the lake.

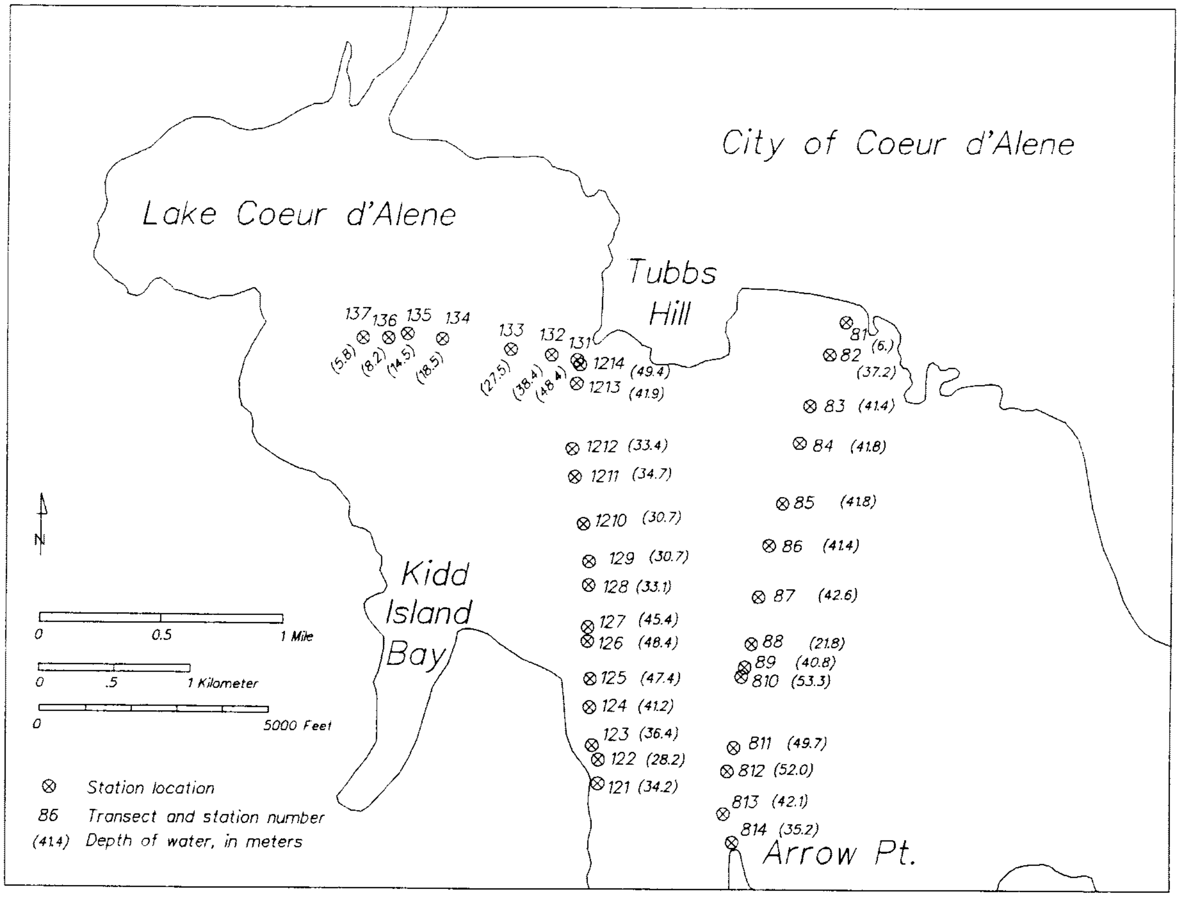
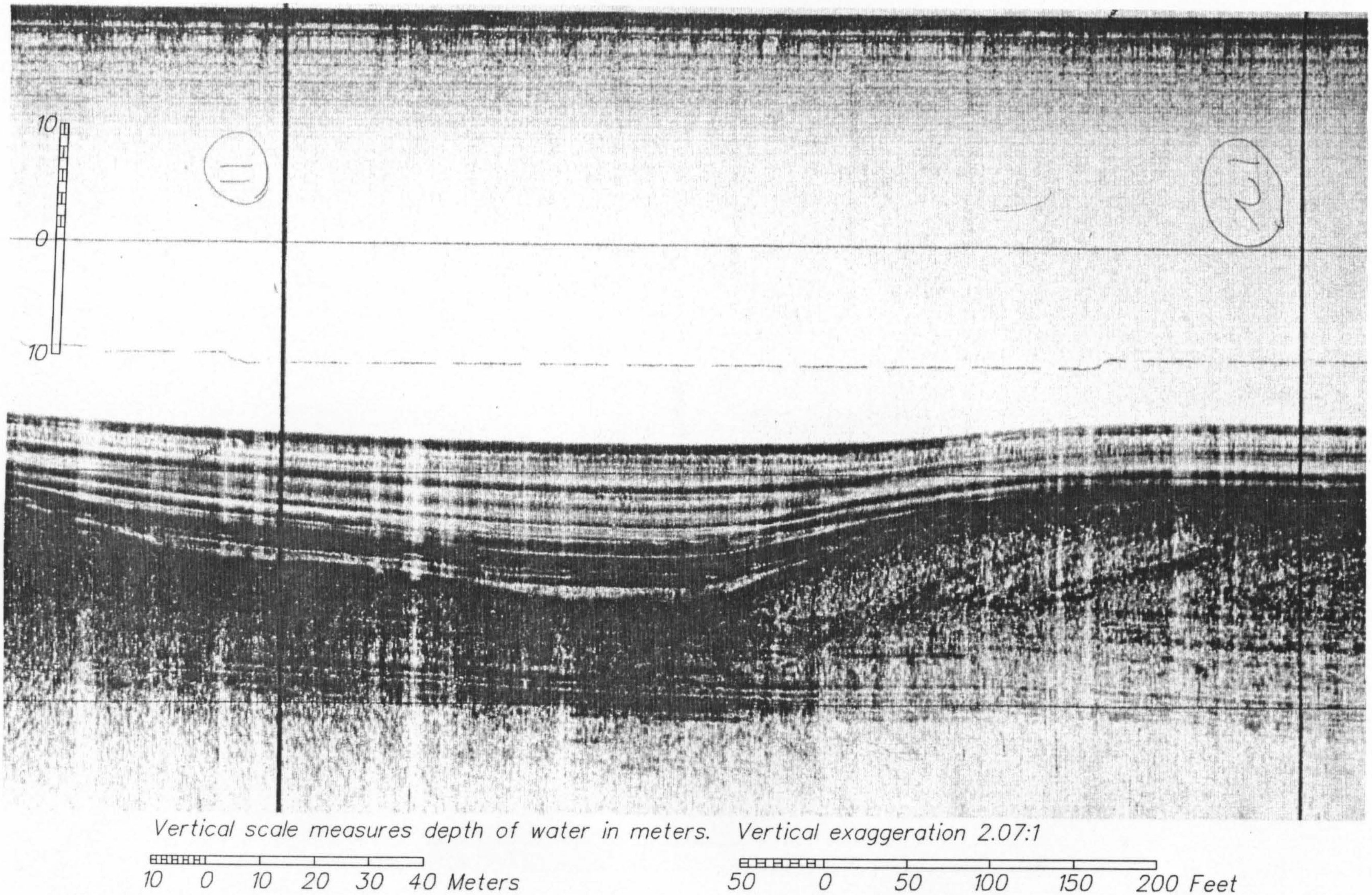


Figure 27. Location and depth at each station of three seismic transects of the northern end of Lake Coeur d'Alene.

Heavy Metal Contamination

The sediments of Lake Coeur d'Alene and its tributaries are enriched in heavy metals. Maxfield and Wai, *et al.*, (1971) found Pb concentrations in the Coeur d'Alene river delta which ranged from 3,700-4,148 mg/kg. Cadmium values ranged from 8.0 to 43 mg/kg and Zn level were as high as 3,800 mg/kg. Several researchers (Funk, Rabe and Filby, 1973; Molnau and Kessler, 1985; Horowitz, Elrick and Cook, 1991) have noted that most of the southern portion of the lake and most of the sheltered bays do not contain elevated concentrations of heavy metals. Molnau and Kessler (1985) found no major problems with Pb, NO_3, Zn or Hg in Kidd Island Bay.

The most comprehensive study of lake sediments to date was performed in 1989-1992 by Horowitz, Elrick and Cook. The results indicate that in some areas the lake sediments contain nine times as much Zn as background levels, 100 times as much Hg, 132 times as much As, and up to 320 times as much Pb. The upper two cm (0.8 in) of lake bottom sediments contain highly elevated levels of Sb, As, Cd, Cu, Pb, Hg, Ag and Zn, as indicated in Table 3.



Vertical scale measures depth of water in meters. Vertical exaggeration 2.07:1

Figure 28. The seismic profile along Transect 12, Station 11 to Station 12, shows the thickening and thinning fine sediments due to the irregular surface of the coarse deposits below.

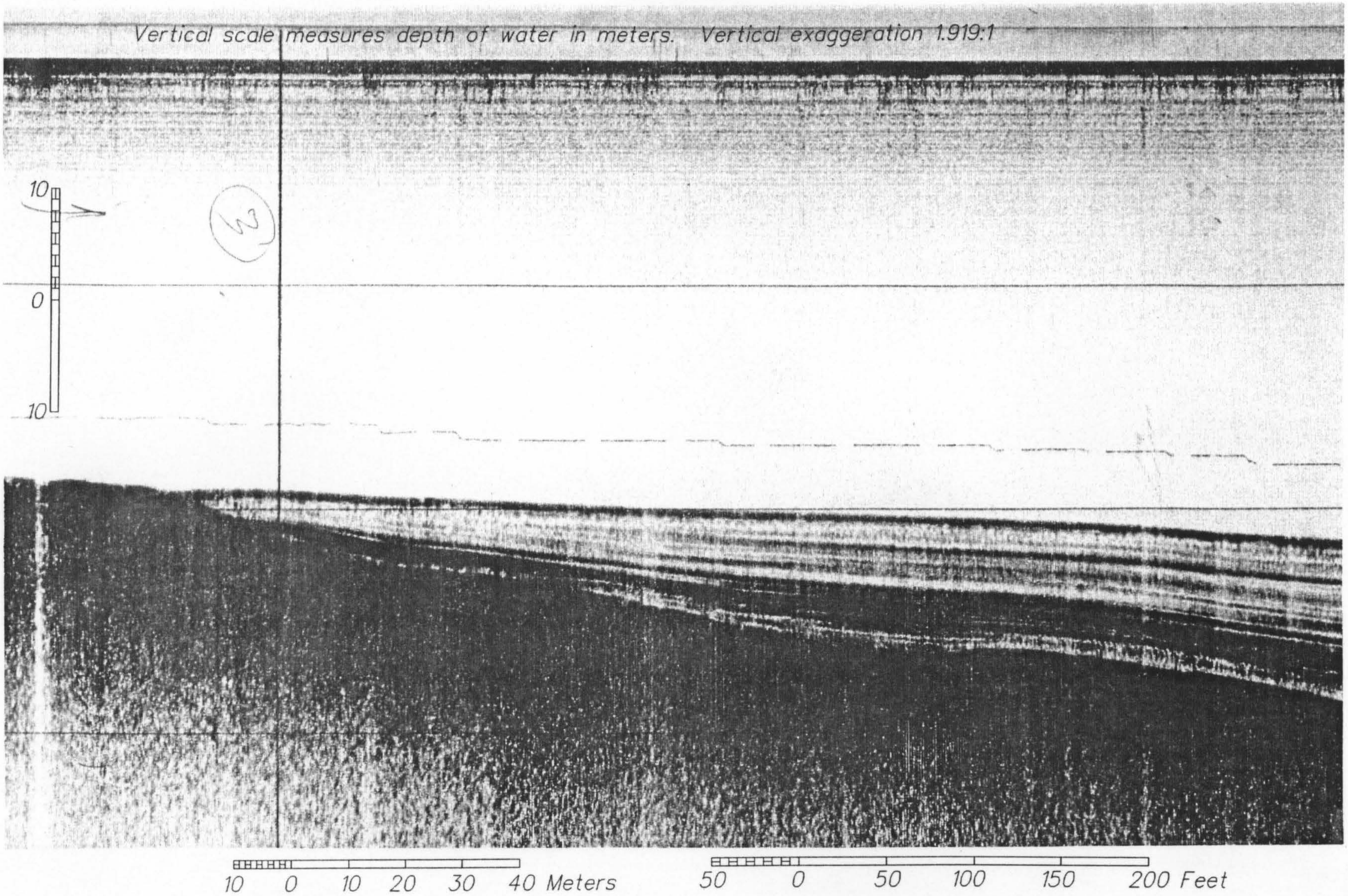


Figure 29. The fine sediments thin out approximately 400 feet from the shore of the lake.

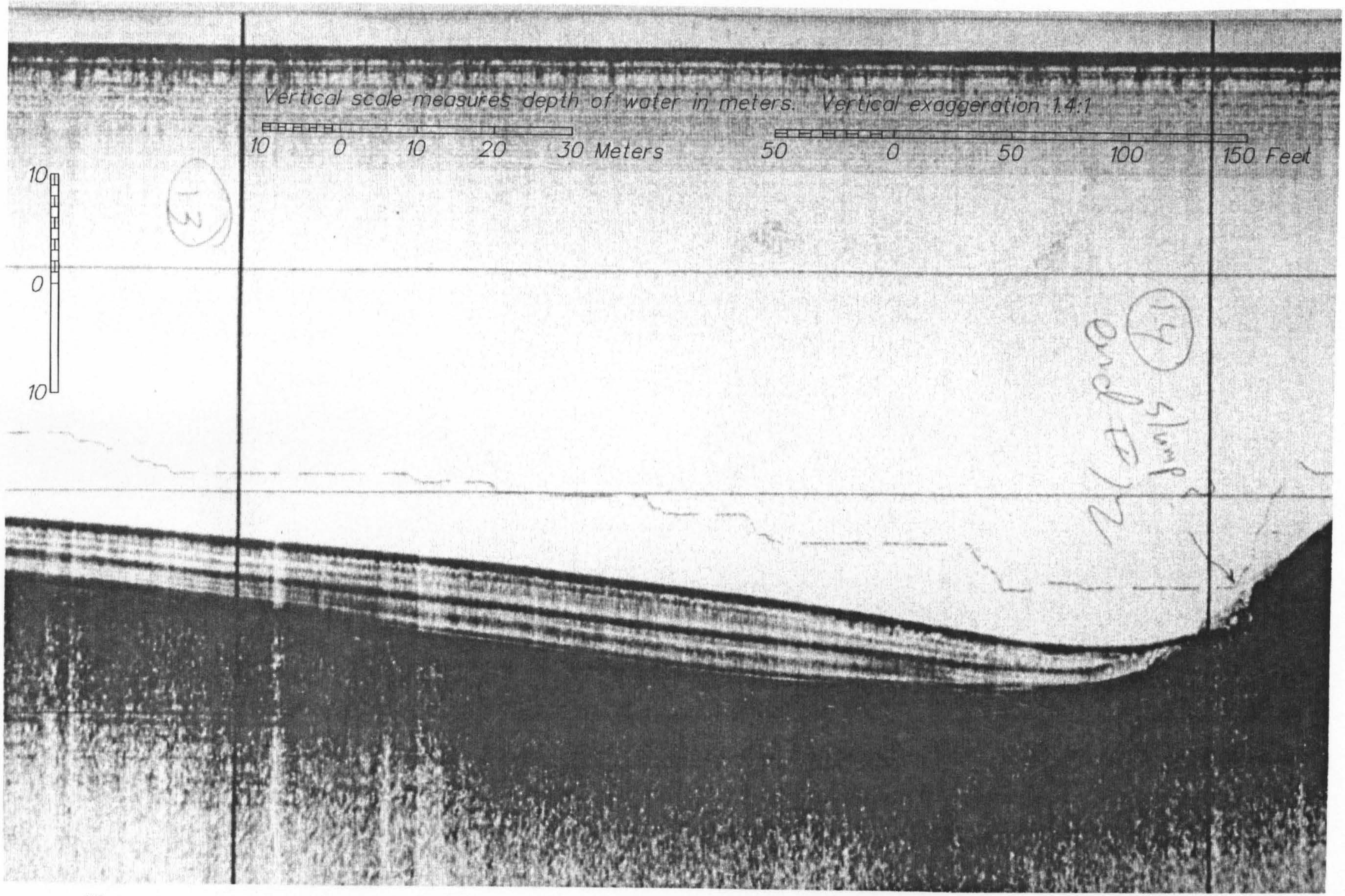


Figure 30. Transect 12, from Station 12 to 13, shows the abrupt contact of fine lake bed sediments with crystalline basement rock.

Element	Minimum	Maximum	Mean	Median	Uncontaminated Median
Ag (ppm)	<0.5	21.0	6.0	4.0	<1.0
Cu (ppm)	9	215	72	70	25
Pb (ppm)	14	7700	1900	1800	24
Zn (ppm)	63	9100	3600	3500	110
Ni (ppm)	4	104	21	21	16
Co (ppm)	5	43	23	26	12
Cd (ppm)	<0.5	157	62	56	3
Cr (ppm)	<1	102	41	41	41
Hg (ppm)	0.02	4.9	1.8	1.6	0.05
As (ppm)	2.4	660	151	120	5
Sb (ppm)	0.5	96	23	19	1
Se (ppm)	0.1	0.6	0.3	0.2	0.2
Fe (wt. %)	1.9	16.4	5.1	4.9	3.0
Mn (wt. %)	0.01	2.46	0.67	0.65	0.05
Al (wt.%)	2.9	9.0	7.5	8.0	6.8
Ti (wt. %)	0.13	0.64	0.34	0.34	0.40
TOC (wt. %)	0.3	15.6	2.5	2.2	2.5

Table 3. Quantitative trace metal chemistry, from about 172 samples of the upper 2 cm of Lake Coeur d'Alene sediments (from Horowitz, Cook and Elrick, 1992).

Horowitz, Elrick and Cook (1992) recognized a pattern in which the highest heavy metal concentrations were found where water moving changes course and current velocity decreases. Presumably, due to the decrease in the stream capacity (ability to transport sediment), heavy metals are deposited. Other processes, such as wind/wave transport and postdepositional remobilization, may also affect the trace element distribution patterns (Horowitz, Elrick and Cook, 1992).

Several areas of the lake contain bottom sediments with particularly high metal concentrations. Some of the highest concentrations of Ag, As, Cd, Cu, Hg, Pb, Sb and Zn were found in sediments in and around Harrison Slough, near the mouth of the Coeur d'Alene River. High concentrations of As, Hg Pb and Zn were found south of Harlow Point. A deep section of the center of the main stem of the lake contains particularly high levels of As, Cd, Hg, and Zn. Near the mouth of Mica Bay, Ag, Cu, Hg, Pb, and Sb are high. Ag, Cu, Cd, Hg, Pb, and Zn are high near the mouth of Wolf Lodge Bay. In the vicinity of the Rathdrum Aquifer recharge zone, near Independence Point, Tubbs Hill and Silver Beach, the sediments are elevated in Cu, Cd, Hg, Pb, and Zn.

Horowitz, Elrick and Cook found that the vast majority of surface sediment samples collected from the main body of the lake were tan to brown and visually appeared to be fine- to very-fine-grained ($<63\mu m$). Many samples contained a very thin surface veneer of fine-grained, reddish material, which may have been fine-grained mining and ore processing waste from the river banks and flood plain of the Coeur d'Alene River, or possibly authigenic Fe and Mn oxides that were formed by postdepositional metals cycling (Horowitz, Elrick and Cook, 1992).

Detailed grain size and geochemical analyses were performed on selected samples. In the three samples from the north end of the lake, farthest from the mouth of the Coeur d'Alene River, the <2 μm (occasionally 8-16 μm) fractions contribute the highest concentration of trace elements (Horowitz, Elrick and Cook, 1992). The pattern of significantly higher metals concentrations in the smaller size fractions is well documented in the literature (Moore, Brook and Johns, 1989). Metals in this small size fraction are likely to be more mobile, because they exist as adsorbates on clays or as amorphous precipitates and coprecipitates. Figures 31 and 32 show the concentrations of twelve metals in the <2 μm size fraction of sediment at seven sampling stations in the lake.

3.3.2 Lake Processes

Eutrophication

Eutrophication is the term used to describe the biological and chemical effects of an increase in concentration of plant nutrients (nitrogen and phosphorous) on aquatic ecosystems. The Organisation (sic) for Economic Co-operation and Development (OECD) defines eutrophication as the "nutrient enrichment of waters which results in the stimulation of an array of symptomatic changes, among which increased algae and macrophytes, deterioration of water quality and other symptomatic changes, are found to be undesirable and interfere with water uses" (Ryding and Rast, 1989, pg. 1).

Eutrophication is a normal development in the life span of a lake. In natural situations, the eutrophication process takes place slowly over several decades or centuries so that the change from oligotrophy to eutrophy is almost imperceptible. By contrast, the rapid input of nutrients (phosphate, nitrogen and CO_2) from agricultural land drainage and industrial and domestic sources may cause the productivity of a lake to increase rapidly. The result may be excessive growth of phytoplankton, reduced transparency, loss of less tolerant fish species, littoral zones choked with aquatic weeds, decaying blue-green algae releasing foul odors and tastes, and increased organic content which results in decreased dissolved oxygen in the water (Hammer and MacKichan, 1981).

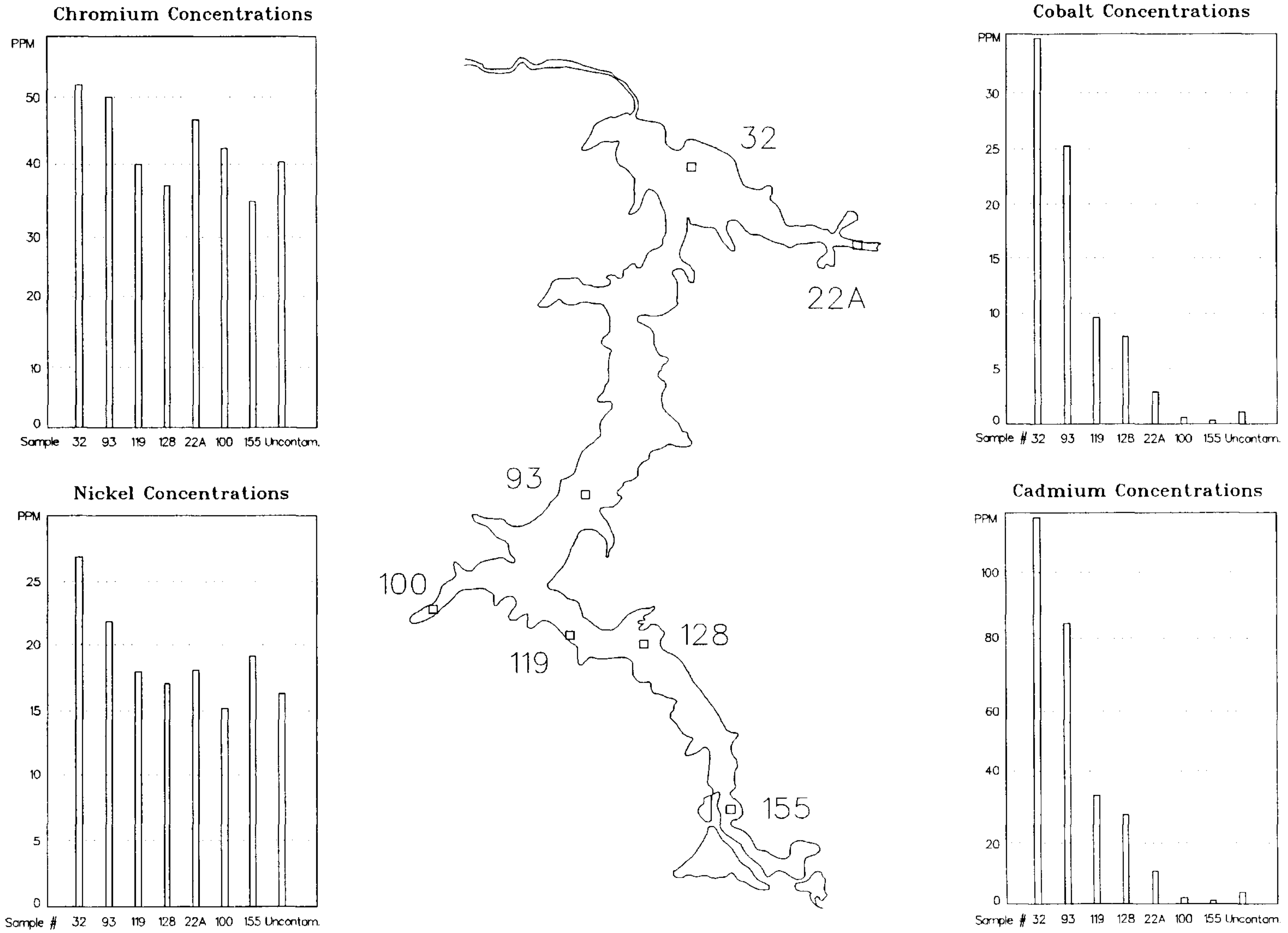
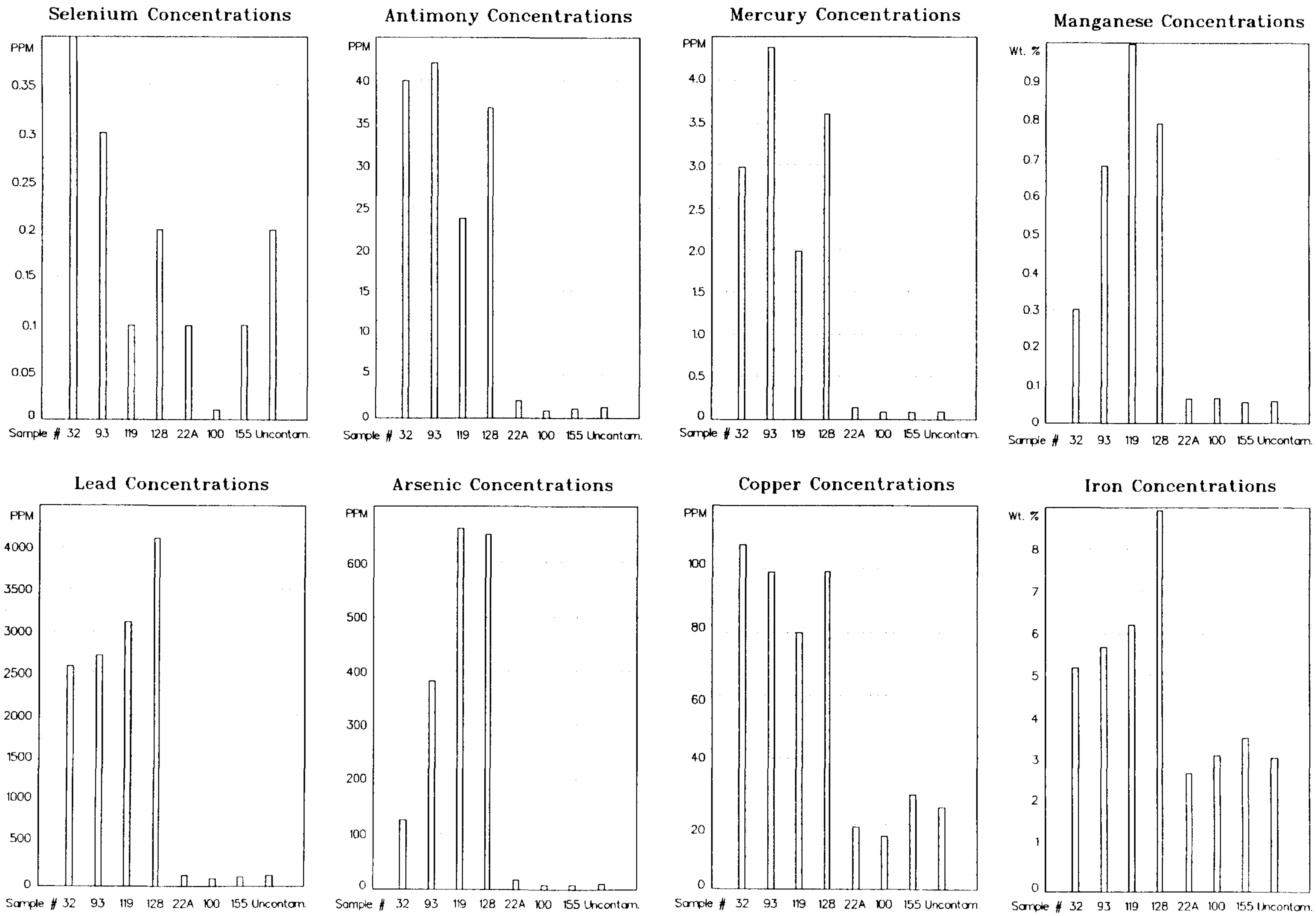


Figure 31. Concentrations of chromium, cobalt, nickel, and cadmium in the <2 μm size fraction at seven sampling stations in Lake Coeur d'Alene.


Selenium Concentrations

Antimony Concentrations

Mercury Concentrations

Manganese Concentrations

Lead Concentrations

Arsenic Concentrations

Copper Concentrations

Iron Concentrations

Figure 32. Concentrations of selenium, antimony, lead and arsenic, mercury, manganese, copper and iron in the <2 μm size fraction at seven sampling stations in Lake Coeur d'Alene.

Trophic State	Phosphorous (μg/l)	Chlorophyll a (μg/l)	Secchi Disk Transparency (m)	Primary Productivity (μC/m^2/day)
ultra-oligotrophic	<3	<0.3	>16	<50
oligotrophic	3-9	0.3-2	7-16	50-250
mesotrophic	9-24	2-6	2-6	250-1000
eutrophic	24-75	6-40	0.75-2	1000-2000
hyper-eutrophic	>65	>40	<0.75	>2000

(a.) From Wetzel (1983).

Trophic State	Phosphorous (μg/l)	Chlorophyll a (μg/l)	Chlorophyll a (mcg/l)	Secchi Transp. (meters)	Secchi Disk Transp. (mean, m)
ultra-oligotrophic	<=4	<=1	<=2.5	>+12	>=6
oligotrophic	<=10	<=2.5	<=8	>=6	<=3
mesotrophic	10-30	2.5-8	8-25	6-3	3-1.5
eutrophic	35-100	8-25	25-75	3-1.5	1.5-0.7
hyper-eutrophic	>=100	>=25	>=75	<=1.5	<=0.7

(b.) From OECD [Organisation (sic) for Economic Cooperation and Development], Paris, 1982, published in Harper (1992).

Table 4. Classification of the trophic status of lakes from (a) Wetzel, 1983 and (b) Harper, 1992.

A lake is said to be eutrophic if it fits certain criteria for nutrient concentration, biological content and visibility. These parameters measure the fertility of the impounded water, which is dependent on both the chemical and biological characteristics of the water body. Eutrophic lakes are nutrient rich and green from dense phytoplankton growth. These lakes contain lush growths of aquatic weeds, blooms of algae, and large populations of tolerant fish (Hammer and MacKichan, 1981). Oligotrophic lakes are clear, blue, nutrient-poor and biologically unproductive. Two classification schemes for the degree of fertility of lakes are given in Table 4.

The criteria listed in Table 4 represent attempts to measure the *process* of eutrophication. The process is characterized by (1) decreasing hypolimnetic dissolved oxygen concentrations, (2) increasing nutrient concentrations, (3) increased suspended solids (mostly organic material), (4) population changes from diatoms to dominantly blue green algae and/or green algae, (5) decreasing light penetration and (6) increasing phosphorous content of sediments. These changes within the lake system affect the chemistry of both the water column and the lake sediments.

Three stages in lake evolution have been distinguished. The first is a long period when surface mud remains permanently oxidized and sediments accumulate nutrients. This generally equates to oligotrophy. During the second period (mesotrophy/eutrophy), the mud surface becomes reduced, at first intermittently, releasing nutrients and other ions back into the water body. The third period, eutrophy or hypereutrophy, involves the permanent deoxygenation of the hypolimnion and reducing conditions in the mud (Harper, 1992).

Eutrophic and oligotrophic lakes differ seasonally in the amount of dissolved oxygen in their waters and the degree of thermal stratification. Figure 33 shows the seasonal differences in the degree of thermal stratification and the amount of dissolved oxygen in the water of eutrophic and oligotrophic lakes.

Thermal Stratification

Lake Coeur d'Alene is dimictic: it undergoes two periods of thermal stratification and both a spring and fall overturn. During the spring and summer, the upper few feet of lake water receive solar and atmospheric radiation. The water becomes warmer and lighter, and floats on top of colder, denser water. This warm layer, the epilimnion, is well mixed by wind currents and is therefore homothermal (isothermal). The depth of the epilimnion increases as spring and summer progress.

The temperature drops off sharply below the epilimnion, in the zone known as the metalimnion. The thermocline, the depth at which the maximum temperature gradient occurs, serves as a barrier between the epilimnion above and the hypolimnion below. The hypolimnion is the deepest zone of the stratified lake. It contains the lowest temperatures, is isothermal, and generally has almost no circulatory currents.

A stable, stratified lake undergoes "overturn" in the fall, when atmospheric temperatures decline and solar radiation decreases. The epilimnion loses heat to the atmosphere, so the water becomes colder and denser and therefore sinks. Convective currents develop, which break through the thermocline and mix the lake waters.

Thermal stratification is less pronounced during the winter, but again the densest water occupies the deepest reaches of the lake. The bottom water is at 4°C and the surface water is colder and lighter. Ice often forms at the lake surface. In the spring, the surface of the lake is warmed, causing a change in the density of the water. The water column becomes unstable again and mixing occurs.

Dissolved Oxygen Sources

The two principal sources of dissolved oxygen (DO) in Lake Coeur d'Alene (and most lakes) are (1) input from the atmosphere and (2) oxygen liberated during algal photosynthesis. In the first case, water must circulate in order to establish equilibrium with the atmospheric concentration of oxygen. This

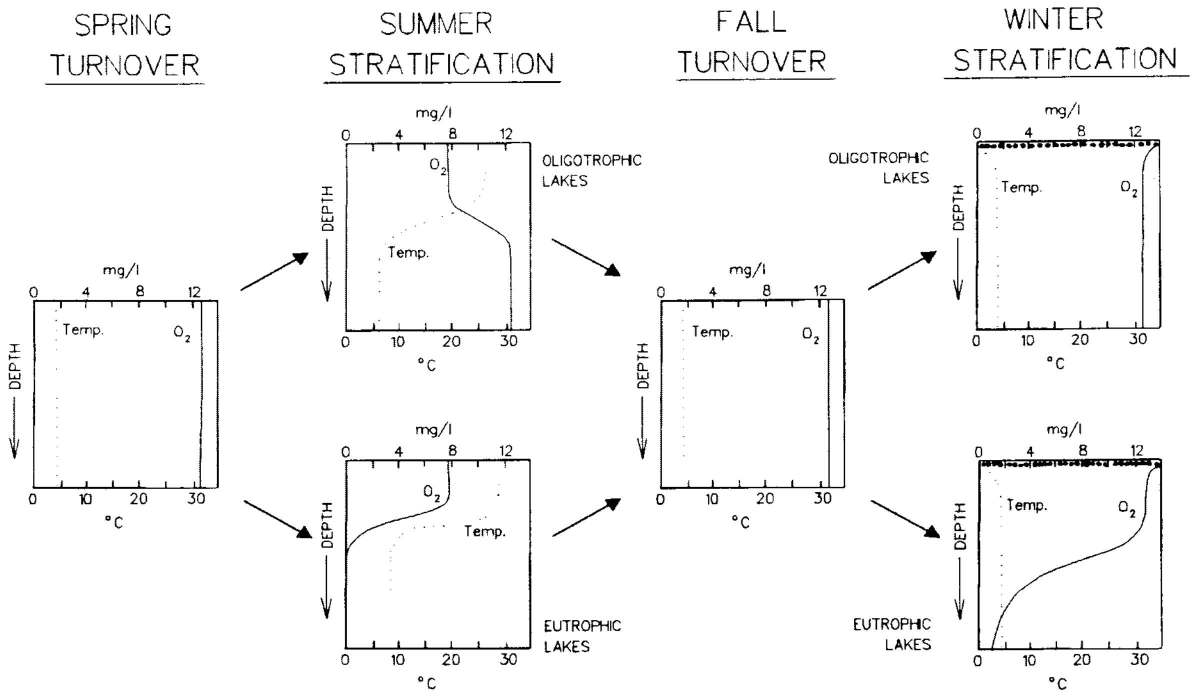


Figure 33. Idealized vertical distribution of temperature and dissolved oxygen during the four main seasonal phases of an oligotrophic and a eutrophic dimictic lake (from Harper, 1992).

circulation occurs in the epilimnion as a result of wind-induced currents. Circulation is achieved lake-wide by seasonal overturn in the spring and fall. Water mixes, raising the DO content throughout the lake to near atmospheric.

In oligotrophic lakes, DO is controlled primarily by thermal stratification. The hypolimnion contains more dissolved oxygen than the epilimnion during the spring and summer because cold water is able to dissolve more oxygen than warm water.

In eutrophic lakes, the dissolved oxygen levels established in the spring based upon temperature are greatly modified by biological activities. Algae in the epilimnion store energy through the process of photosynthesis, according to the following simplified reaction:

$$6CO_2 + 6H_2O + \text{energy} \rightarrow 6C_6H_{12}O_6 + 6O_2$$

Photosynthesis produces high concentrations of DO and localized centers of highly negative *pe* (redox potential). The epilimnion can become supersaturated with oxygen due to algal photosynthesis on sunny days. Daytime photosynthesis may also elevate the pH of the epilimnion. At night, photosynthesis ceases, the algae continue to respire and dissolved oxygen is reduced. The production of organic matter, and therefore the redox potential, DO content, and typically the pH, is highest during the summer.

Dissolved Oxygen Sinks

When productivity is high in the epilimnion, dead organisms and faeces sink to hypolimnion and are decomposed by bacteria in the water column and sediments. The decay process is essentially the reverse of the photosynthetic process:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy}$$

The consumption of oxygen due to bacterial decomposition of organic matter causes the lower layers to experience oxygen depletion. The balance between photosynthesis and respiration is largely responsible for regulating the redox intensity of lake waters (Stumm and Baccini, 1978).

The rate of oxygen depletion in the hypolimnion will increase as production and the quantity of organic debris falling from the epilimnion increases. The oxygen content of the hypolimnion is reduced progressively during the period of summer stratification, usually most rapidly at the deepest portion of the lake basin (Kramer, 1988). The rate and extent of oxygen depletion is also affected by the depth of the lake, the volume of the hypolimnion, and the length of time of stratification. Highly eutrophic lakes become anaerobic near the bottom with noticeable production of hydrogen sulfide (Kramer, 1988).

A eutrophic lake also exhibits a DO reduction during winter stratification, which can become severe during prolonged periods of ice and snow cover (Hammer and MacKichan, 1981). The exchange of oxygen with the atmosphere virtually ceases when the lake is covered with ice.

Redox Reactions

The concentration of dissolved oxygen is a reflection of the redox status of a lake because O_2 is the first species to be reduced when organic material is oxidized. Oxidation-reduction reactions involve the transfer of electrons from donor atom to acceptor atom. The element which gives up an electron is oxidized; that which gains an electron is reduced. Every oxidation reaction is accompanied by a reduction. The oxidation of manganese, for example,

$$2Mn^{2+} = 2Mn^{4+} + 4e$$

involves the reduction half reaction:

$$O_2 + 4H^+ + 4e = 2H_2O$$

so that the complete reaction is given as:

$$2Mn^{2+} + O_2 + 4H^+ = 2Mn^{4+} + 2H_2O$$

The redox potential is a measure of the tendency of an ion to either lose or gain electrons. Redox potential is often measured by means of a hydrogen electrode and is commonly reported in units of millivolts. Oxidation potential may also be written in terms of a theoretical concentration of free electrons known as p*e*.

The relationship between dissolved oxygen content and the redox potential of water can be derived from the Peters-Nernst equation:

$$Eh = E^{\circ}_{H} + (2.3RT/nF)\log[2H^{+}/O]$$

At 25°C

$$Eh = E^{\circ}_{H} + (0.059/2)\log[H+]^{2}\log P_{O2}^{1/2}$$

$$= E^{\circ}_{H} - 0.059pH + 0.01475\log P_{O2}$$

The relationship may also be written in terms of p*e*:

$$pe = 13.75 + \tfrac{1}{4}\log P_{O2} \quad (25^{\circ}C, pH=7)$$

Equations such as this can be derived for all redox species in natural waters, although only a few elements (C, N, O, S, H, Fe and Mn) dominantly participate in aquatic redox processes (Stumm and Morgan, 1981). These redox reactions, although microbially catalyzed, tend to occur in the order of thermodynamic possibility. Figure 34 shows the order of redox reactions with decreasing p*e* (redox potential) at a pH=7 (slightly lower than the *average* pH in Lake Coeur d'Alene and higher than reported *late summer* pH in the Spokane River [Section 3.3.3]). As organic matter is consumed in the hypolimnion (or elsewhere in the water column) first O_2 is reduced, then NO_3^-, NO_2^-, $MnO_2(s)$, $FeOOH(s)$ and so on. In a stratified, eutrophic lake these reactions are reflected in the vertical distribution of species (Stumm and Morgan, 1981).

The balance between respiration and photosynthesis is largely responsible for regulating the redox intensity of lake waters (Stumm and Baccini, 1978). The redox potential of water at equilibrium is relatively insensitive to changes in oxygen concentration and extent of saturation, according to Stumm and Morgan (1981), because p*e* is influenced by the 4th root of the partial pressure of oxygen (as shown in the last equation). If the oxygen content is decreased by 99 percent, the redox potential would be reduced by only about 30 millivolts (Stumm and Morgan, 1981). Measurable changes in dissolved oxygen will have only slight effects on redox potential and the mobility of metals in solution. However, once DO is depleted, other species will participate in redox reactions. The partial pressure of oxygen (P_{O2}) may also continue to decrease when a standard DO meter reports 0% DO saturation. Therefore, a 0% dissolved oxygen reading does not guarantee that the hypolimnion of a lake is under strongly reducing conditions, but rather that the possibility exists.

The mobility of some metals will not be affected directly by reducing conditions in the hypolimnion, but will respond indirectly. Zinc and Cd, for example, are conservative with respect to redox. However, the release of 'redox conservative' heavy metals from sediments may be tied to the mobility of Fe and (particularly) Mn which are sensitive to changes in redox potential. The behaviors of various metals are discussed in detail in Chapter 4.

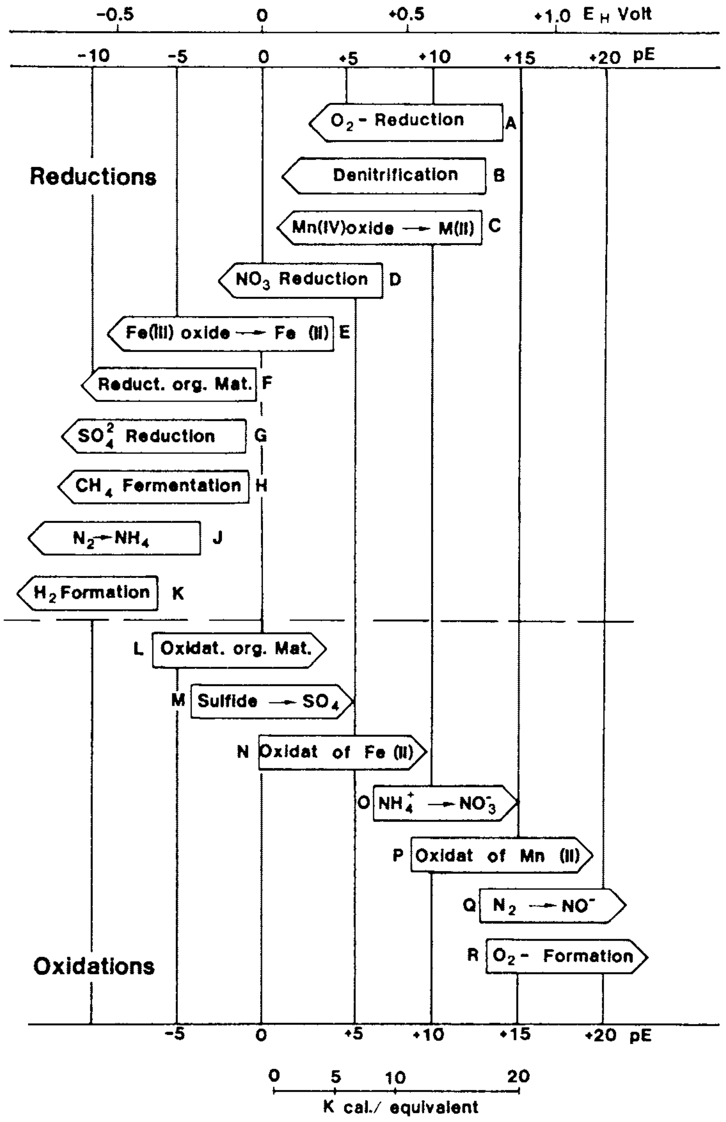


Figure 34. Sequence of biologically mediated redox processes calculated for pH = 7 (from Stumm and Morgan, 1981, pg.460).

3.3.3 Lake Coeur d'Alene Water Quality

Trophic Status

Several investigators have studied the trophic status of Lake Coeur d'Alene. Dunigan (1972) reported that the northern portion of the lake was oligotrophic, some middle and southern portions tended toward mesotrophy. The southernmost portion (Chatcolet) fit a eutrophic classification, according to Parker (1972). Molnau and Kessler (1985) reported that the nitrate content of sediments in Kidd Island Bay was greater than those listed by Wetzel (1983) for eutrophic lakes in Wisconsin. The nitrate concentration in the water column, however, was not elevated. One characteristic of eutrophication is the liberation of nitrogen from surficial sediments into the water column, which increases eutrophication in a "snowball" effect. This process did not appear to be happening, so Molnau reported that nitrate was not a significant problem in Kidd Island Bay. Yearsley (1980) reported that the Spokane River is reportedly oligotrophic to mesotrophic.

Secchi disk transparencies of Lake Coeur d'Alene, from more recent studies (published in Harenberg, *et al.*, 1991) indicate that Lake Chatcolet is indeed eutrophic. In the vicinity of Blue Point, near Harrison, Lake Coeur d'Alene was eutrophic from March to June, 1991, and mesotrophic from July to September, based on Secchi transparencies. Northeast of University Point, near Harrison, the lake shifted from eutrophic to mesotrophic to oligotrophic from January to September, 1991. Many of the northern bays were oligotrophic at that time. The lateral lakes of the Coeur d'Alene River were eutrophic to mesotrophic.

The USGS study (in progress) will attempt to model the Coeur d'Alene basin, identify nutrient sources, quantify nutrient input to the lake, and make predictions about changes in lake chemistry and aquatic biota. Predictions of the rate and degree of eutrophication presumably will be available after the completion, calibration and verification of the eutrophication model. Until then, predictions about metal migration must address a whole spectrum of possible lake chemistry conditions. Information can be drawn from similar sites worldwide, but particular emphasis must be placed on current conditions in Lake Coeur d'Alene.

Lake Stratification

Lake Coeur d'Alene is subject to seasonal thermal stratification and seasonal changes in dissolved oxygen with respect to depth. Figures 35, 36 and 37 graphically illustrate the stratification with respect to temperature and DO at a sampling station near Tubbs Hill in 1991. The depth of water is approximately 135 feet (40 meters) at the station.

Dissolved oxygen reached a low of 68% (7.7 mg/l at 6.7°C) at the sampling station 1.3 miles southeast of Tubbs Hill in September, 1991. Levels as low as 52% at depth northeast of Blue Point, 72%

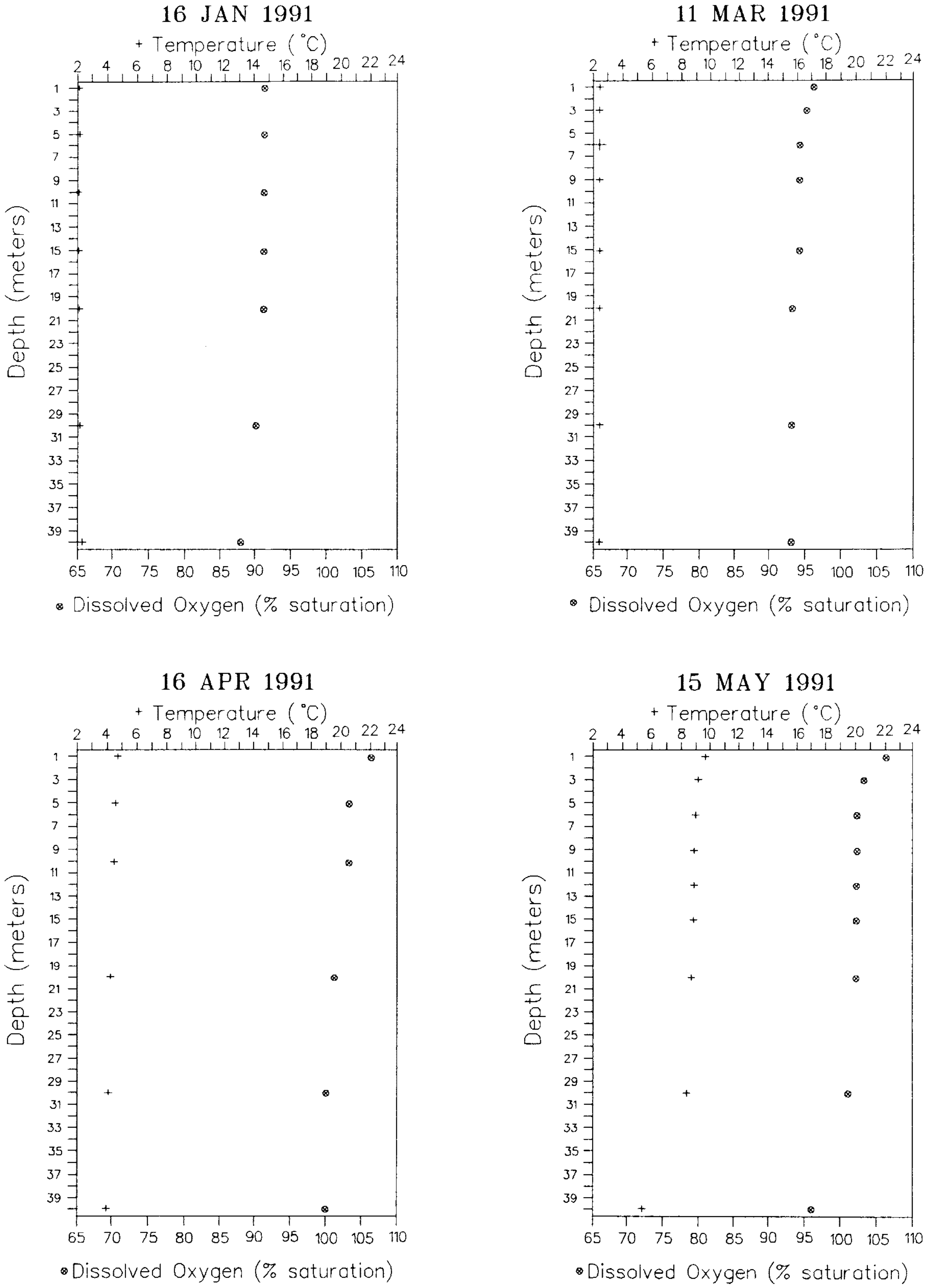


Figure 35. Temperature and dissolved oxygen in the Lake Coeur d'Alene Water Column near Tubbs Hill, on January 16, March 11, April 16 and May 15, 1991. (Data from USGS Water Resources Data, Idaho, Water Year 1991.)

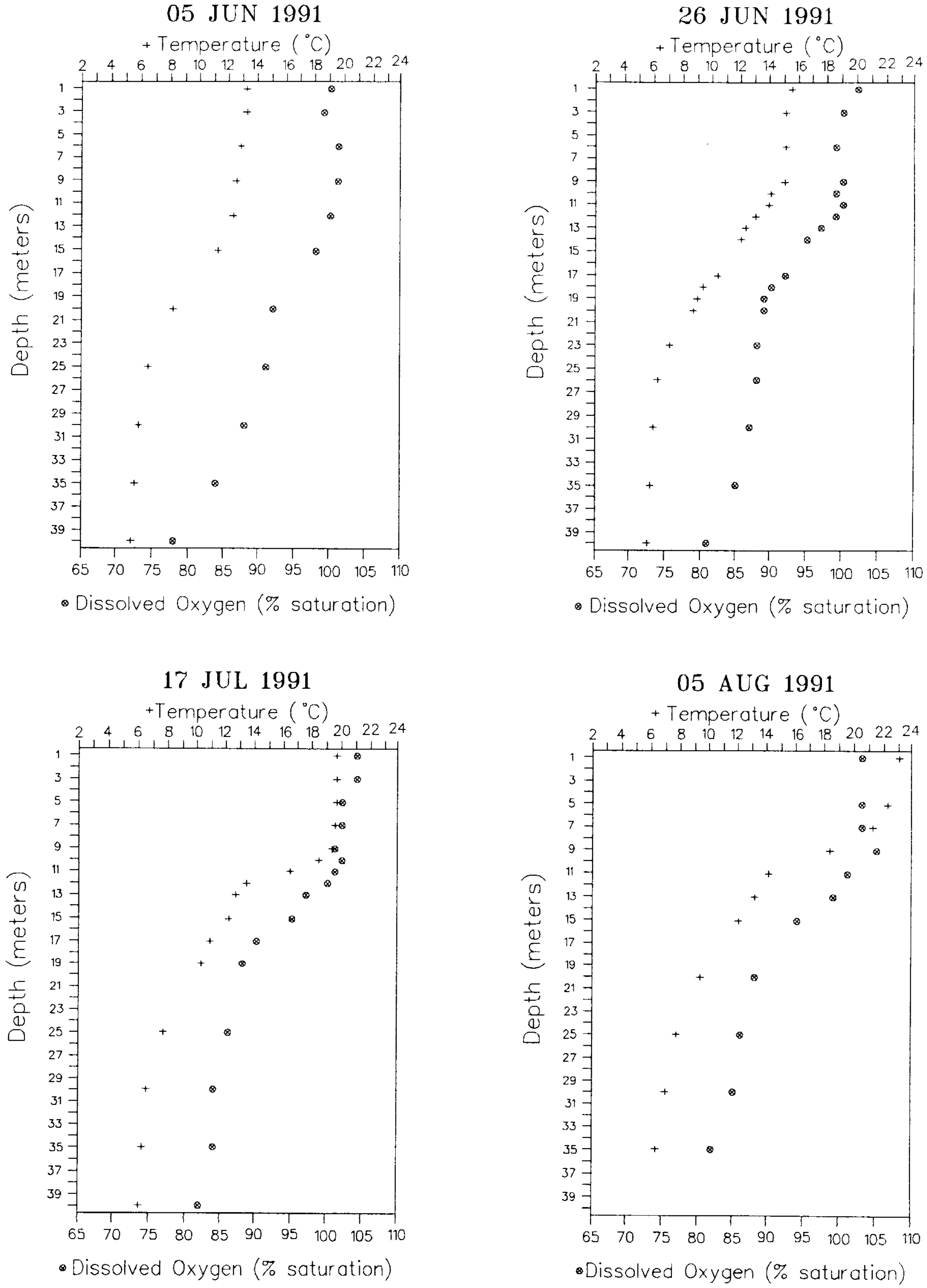


Figure 36. Temperature and dissolved oxygen in the Lake Coeur d'Alene Water Column near Tubbs Hill, on June 5, June 26, July 17 and August 5, 1991. (Data from USGS Water Resources Data, Idaho, Water Year 1991.)

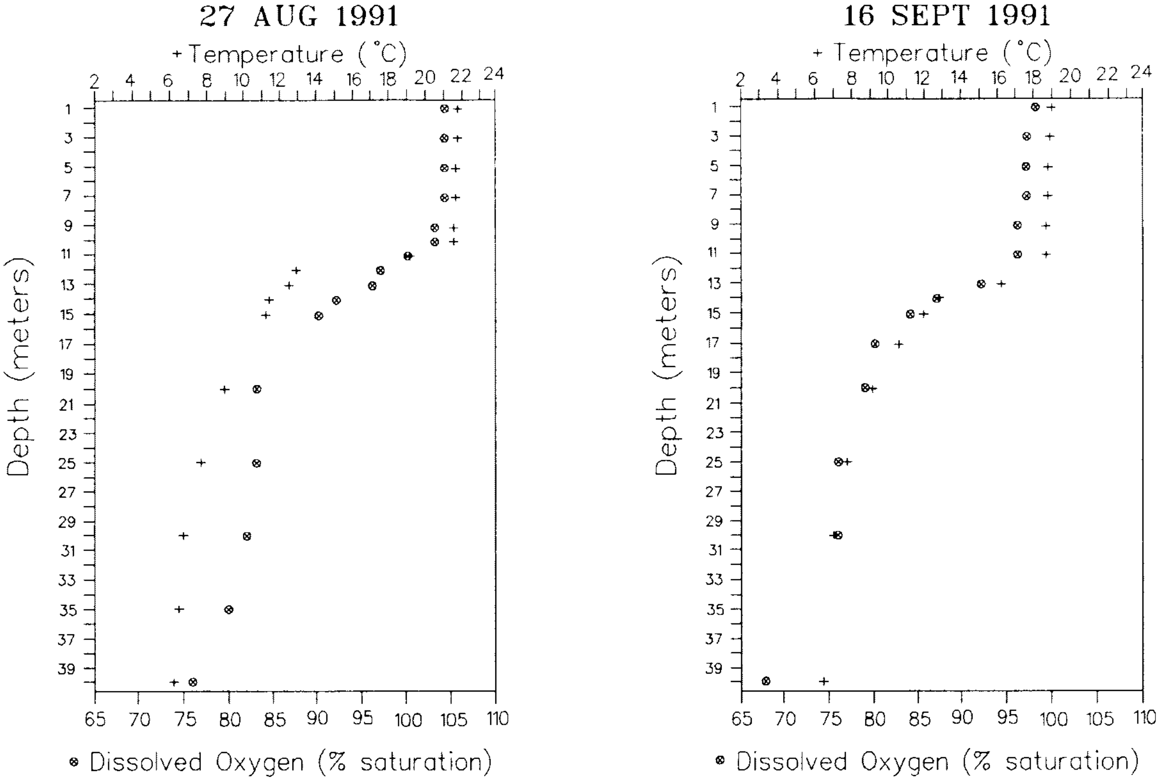


Figure 37. Temperature and dissolved oxygen in the Lake Coeur d'Alene Water Column near Tubbs Hill, on August 27 and September 16, 1991. (Data from USGS Water Resources Data, Water Year 1991.)

at depth in Beauty Bay, and 0% in Lake Chatcolet were recorded at that time. Phosphorous levels in the water (euphotic zone) did not appear to be elevated as a result of DO conditions.

Dominant Ions

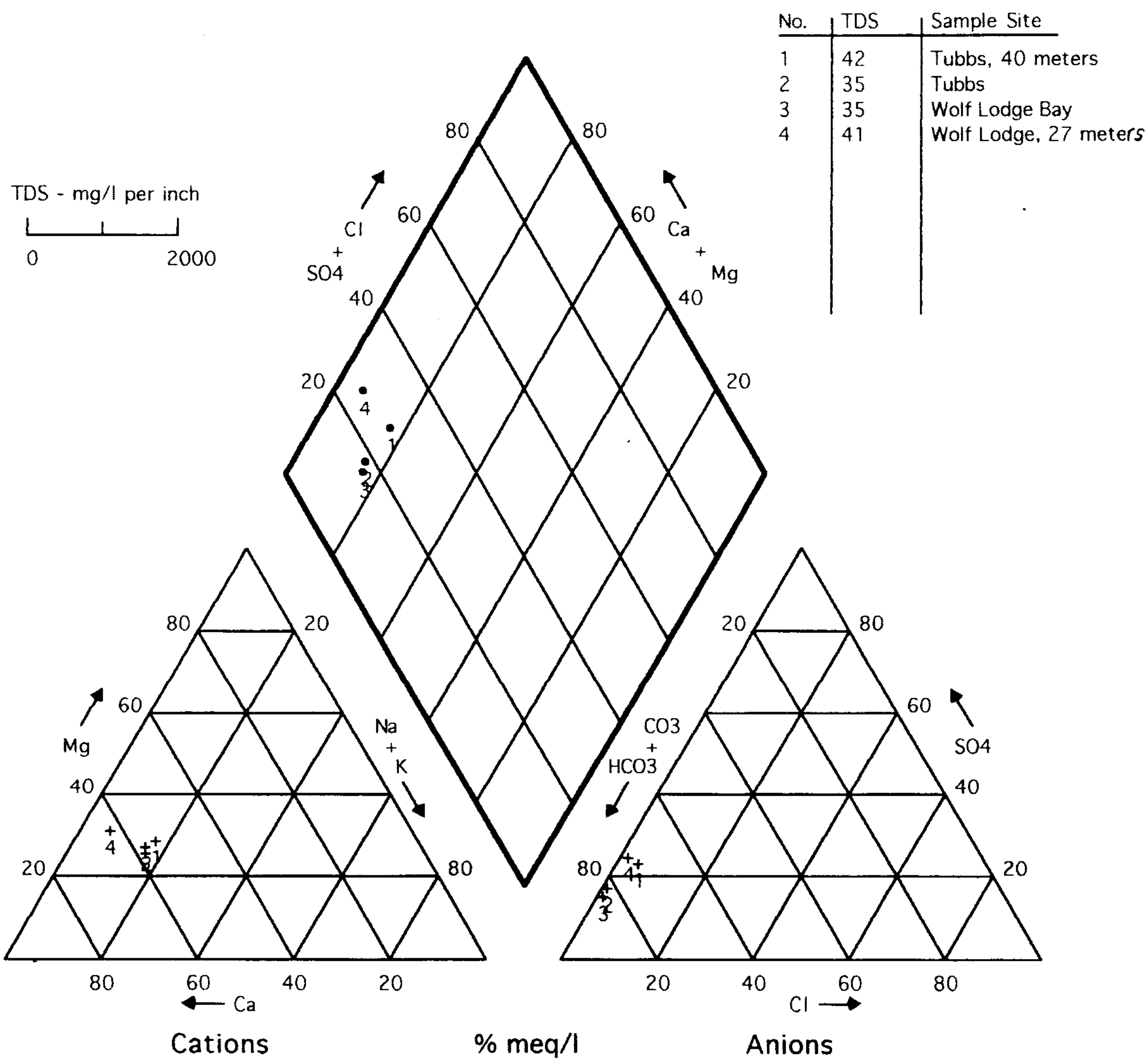
Calcium is the dominant cation in water of both the Spokane River and Lake Coeur d'Alene, followed by magnesium and sodium (Sagstad, 1977; Harenberg, 1991). The dominant anionic constituent is carbonate. The trilinear diagram in Figure 38 illustrates that these are calcium-carbonate type waters. The low concentrations of chlorine and sulfate may be significant to the stability of certain metals in sediments.

Acidity/Alkalinity (pH)

Eutrophic lakes generally experience elevated pH in the epilimnion, as a result of excessive O_2 produced during algal photosynthesis. pH values from 9 to 10.5 or higher have been documented in the epilimnion of eutrophic lakes worldwide. The pH of the hypolimnion is primarily affected by CO_2. Hydrolysis reactions of metal ions can also affect pH, if the concentration of metals is sufficiently high.

A generalized diagram for the distribution of pH, CO_2, temperature and O_2 with depth is given in Figure 39.

Iron and aluminum are believed to be the most significant metallic contributors to the hydrolysis regulation of pH in most *acid* waters (Hem, 1989). In Lake Coeur d'Alene, reducing conditions in the hypolimnion could contribute to the maintenance of neutral pH. The reduction of ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}) consumes H^+ and decreases acidity, although the hydrolysis reactions tend to be slow. Similarly, the reduction of Mn consumes the hydronium ion and increases pH.



No.	TDS	Sample Site
1	42	Tubbs, 40 meters
2	35	Tubbs
3	35	Wolf Lodge Bay
4	41	Wolf Lodge, 27 meters

Figure 38. Trilinear diagram illustrating the composition of Lake Coeur d'Alene and Spokane River water in terms of dominant anions and cations.

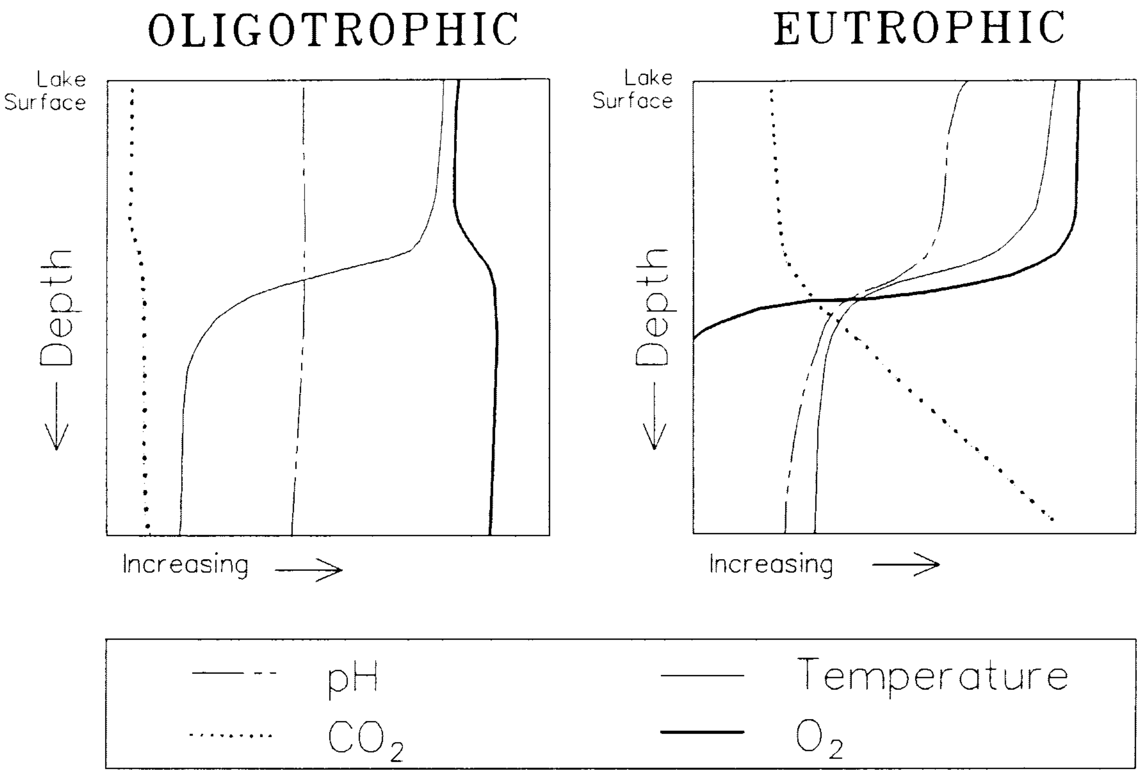


Figure 39. Generalized distribution of pH, CO_2, temperature and DO in a stratified lake.

Contrarily, the production of CO_2 drives pH lower. In the hypolimnion, CO_2 is released during the destruction of organic substances. The addition of CO_2 tends to increase the concentration of H^+ and therefore contributes to acidity in a three step reaction:

$$CO_2(g) + H_2O(l) = H_2CO_3(aq)$$

$$H_2CO_3(aq) = H^+ + HCO_3^-$$

$$HCO_3^- = H^+ + CO_3^{2-}$$

These reactions are part of an interactive system by which inorganic and microbially-mediated reactions tend to equilibrate. Bicarbonate (HCO_3^-) dominates over the pH range of Lake Coeur d'Alene waters. The rate of the carbonate reaction (above) is much faster than those of hydrolysis reactions involving Fe and Mn.

A third factor which is likely to influence pH in the hypolimnion of Lake Coeur d'Alene is the availability of solid $CaCO_3$. It is likely that carbonate material in the sediment acts as a buffer to maintain relatively neutral to alkaline conditions. The pH in Lake Coeur d'Alene generally ranges from 6.5 - 8.1, as measured by Paul Woods (Harenberg, 1991).

Towatana (1990) similarly hypothesized that a pH change would be buffered by carbonate gangue materials in the Smelterville Flats area on the Coeur d'Alene River. There, a recognized increase in Zn concentrations should have been accompanied by a decrease in pH due to sulfuric acid generation. The excess of carbonate in the system prevented the acidification of the water (Swope, 1990).

River water generally has a pH in the range of 6.5 to 8.5. Yearsley (1980) recorded pH values as high as 7.6 in the Spokane River near the outlet of the lake and as low as 6.3 in the deep waters near Ford Rock, where dissolved oxygen was low. Seitz and Jones (1981) measured pH values from 7.3 to 8.8 in June, August and November. A much lower pH was recorded in August, 1988, however (Yearsley and Duncan, 1989). Water leaving Lake Coeur d'Alene had a minimum pH of 5.85 and a mean of 6.05.

The mean pH of 73 groundwater samples from the Rathdrum Prairie Aquifer is 7.4, with a standard deviation of 0.6 pH units (data from Parliman, Seitz and Jones, 1980). The lowest recorded pH was 6.1, with a high of 8.2. Groundwater from wells within one mile of the Lake Coeur d'Alene/Rathdrum Prairie Aquifer recharge zone had a mean pH of 7.7. Most groundwaters in the United States have pH values ranging from about 6.0 to 8.5. The pH of water in Lake Coeur d'Alene and the adjacent aquifer recharge zone is likely to remain within these limits for natural waters. (A possible exception could occur in areas which once contained log yard wastes. Leachates derived from wood and bark are known to cause a drop in pH and a decrease in dissolved oxygen. An investigation into this topic is beyond the scope of this paper.)

Redox Conditions

Redox potential will be lowest where and when dissolved oxygen is depleted. No cases of a complete lack of dissolved oxygen in Lake Coeur d'Alene or the Spokane River have been reported. As part of this study, redox conditions were determined from samples collected by the USGS in 1991. The dissolved oxygen levels in Lake Coeur d'Alene were as low as 82% at depth in samples which later underwent a complete chemical analysis for major anions and cations. The redox status of these samples was calculated from dissolved oxygen using the ion speciation program PCWATEQ. The sample from Wolf Lodge Bay, on August 16, had $pe = 14.854$ and $Eh = 0.827$ V. The sample from near Tubbs Hill, at 40 meters in depth, had $pe = 15.162$ and a corresponding $Eh = 0.840$ V, $\log P_{CO_2} = 3.93$ and $\log P_{O_2} = -3.41$. Reducing conditions would have both negative Eh and pe values. The water samples from Lake Coeur d'Alene in August, 1991, reflect very oxidizing conditions.

Nitrate/Phosphate Content

Photosynthesis consumes nitrogen and phosphorous in equal ratios, so that the rate of biological productivity is dependent on the concentration of the less abundant element. In Lake Coeur d'Alene, phosphorous appears to be limiting. As long as phosphorous loadings to the lake are small and as long as dissolved oxygen exists at the sediment-water interface, the sediments will be a sink for phosphates. A well documented phenomenon in lakes, however, is that when reducing conditions persist in the hypolimnion, sediments release phosphorous accumulated in previous years. This process does not appear to be occurring yet in Lake Coeur d'Alene.

4.0 HYDROGEOCHEMISTRY OF METALS

4.1 Phase Associations

An understanding of the occurrence and behavior of metals in natural waters and sediments is crucial to predicting the mobility of metals in water and sediments of Lake Coeur d'Alene. As lake chemistry changes due to eutrophication, each metal will respond differently to changes in dissolved oxygen, p*e* and pH.

Heavy metals with elevated concentrations in Lake Coeur d'Alene sediments include Sb, As, Hg, Cu, Cd, Zn, Ag, Co and Pb. The term "heavy metal" is operationally defined as "any of the metals that react readily with dithizone (C_6H_5N)" (Bates and Jackson, 1990, p. 302).

The chemical characteristics of these metals determine their behavior and migration potential. This section addresses the concepts of phase, pH, and Eh in light of metal remobilization from sediments and migration in surface water and groundwater. Brief summaries of the chemical characteristics of selected metals found in the Coeur d'Alene Basin are included, followed by predictions of metal mobility and the results of groundwater monitoring in the study area.

4.1.1 Phases of Metals in Water and Sediment

Most metals can exist in different phases, which are physically separable and have different characteristics and affinities. A phase or species is understood as the "molecular representation of a specific form of an element" (Landner, 1987). Four general phases are recognized: (1) ions and complexes in solution, (2) cations adsorbed on clays and organics, (3) colloids and coprecipitates and (4) inert, crystalline compounds. One organizational scheme for understanding the phases (or species) of metals, given by Grahn and Hakanson (1986), is shown in Figure 40. The concentration of metal in each phase depends on pH, Eh, amount of organic carbon, temperature, etc. Phase associations are useful for predicting the migration and biological impact of metals.

Metals species "in solution" include ions, chelates, and organic and inorganic complexes. By convention, the "dissolved" fraction of metals are those which will pass through a 0.45 μm filter. This may actually include organic and inorganic colloids as well as ions in solution. Metals in solution will potentially migrate at the rate of groundwater or surface water advection. Theoretically, some infinitely small concentration of solubilized metals exists in all natural waters.

The exchangeable fraction consists of cations adsorbed on particles (usually clays or organics) by adsorptive bonding. This is usually the smallest fraction for most toxic metals. Metals in this phase have a high migration potential, because they may desorb when conditions change.

Metals may also exist as colloids, such as hydroxides and oxyhydroxides. Metals can travel as colloids in groundwater or be coprecipitated as hydroxides of Fe or Mn or as carbonates on sediment

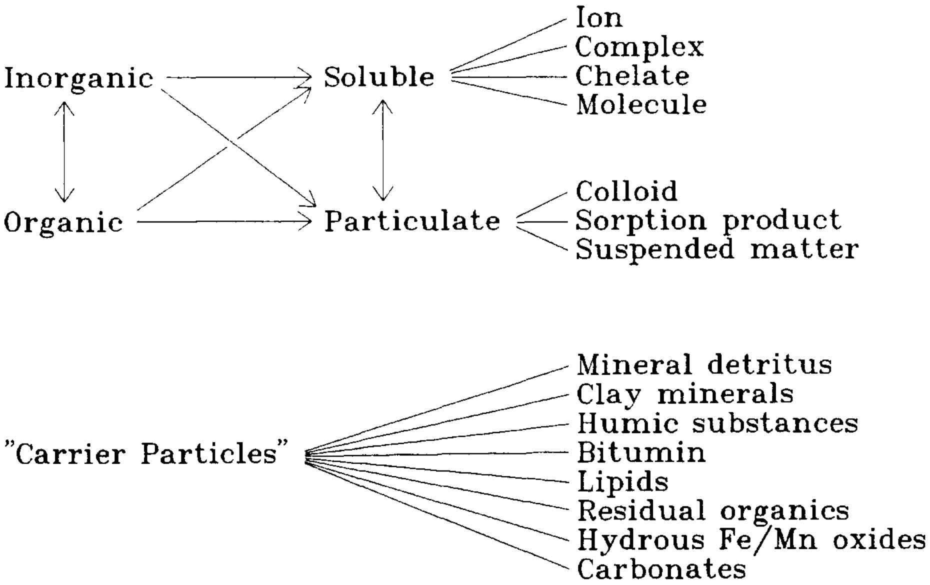


Figure 40. An organizational scheme for understanding phases of metals in water and sediment (from Grahn and Hakanson, 1986, after Biejer, *et al.*, 1977).

particles. The bulk of heavy metals in the sediments of Lake Coeur d'Alene are in solid Fe oxide precipitates or in iron oxide complexes.

Metals are often incorporated in organic particles, which may be picked up by feeding organisms. In some cases, this leads to the bioaccumulation of metals, although bioaccumulation of most metals is rare. Metals incorporated into the organic fraction may be the most difficult to model and predict, because the variety of organic materials is large, and some of these materials contribute to metal mobility while others do the opposite.

The inert fraction of metals is in the form of crystalline particulate matter (or amorphous solids) which may be carried in suspension by water with sufficient velocity or deposited in surficial sediments. The earliest metal loadings to Lake Coeur d'Alene probably came in the inert/refractory phase. Metals in this phase are unlikely to be taken up by freshwater biota. The inert fraction is unlikely to pose a health threat, but can change phase, in time, under certain conditions.

Heavy minerals (inert/refractory phase) make up 0.4 to 3.0 weight percent of sediments in three samples taken from the north end of Lake Coeur d'Alene (Horowitz, Elrick and Cook, 1992). The heavy fraction contains minerals such as galena, sphalerite, titanium oxides, tetrahedrite, monazite, arsenopyrite, chalcopyrite and various iron sulfides, many of which are coated by iron oxide rinds.

Determination of Metal Phase

Laboratory analysis is required to determine the phases of metals in water and sediment. The bulk concentration of metals can be separated into physico-chemically defined fractions by (1) chemical extraction, (2) ion-exchange and gel chromatography, (3) filtration, centrifugation and sieving, (4) selective solvent extraction, (5) sorption and complexation reactions with synthetics, and (6) numerical chemical modelling. Dr. Art Horowitz, of the USGS in Atlanta, Georgia, determined the phases of metals in Lake Coeur d'Alene sediments by selective extraction. Each phase (or partition) is "operationally defined" and metal concentrations will vary for different extractants.

Following separation into phases, the amount of metal in each phase is determined by any of several detection methods. Atomic Absorption spectrometry (AAS), both in the flame, graphite furnace and hydrite generation mode, is most often used because of its operational ease, high sensitivity and low detection limits (10^{-10} - 10^{-12} g) (Landner, 1987).

Metal Transfer Between Solid and Aqueous Phases

Metals which reach the aqueous environment are often bound up in sediments. Sediments have a high affinity for metals, but the incorporation or fixation of metals in sediments may not be permanent. Sediments often serve as a temporary sink for metals until conditions favor the release of selected elements. Sediments then become secondary release mechanisms.

The phase of metals is affected by the availability of clays, pH conditions (which affect the degree of hydrolysis, precipitation, and adsorptive behavior), redox potential (oxidation state), the amount of complexing agents (OH^-, CO_3^{-2}, PO_4^{-3}, SO_4^{-2}, and organics such as humic and fulvic acids), the salinity and concentration of competing elements, and residence time.

Adsorption affects whether a metal will remain in solution or will be bound in sediments or colloids. Adsorption occurs when a metal, dissolved ion, or molecule becomes attached to the surface of a pre-existing solid substrate. Metals may adsorb onto particles which have negatively charged OH groups. Adsorptive particles include clay minerals ($SiOH^-$, $AlOH_2^-$, $AlOH^-$), freshly precipitated iron hydroxides (FeOH), amorphous silicic acids, organic substances (carboxylic and phenolic groups) and all fine grained materials with large surface areas.

The adsorption process is highly dependent on pH because H^+ also competes for exchange sites. At low pH there is very little adsorption and at high pH almost all cations are adsorbed. The pH range of adsorption varies for different metal ions. Heavy metals are released (desorbed) with increasing hydronium (H^+) ion (decreasing pH).

Cation exchange is the process of releasing a charged metal (or cation) in favor of another metal ion. Cations are often sorbed from solution as other cations are released. This process, known as cation exchange, can 'clean' water by binding metals and can contaminate water by releasing bound cations.

Clay minerals, zeolites, colloidal oxyhydroxides and natural organic compounds all exhibit ion exchange behavior. The exchange capacity is a property of the soil or lithology and is defined as the sum of the exchangeable cations, expressed in meq/ℓ. A medium with a high cation exchange capacity (CEC) has the potential to bind up larger amounts of metals than one with a low CEC. Smaller sized particles have increased surface area and thus have a higher CEC. Montmorillonite clays are extremely fine and typically adsorb the greatest concentration of metals. The relationship of the CEC of common clays is:

kaolinite < chlorite < illite < montmorillonite.

Adsorption is considered to be temporary because of competition for exchange sites by abundant Ca^{+2}, Na^{+2}, H^{+}, and K^{+}. The adsorption of metals onto oxide/hydroxide surfaces is discussed further in Section 4.1.4.

Coprecipitation is related to adsorption, except that the metal is not attached to a pre-existing phase. The dissolved species is incorporated as a minor constituent in a solid phase as it is precipitating. It can be very difficult, in natural systems with Fe and Mn hydroxides, to determine whether metals were adsorbed to the surface of preexisting (already precipitated) Fe/Mn oxyhydroxides or were coprecipitated. Coprecipitation is probably the most important process for attenuating heavy metal migration in the subsurface environment.

Complexation by organic materials and cation exchange on the surfaces of organics may immobilize metals. Organics have more exchange sites than clays and can (temporarily) bind a significant amount of metals. Dissolved organics can increase metal solubility by complexing and can affect whether metals occur in the reduced or oxidized form. Dissolved organics can alleviate the toxicity of some metals by altering the availability to freshwater biota. Organics influence adsorption and affect the stability of metal containing colloids.

Organic acids ("humic acids") include humins, humic acids, fulvic acids, and yellow organic acids. These acids are important products of the decomposition of organic material. A positive correlation often exists between the content of organic materials and the concentration of metals in aquatic sediments. Laboratory analyses of water and sediment samples often give a value for total organic carbon (TOC). A higher amount of TOC often corresponds to more metals in solution. TOC is only one factor in a complicated system, however. Organo-metallic complexes may attenuate *or* facilitate the movement of metals in the subsurface environment. The median TOC concentration in surficial sediments of Lake Coeur d'Alene is not higher than the median uncontaminated (background) concentration (Horowitz, Elrick and Cook, 1992).

The *precipitation* process removes metals from solution and is dependent on the concentrations of ions in solution, p*e* and pH. Precipitates form when the concentration of ions in solution exceeds the solubility constant, Ksp. $Ksp = [A]^a[B]^b$, where A is the activity or concentration of species A and a is the stochastic amount. Dissolution of the solid phase occurs when the solubility product (a function of the activities of ions in solution) is less than the solubility constant (Ksp). The conditions under which precipitation or dissolution will occur are calculated thermodynamically and shown as stability relations (or fields) in Eh-pH or p*e*-pH diagrams. Such information is given for several metals in Section 4.2.7.

Metals commonly precipitate as hydroxides, sulfides, chlorides, sulfates, and carbonates. Hydroxides are precipitates of amorphous or very fine metastable crystalline precipitates with a disordered crystal lattice. Hydroxides precipitate from strongly oversaturated solutions and convert to stable phases over time. Sulfides are insoluble at neutral pH. Carbonate solubility depends on the partial pressure of carbon dioxide (PCO_2). Generally, chlorides and sulfates of heavy metals are readily soluble. Carbonates, hydroxides, and sulfides dissolve with great difficulty.

Redox conditions affect the solubility of metals. Redox is reflected by the availability and concentration of dissolved oxygen. Metals in higher oxidation states are generally less soluble than their reduced forms, so as redox potential increases, solubility increases. This is especially true for Fe and lead; reduced iron (Fe^{2+}) is more soluble than oxidized iron (Fe^{3+}). Cadmium is an exception to this in that the solubility of Cd increases with decreasing redox potential.

4.1.2 Phases of Metals in Lake Coeur d'Alene Sediments

The phase associations of trace elements in four sediment samples from Lake Coeur d'Alene, from Horowitz, Elrick and Cook (1992), are given in Figure 41. Significant concern may be warranted because most metals are associated with the iron oxide phase. Metals in this phase are typically more readily mobile and more available to aquatic plants and animals than metals in the sulfide or refractory (inert) phases.

These phase associations were determined by a sequential extraction procedure. Horowitz, Elrick and Cook determined that approximately 95% of the Pb, 90% of the Cd, 80% of the Zn, 75% As, and 55% of the Cu are associated with an operationally defined iron oxide phase. The remaining portion of these elements appear to be associated with either an operationally defined organic/sulfide phase or are tightly bound in mineral lattices.

The phase of Ag is highly variable. In sample 128, approximately 58% of the Ag is associated with the iron oxide phase, but in Sample 32, 100% of the Ag is associated with the organic/sulfide phase. Antimony appears to be dominantly held in the refractory (lattice-bound) phase.

4.2 Chemical and physical characteristics of selected metals

4.2.1 Arsenic

Arsenic is commonly considered nonmetallic or a metalloid, in part because it tends to form oxyanions rather than cations in water (Fergusson, 1990). Minerals containing As include: arsenopyrite (FeAsS), orpiment (As_2S_3), realgar (As_4S_4), native As, arsenolite (As_2O_3), loellingite ($FeAs_2$) and many others.

Mining and agriculture are principle sources of As products. Sodium arsenite has been used as an herbicide. Copper and Cr salts of As are used as wood preservatives. Arsenic is also used in

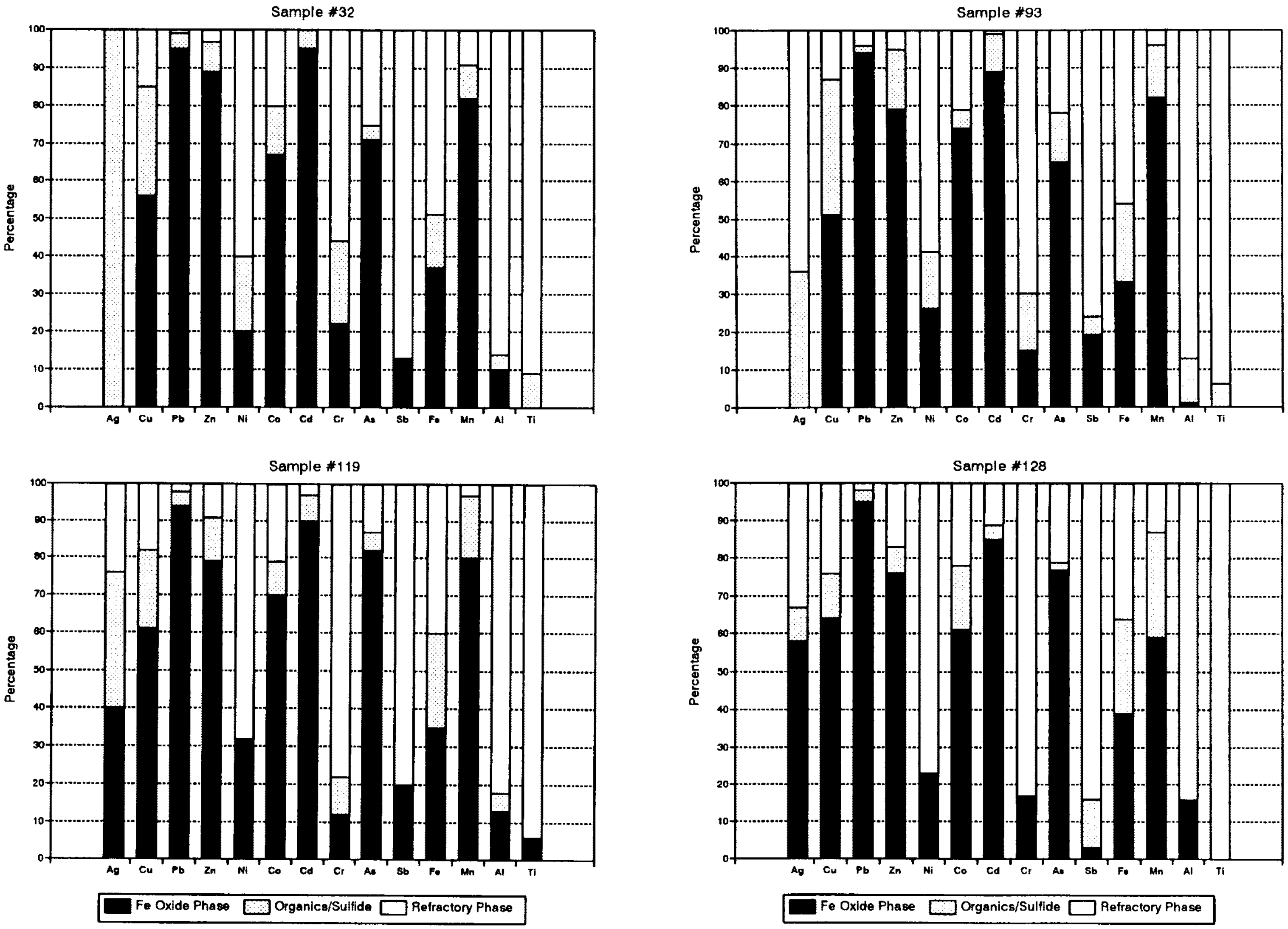


Figure 41. Phase associations of trace elements in four samples of Lake Coeur d'Alene sediments.

insecticides, rodenticides, plant desiccants, pharmaceuticals, textile dying and detergents.

Arsenic has an atomic mass of 74.92 and atomic number 33. Gray, elemental As has a density of 5.73 g/cm^3 and a melting point of 814°C at 36.5 bars. Gray As sublimates at 604°C, 1 bar pressure. Yellow, elemental As is unstable and has a density of 2.03 g/cm^3 at 18°C. Both are forms of metallic As, which is not soluble in most common solvents (Leonard, 1991). White As, As_2O_3, can exist in several forms which have various densities and melting points. Other forms of As include arsenious halides such as AsF_3, $AsCl_3$, and $AsBr_3$, arsenic pentoxide (As_2O_5), arsenic pentasulfide (As_2S_5), arsenic pentaselenide (As_2Se_5), arsenates and compounds containing As in the -3 oxidation state, including Na_3As, Ca_3As_2, Zn_3As_2 and AlAs.

Speciation of As is critical, because organic and inorganic forms can coexist and the form of As has a large effect on toxicity (Leonard, 1991). Arsenic occurs as As^{5+}, As^{3+}, As^0 and As^{3-} in natural waters. The most common arsenic species are As^{5+}, As^{3+} and methylated arsenic. As^0 and As^{3-} occur only under strongly reducing conditions, and are rare in the natural water environment (Moore and Ramamoorthy, 1984).

Arsenic mobility in water increases in the 3+ (arsenite) state (Fergusson, 1990). Arsenite is a hard acid which preferentially complexes with oxides and nitrogen. When combined with Fe and aluminum compounds, As^{3+} is relatively immobile (Sakata, 1987). Arsenites predominate under mildly reducing conditions (Moore, 1991; Fergusson, 1990).

As^{5+} is most common in well oxygenated waters and at high Eh. Arsenate (Arsenic V) is a soft acid which preferentially complexes with sulfides (Moore, 1991). As^{5+} is relatively immobile when combined with Fe and Al compounds (Brannon and Patrick, 1987). Most arsenates have a low solubility in water and salts of As with Cu and Cr are useful as wood preservatives because they do not leach out of wood.

Fresh water normally contains 0.15-0.45 μg/l of As, which occurs mainly in the organic form (Fergusson and Gavis, 1972). According to Bowen (1979) the concentration of As in freshwater) is somewhat higher: 0.2 - 230 μg/l. Some waters have been known to contain more than 1000 μg/l (Leonard, 1991).

A speciation scheme for As in a stratified lake is given in Figure 42. Arsenate is dominant in the oxygenated epilimnion and arsenite is more common in the oxygen deficient hypolimnion. Further reducing conditions may lead to the formation of arsenic sulfides and insoluble arsenate compounds (Fergusson, 1990).

Arsenic is predominantly bound to sediments in most water courses (Moore, 1991). Relatively high levels, up to 60 mg/kg or even 675 mg/kg, have been observed in freshwater sediments (Leonard, 1991). The metalloid combines strongly with sulfur and carbon in organic compounds. The sorption of As^{3+} and As^{5+} by humic acids and other organic matter is dependent on pH and organic concentration of the sediments (Faust, Winka and Belton, 1987).

Desorption of As from sediments is controlled by pH, As concentration in the interstitial water of sediments, and changes in the total Fe, extractable Fe, and $CaCO_3$ equivalent in sediments (Brannon and Patrick, 1987). Experiments comparing sandy lake sediments with organic lake sediments have shown that very little total As is released from organic sediments in aqueous systems, but substantial quantities of total As are released from sandy sediments (Faust, Winka and Belton, 1987). Arsenic is incorporated into the sandy sediments by coprecipitation onto iron oxyhydroxides. The release of As from sandy sediments is due to the slow dissolution of the iron oxyhydroxides.

The background level of As in soil is about 6 mg/kg (Bowen, 1979) to 7 mg/kg (Leonard, 1991). Arsenic occurs in soils mainly as arsenate under oxic conditions. The species is strongly and sometimes irreversibly sorbed onto clays, Fe and Mn oxides/hydroxides and organic matter. The amount of sorption relates to the As concentration, time and the Fe and Mn content of the soil. Increasing the pH of soil (by liming) increases the mobility of As because calcium arsenate is more soluble than Al and Fe arsenates (Fergusson, 1990). The mobility of As also increases under reducing conditions, because of the increase in the proportion of arsenite.

4.2.2 Lead

Lead is the 36th most abundant element in the earth's crust (Moore, 1991; Merian, 1991). The average crustal abundance of Pb is 16 ppm (Nriagu, 1978). The element is found in over 200 minerals on earth, but is concentrated in galena (PbS), gelesite ($PbSO_4$), and cerrusite ($PbCO_3$) (Moore, 1991). Lead is ubiquitous, found in all environmental media: air, soil, rocks, water, sediments. Naturally occurring isotopes include: ^{208}Pb(52%), ^{206}Pb (24%), ^{207}Pb (23%), ^{204}Pb (1%) and radioactive ^{210}Pb from radon decay (Ewers and Schlipkoter, 1991).

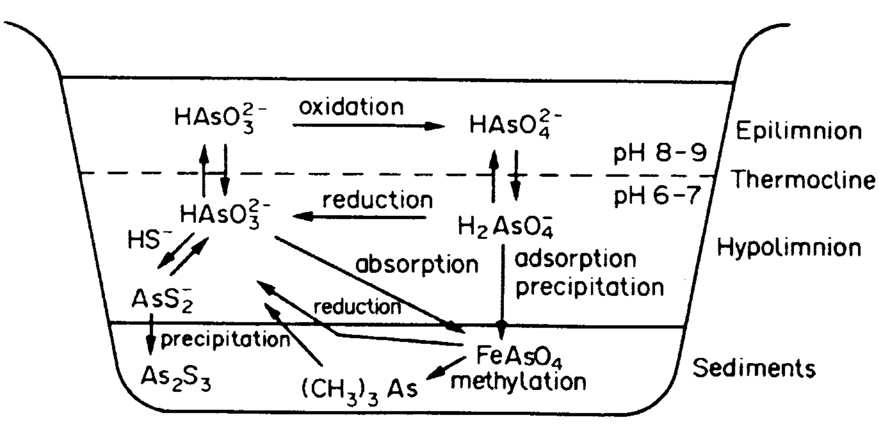


Figure 42. Schematic representation of arsenic speciation in a stratified lake (from Fergusson, 1990).

Lead is a bluish-white, soft metal. The Group IVa metal has the chemical symbol Pb, atomic number 82 and atomic mass 207.19. Lead vaporizes at 1740°C and has a notably high density (11.34 g/cm^3) and low melting point (327.5°C) (Ewers and Schlipkoter, 1991).

Lead exists in three oxidation states: Pb^0, Pb^{2+}, and Pb^{4+}. The aqueous phase of Pb is almost exclusively Pb^{2+}. Similarly, Pb exists at the +2 oxidation state in most inorganic compounds.

Lead is relatively insoluble in natural waters because it tends to form complexes with many of the major anions. These low solubility complexes include hydroxides, carbonates, sulfides and (less commonly) sulfates. $PbCO_3$ (cerussite), $Pb(OH)_2$ and $Pb_3(OH)_3(CO_3)_2$ (hydrocerussite) are the least soluble forms of Pb in oxidizing systems. In reduced systems where sulfur is present, the stable solid is PbS (galena). Lead also partitions favorably with humic and fulvic acids, to form insoluble organic complexes (Moore, 1991; Hem, 1976; Ewers and Schlipkoter, 1991).

Sorption to sediments is the common fate of Pb in aquatic systems. Moore (1991) reported that, in numerous studies, Pb is commonly bound to the smallest size fractions in sediments. At the surface of the sediment column (only), lead carbonate complexes may be common. Fe-Mn hydrous oxides of Pb may be abundant in the sediment column. Lead sulfide is dominant in anaerobic sediments (Moore, 1991). The clays montmorillonite and kaolinite adsorb Pb over a wide range of pH, because of their cation exchange capacities, but illitic clays do not fix Pb. A study of landfill leachate has shown that montmorillonite can remove five times more Pb than kaolinite. At $pH<6$, $H+$ ions competed with Pb for adsorption sites, but at $pH>6$ a sharp rise in Pb adsorption was observed due to the formation of hydroxyl Pb species. The precipitation of heavy metal hydroxides and carbonates was the primary mechanism for Pb attenuation in clayey materials.

Although sediments tend to fix Pb, Pb may also slowly desorb from sediments. McKee (1989) found that the sediment-bound Pb in lake Superior may ultimately appear in the pore water and be recycled to the overlying water. The median concentration of Pb in river and lake water of the United States is about 2 ug/l (Lovering, 1976). Hem (1976) states that the concentration of dissolved Pb in most natural water systems (which usually contain dissolved carbon dioxide and have a pH near 7) is very low--commonly less than 10 μg/l. Moore (1991) reports that approximately 75% of Pb in rivers is in suspension; 25% is in solution.

Levels of dissolved Pb in aqueous systems do not appear to be influenced by redox conditions, although pH strongly influences solubility. Above pH 8.0 the solubility of Pb is less than 10 μg/l regardless of the alkalinity. Near pH 6.5, in water having low alkalinity, the solubility of Pb could approach or exceed 100 μg/l. Lead solubility will be low in alkaline and moderately mineralized waters. Where the pH is below 7.0, the equilibrium solubility of Pb may be well over 100 μg/l. In most natural waters, the concentration of soluble Pb is less than that predicted by equilibrium solubility calculations (Harrison, Laxen and Wilson, 1981; Hem, 1976).

Concentrations of Pb in groundwater will generally be low, except in groundwater with low pH or high chloride content and with relatively high temperatures (Lovering, 1976). Where waters are near neutral pH and contain dissolved carbon species, soluble Pb concentrations could be a few tenths of a milligram per liter, although commonly values are less than 10 μg/l.

Lead is generally considered to be immobile in soils. However, Pb can be leached by organic acids and travel in solution as soluble Pb organic complexes. Wai and Mok (1989) studied of the leaching of Pb from sediments of the lower Coeur d'Alene River. They examined the release of metals as a function of pH. The results shown in Table 5 indicate that at extremely low pH values, the sediments of the main stem of the Coeur d'Alene River (and presumably those of Lake Coeur d'Alene) are likely to release Pb. However, at the pH range of natural waters, Pb is unlikely to leach from sediments in significant quantities.

4.2.3 Copper

Copper comprises 0.005 to 0.009% igneous rocks by weight (Scheinberg, 1991). The primary Cu mineral is chalcopyrite ($CuFeS_2$), followed by metallic Cu, chalcocite (CuS_2) and bornite (Cu_5FeS_4). Natural Cu consists of an isotopic mixture of 69.1% ^{63}Cu and 30.9% ^{65}Cu (Scheinberg, 1991).

The red metal has atomic number 29, atomic mass 63, density 8.93 g/cm^3, melting point 1083°C, and boiling point 2590°C. Copper is a transition element and has four oxidation states: Cu^0, Cu^+, Cu^{2+}, and Cu^{3+}. Cu^{2+} is the stable oxidation state in aqueous solutions. Like all bivalent transition metal cations, Cu^{2+} is an intermediate receptor between hard and soft acids.

Copper shows a pronounced tendency to form complexes with organic and inorganic ligands. Copper readily forms organo-metallic complexes with humic and fulvic acids, as well as complexes with carbonate, nitrate, sulfate and chloride. Under reducing conditions, Cu forms relatively insoluble complexes with sulfides.

Copper also binds to clays. In soils, Cu fixed in excess of the cation exchange capacity of the clay may be precipitated as $Cu(OH_2)$. An increase in pH in soil or water will increase the amount of Cu

Table 5. Leaching concentrations of lead from the sediments of the Coeur d'Alene River at various pH (from Wai and Mok, 1989).

pH	2.7	4.3	6.3	8.3	11.4
ug/kg of dry sediment	3302.58	474.53	0.73	2.72	16.40

fixation. In bottom sediments, Cu has a strong affinity for hydrous Fe and Mn oxides, carbonate materials, clays and organic matter.

The median concentration of "dissolved" ($<0.45\ \mu m$) Cu in freshwater lakes and rivers is 3 $\mu g/l$, with a range of 0.2 to 30 $\mu g/l$ (Bowen, 1979). Pristine rivers, such as the river Rhone, contain about 0.8 mg/l dissolved Cu (Huynh Ngoc, Whitehead and Oregonie, 1988). Copper in natural waters is commonly in quite stable organic complexes (Bowen, 1979; Moore, 1991). In fact, in some freshwaters, more than 90% of Cu may be bound to humic acids (Mantoura, Dickson and Riley, 1978). In one river in Canada, Tesier and Campbel (1978) found Cu in the following forms: organic 31-52%, residual 22-41%, Fe-Mn hydroxides 12-20%, carbonates 8-14%, exchangeable 1-1.2%.

Moore (1991) states that Cu is highly toxic to most species of aquatic plants, and is routinely used as an algicide and herbicide. Copper is known as one of the most toxic heavy metals to fish.

4.2.4 Cadmium

Cadmium is the 67th most abundant element (Merian, 1991), although Moore (1991) reports that Cd is the 64th. Common Cd minerals include greenockite (CdS), hawleyite, and otavite, which are commonly associated with sphalerite (ZnS).

Cadmium is a relatively soft, silver-white, lustrous and ductile metal. The atomic number is 48, atomic mass is 112.4. Cadmium has a melting point of 320.9°C, a boiling point of 767°C, and a density 8.64 g/cm^3 at 20°C. Naturally occurring isotopes of Cd include: ^{114}Cd (28.9%), ^{112}Cd (24.1%), ^{111}Cd (12.7%), ^{110}Cd(12.4%), ^{113}Cd(12.3%), ^{116}Cd(7.58%), ^{106}Cd (1.2%) and ^{108}Cd(0.87%).

The nontransition element exists in a single valence state: Cd^{2+}. Cadmium is a soft acid, has a pronounced tendency to form complexes and is commonly associated with Zn (Moore, 1991).

Cadmium is relatively mobile in aquatic systems, existing as Cd^{2+}, $Cd(OH)_2(aq)$, $Cd(OH)_3^-$, $CD(OH)_4^{2-}$, and $CdCO_3$, and in various other organic and inorganic complexes. The solubility of Cd decreases rapidly from a pH of 4 to 9 (due to the formation of solid $Cd(OH)_2$) and then increases slightly from a pH of 9 to 11 (Hem, 1985; Moore, 1991). Because the 2+ valency predominates in freshwater, redox potential has little effect on Cd speciation.

Cadmium in freshwaters preferentially complexes with the following ligands: humic acids > $CO_3^{2-} > OH^- > Cl^- > SO_4^{2-}$ (Moore, 1991). Salts of Cd with strong acids are readily soluble in water. Less soluble are the sulfide, carbonate, fluoride and the hydroxide (Stoeppler, 1991[b]).

The concentrations of dissolved and particulate-bound Cd in rivers and lakes are often below 0.1 $\mu g/l$. Sediments of unpolluted lakes and rivers usually have Cd concentrations ranging from 0.04to 0.8 mg/kg. Cadmium in the sediments of polluted rivers may range from 30 to 400 mg/kg and the sediments of extremely polluted rivers can reach 800 mg/kg Cd or higher (Stoeppler, 1991[b]). Bowen

(1979) reports a median concentration of 0.1 μg/l Cd in freshwater, with a range of 0.01 to 3.0. Cadmium is believed to be complexed primarily with organics in the aqueous system.

Sorption of Cd to suspended solids such as clay is an important, often dominant, fate process in freshwaters. Coprecipitation with hydrous iron, aluminum-manganese oxides and carbonate materials also periodically dominates the fate of Cd (Moore, 1991).

4.2.5 Mercury

The most common ore of mercury is Cinnabar (HgS). Mercury has atomic number 80, atomic mass of 200.59, density 13.55 g/cm^3, melting point -39.8°C, and boiling point 357°C. Six main natural isotopes occur: ^{202}Hg (29.8%), ^{200}Hg (23.1%), ^{199}Hg (16.8%), ^{201}Hg, (13.2%), ^{198}Hg(10%) and ^{204}Hg (6.8%), ^{196}Hg (trace) and ^{203}Hg (trace).

Mercury exists in three oxidation states in natural waters: Hg^0, Hg^+, and Hg^{2+}. In well-aerated waters (Eh>0.5 V) Hg^{2+} dominates. Hg^0 may develop under reducing conditions (Moore, 1991). Mercury forms several inorganic compounds in water. Hg bonds with chloride and also hydrolyzes to $Hg(OH)_2$. $Hg(OH)_2$ is the dominant species at pH>4, given Cl^- concentration <10-5 M. When Cl occurs at higher concentration (0.01 M) the region of predominance of $Hg(OH)_2$ shifts to pH>6 (Moore, 1991). $HgCl_2$ is highly soluble in water and highly toxic. Hg_2Cl_2 is less soluble and less toxic (Weast, 1986). An excess of the sulfide ion stabilizes bivalent Hg as hydrosulfide or sulfide complexes, even at low redox potentials (Moore, 1991). HgS is the least soluble inorganic form of Hg (Weast, 1986).

Mercury forms stable complexes with a variety of organic ligands, amino acids, and hydroxycarboxylic acids. Organic complexes dominate Hg speciation in pH 3-5. The most renowned organic complex, methylated mercury, $(CH_3)_2Hg$, is a highly mobile, toxic species which is readily bioaccumulated by aquatic plants and animals. This organic form of Hg may affect human health in populations which consume large quantities of affected fish.

Inorganic Hg can be methylated (converted to toxic organic Hg) within sediments. The rate of methylation is typically greatest in the surficial sediments, and decreases with increasing sediment depth (Callister and Winfrey, 1986). Rate of methylation in the water column is extremely slow (below detection). In sediments and the water column the rate of methylation of inorganic Hg generally increases with increasing temperature and with decreasing pH. The rate of methylation decreases with increasing sulfide content and increases with increasing nitrogen content of sediment. With decreasing dissolved oxygen content, the rate of methylation increases. Methylation decreases with increasing chloride content of sediment and water (Callister and Winfrey, 1986; Berman and Bartha, 1986; Nagase, Ose, Sato and Ishikawa, 1984). The concentration of methyl mercury typically represents less than 2% of total Hg in the water column and sediments.

The median concentration of Hg in freshwaters is 0.1 μg/l. The range is 0.0001 to 2.8 μg/l, which occurs mostly as organic species (Bowen, 1979). The Hg level in uncontaminated lakes, given by Fergusson (1990) is 0.02 μg/l.

Mercury concentrations are low in the water column because the metal is usually adsorbed to suspended solids and sediments. The association of Hg with sediments ranges from relatively weak Van der Waals forces (adsorption to clays) to strong covalent bonding, coprecipitation with iron-manganese oxides, and incorporation within crystal lattices (sulfides).

The release of Hg from sediments back into the water column occurs very slowly. Desorption is facilitated to a small degree by low pH of the overlying water, Eh, and the quantity of chloride and other ligands in the water and sediments (Bjornberg, Hakanson and Lundbergh, 1988). Inorganic Hg and methyl Hg are soft acids; they prefer complexation with sulfide over oxygen and will remain as sulfides in sediments rather than dissolve into the water column.

4.2.6 Zinc

Zinc is the 24th most abundant element in the earth's crust. Principal Zn ores are sphalerite (cubic ZnS), wurtzite (hexagonal ZnS), smithsonite aka calamine ($ZnCO_3$), and willemite (Zn_2SiO_4). Major sources of Zn to the environment include domestic wastewater, coal-burning power plants, mining wastes and cement and fertilizer production.

The bluish white, rather soft metal has an atomic number of 30, an atomic mass of 65.39, a density of 7.14 g/cm^3, a melting point at 419.58°C and a boiling point at 907°C. Naturally occurring stable isotopes are ^{64}Zn (48.6%), ^{66}Zn (27.9%), ^{68}Zn (18.8%), ^{67}Zn (4.1%), and ^{70}Zn (0.6%). Eighteen artificial radioactive isotopes are known, most of which have very short half lives.

Zinc is a nontransition, Group IIB, "borderline" metal. It forms bonds with oxygen as well as with nitrogen and sulfur donor atoms. Zinc is conservative with respect to redox. That is, Zn^{2+} is its only oxidation state. The dominant species under aerobic conditions at low to moderate pH is Zn^{2+}. $Zn(OH)_2$ dominates at pH 8 - 11 (Vymazal, 1985).

Zn^{2+} has a strong tendency to react with acidic, alkaline and inorganic compounds. Due its amphoteric properties, Zn forms a variety of salts. Zinc chlorate, zinc chloride, the sulfates and nitrates are readily soluble in water. The oxide, carbonate, phosphates, silicates, sulfides and organic complexes of Zn are practically insoluble in water (Weast, 1986). Zinc binds readily with many organic ligands, and its behavior is highly dependent on Eh, pH and concentration.

Anaerobic conditions lead to the formation of ZnS at any pH within range 1-14. Zinc in two rivers in northern Greece partitioned primarily into the sulfide and Fe-Mn hydrous oxide fractions of the sediments (Samanidou and Fytianos, 1987).

The average composition of Zn in rivers is 7 ug/l (Wedepohl, 1991). Bowen (1979) reports that the median Zn concentration in freshwater is 8 ug/l, with a range of 0.2 to 100 ug/l, most of which is expected to be Zn^{2+} bound to organics. Contrarily, Ohnesorge and Wilhelm (1991) state that in surface waters Zn occurs mainly bound to suspended matter, such as clay, or is precipitated with iron- or manganese oxides.

Sediments are a primary sink for Zn. Sediments from uncontaminated waters typically contain residues of 5 to 50 mg/kg Zn (Moore, 1991).

The toxicity of Zn and most zinc-containing compounds is generally low (Ohnesorge and Wilhelm, 1991). The drinking water guideline is based on aesthetic factors, particularly taste and appearance (Moore, 1991). The 1972 water quality standards suggested an upper limit of 5 mg/l for Zn, because above that limit a significant number of people can detect Zn by taste. "No health effects [to humans] were considered likely" (Hem, 1985, p.142).

4.2.7 Factors Which Contribute to Mobility

The preceding section makes clear that aquatic systems can be very complex environments, geochemically, and that different metals will respond differently to changing lake chemistry. It has been shown that the solubility, mobility and bioavailability of particle-bound metals can generally be increased by four major factors: (1) lowering pH, (2) increasing natural and synthetic complexing agents, (3) increasing salt concentrations (causing increased competition for sorption sites) and (4) changing redox conditions (Forstner and Kersten, 19). In spite of the complexity imparted by competing ions, organic acids and differing rates of reactions, some general conclusions can be drawn from equilibrium thermodynamic calculations. Table 6 lists the relative mobility of selected anions in response to (1) and (4) above: Eh and pH conditions.

Many interactions can be estimated from this simple scheme, which includes data from soil studies and dredged material.

Eh-pH diagrams provide another valuable tool for interpreting/predicting the behavior of metals in the aquatic system. Again, the rates of many reactions are too slow to reach equilibrium in real systems and organisms such as bacteria are able to catalyze redox reactions which would not be expected on thermodynamic grounds. However, Figure 43 shows the *likely* phases of metals under various combinations of Eh and pH in lake water.

Figure 44 illustrates the dominant Zn species under various Eh-pH conditions in a CO_2, S^+, H_2O system. In a calcium carbonate type water, Zn is redox conservative but is sensitive to pH changes within the range of natural waters. This explains why elevated Zn concentrations have been reported in the Spokane River and in Lake Coeur d'Alene. A slight lowering of pH (from about 7.6 to 7.5) liberates Zn^{2+}.

4.3 Effects of Eutrophication on Trace Metals in Lakes

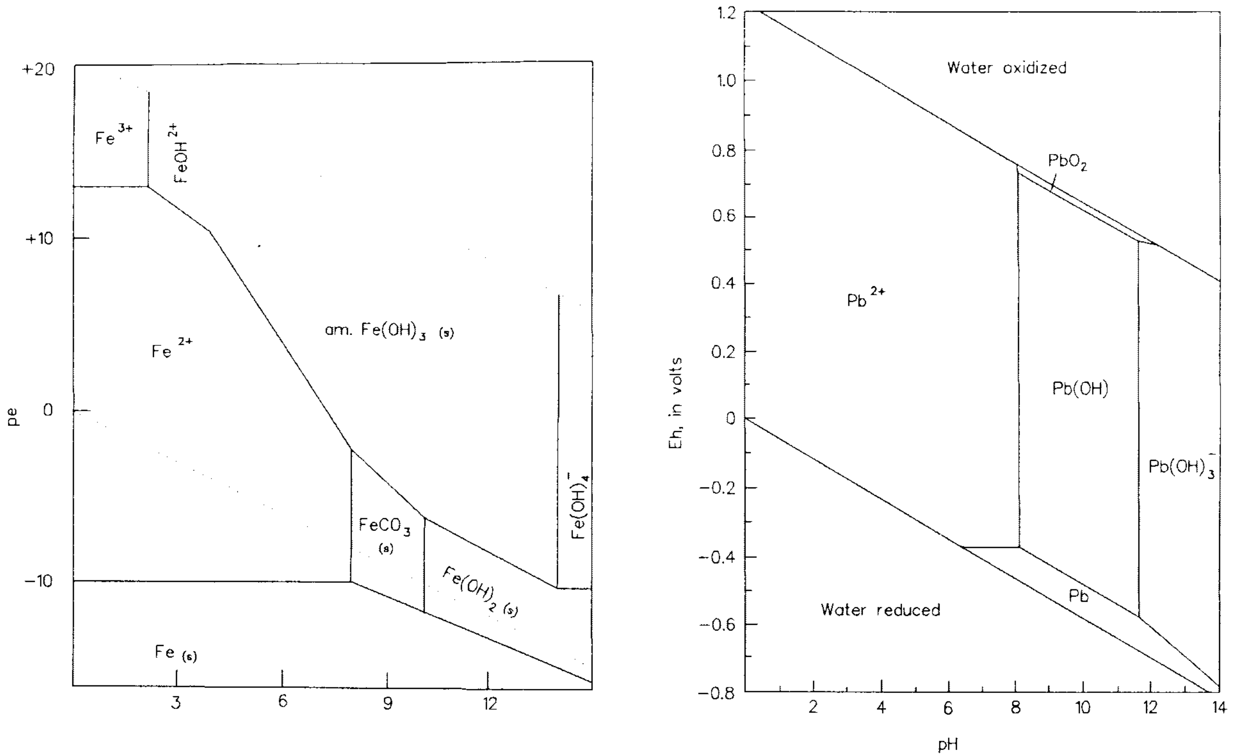
The partitioning of metals between water and sediments will be further complicated by changing lake conditions as a result of eutrophication processes. The cycling of Fe and Mn in the water column and the uptake of metal by aquatic biota may serve to reduce the concentration of metals in the water column under slightly eutrophic conditions. In advanced eutrophy, metals may be removed from water by sulfide precipitation. Eutrophication also affects the pH conditions of lake water. These processes are discussed below.

4.3.1 Manganese Cycling and Metal Scavenging

Metal ions may become reversibly bound to hydrous oxide surfaces and be removed from the water column. The process begins when manganese, silicon, iron and/or carbonate form oxides and oxyhydroxides (as previously mentioned in Sections 4.1.1 and 4.1.3). These solids precipitate, and come in contact with free metal ions while settling through the water column. Some of those free metal ions will adhere to the oxide surface and be transported downward toward the sediment. The tendency of a specific metal ion to bind to oxide surfaces is related to its tendency to react with oxygen donor atoms or to form hydroxo complexes (Sigg, 1987). The complexation of metal ions by oxide surfaces is strongly pH dependent. Figure 45 shows how the extent of adsorption of Cu, Cd and lead to oxide surfaces (in this case rutile, TiO_2, and amorphous silica, SiO_2) changes within a narrow pH range. For each metal ion there is an interval of 1-2 pH units where the extent of adsorption rises from zero to almost 100%. pH is

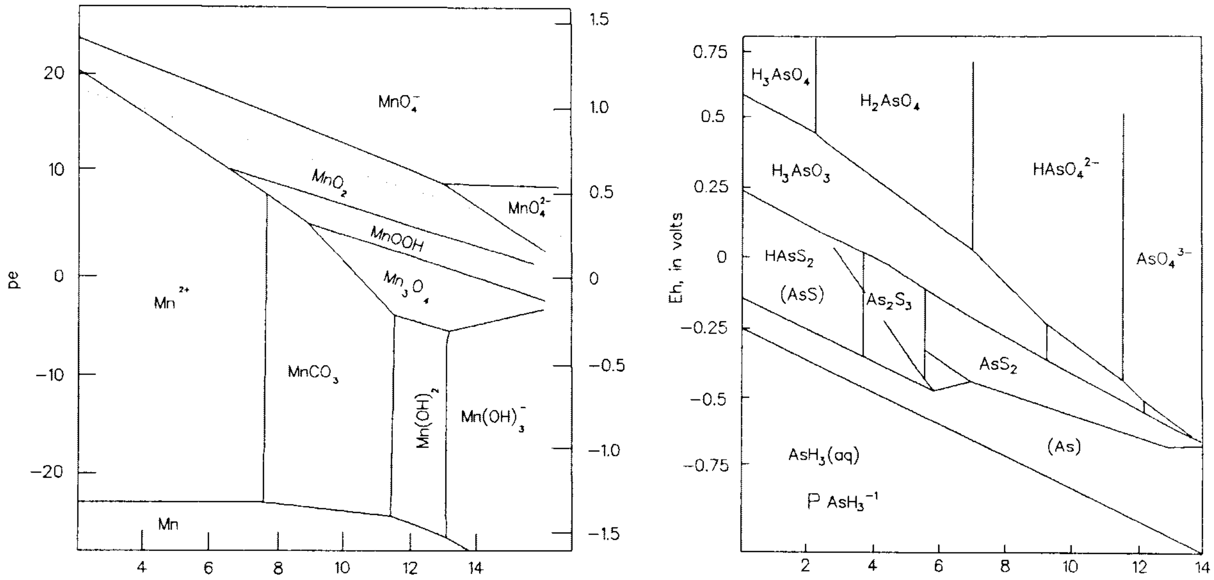
Table 6. Relative mobility of metals with respect to redox and acidity.

Relative Mobility	Electron Activity		Proton Activity	
	Reducing	Oxidizing	Neutral-Alkaline	Acidic
Very low mobility	Al, Cr, Mo, V, U, Se, S, B, Hg, Cu, Cd, Pb	Al, Cr, Fe, Mn	Al, Cr, Hg, Cu, Ni, Co	Si
Low mobility	Si, K, P, Ni, Zn, Co, Fe	Si, K, P, Pb	Si, K, P, Pb, Fe, Zn, Cd	K, Fe(III)
Medium mobility	Mn	Co, Ni, Hg, Cu, Zn, Cd	Mn	Al, Pb, Cu, Cr, V
High mobility	Ca, Na, Mg, Sr	Ca, Na, Mg, Sr, Mo, V, U, Se	Ca, Na, Mg, Cr	Ca, Na, Mg, Zn, Cd, Hg, Co, (Mn)
Very high mobility	Cl, I, Br	Cl, I, Br, B	Cl, I, Br, S, B, Mo, V, U, Se	Cl, I, Br, B



Fe, CO , H_2O system at 25°C, $[Fe]=10^{-5}$ M, $C=10^{-3}$ M, considering the solid phases: amorphous $Fe(OH)_3$, $Fe(CO)_3$ (siderite), $Fe(OH)_2$, and Fe (from Stumm and Morgan, 1981).

Eh–pH diagrams for the Pb–H_2O system. Dissolved Pb activity = $10^{-8.32}$mol/l at 25°C and 1 atm (from Hem, 1972).



Mn–CO_2 system at 25°C, $C=10^{-3}$M (from Stumm and Morgan, 1981).

As, H_2O, S system at 25°C (from Fergusson, 1990).

Figure 43. Eh-pH and p*e*-pH diagrams for arsenic, lead, iron, and manganese.

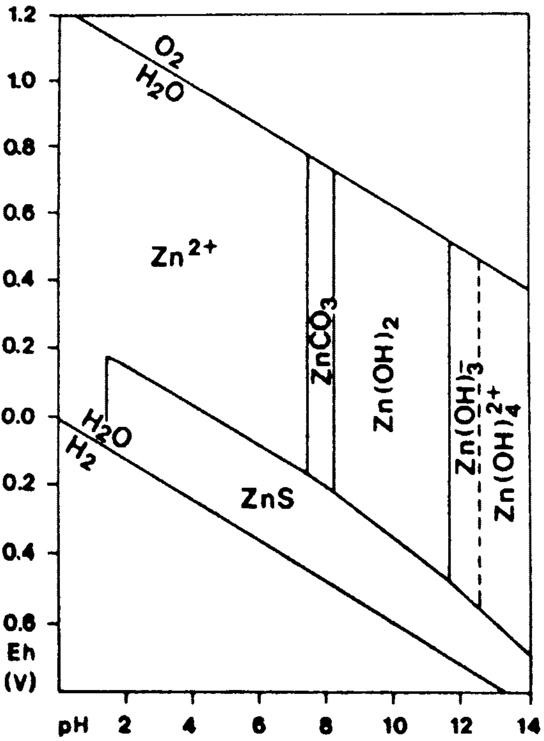


Figure 44. Eh-pH diagram for the Zn, CO_2, S^+, H_2O system at 25°C and 1 atm.

the master variable which governs the extent of adsorption (Schindler and Stumm, 1987.) The extremely large surface area of amorphous Fe and Mn hydroxides explains why FeOOH and MnO_2/MnOOH adsorb significantly more metal ions than do carbonate or silicate precipitates. Iron and manganese effectively scavenge metals from the water column and transport them to down the sediments (Sigg, 1987).

Under reducing conditions in the hypolimnion of a lake, Mn and Fe do not remain in the sediments. The phenomenon of metals cycling is illustrated in Figure 46. Iron and Mn are reduced to Fe^{2+} and Mn^{2+} in the hypolimnion *or* may diffuse upward from the reduced zone of the sediment column. These mobile species migrate upward in the water column until they reach the anoxic/oxic boundary. Upon contact with oxygenated waters, Fe and Mn reprecipitate as oxides (or oxyhydroxides), which again scavenge dissolved trace metals from the water column.

Some authors have postulated that Fe and Mn may act as a transport mechanism for heavy metals in a chemically reduced hypolimnion. However, research indicates that in the deeper parts of lakes, where very active Mn cycling takes place, Mn^{2+} is released from sediments is reoxidized back to MnO_2, and scavenges metals as it settles to the lake floor (Sigg, 1987; Sigg, Sturm and Kissler, 1987). Although it is conceivable that some trace metals could be liberated with Mn^{2+}, the slight reducing conditions which liberate Mn may not be sufficient to liberate trace elements from the sediment. The trace elements, which are adsorbed to oxide and hydroxyl groups rather than to Mn or Fe, may remain in the sediments as low solubility carbonates and hydroxides or may bind to organics in the sediment. Lake

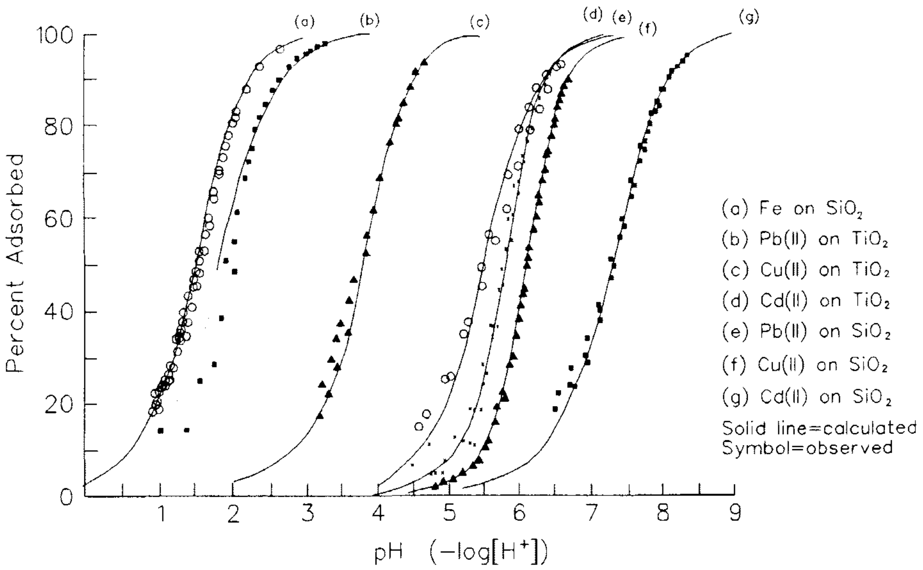


Figure 45. The adsorption of iron, cadmium, lead and copper onto oxide/hydroxide surfaces is strongly controlled by pH (from Schindler, *et al*, 1976; Furst, 1976).

waters which contained Fe and Mn in solution have been found to contain lower levels of Zn, Cu and As than lake waters which lacked an oxide scavenger to coprecipitate trace metals (Jonasson, 1977; Forstner and Wittmann, 1979, 1981).

4.3.2 Uptake of Trace Metals by Aquatic Biota

The biomass is a main factor in controlling the heavy metal balance in lakes (Stumm and Baccini, 1978). The constant ratios of metals to phosphorous in the settling material in lakes indicates that Cu and Zn preferentially bind to biological material (Sigg, 1987). Algal cells have a high affinity for Cu. Copper binds to the surfaces of these cells and is carried down to the sediment when the algae die. In aquatic systems with high biological production and a high sedimentation rate, trace metals, particularly Cu and Zn, may be efficiently eliminated from the water column.

Lakes with high nutrient supply and high biological production will have a correspondingly high sedimentation rate. These lakes may be more effective at reducing trace metal concentrations in the water column and counterbalancing the effects of metals loading (Sigg, 1987). If increased metals loading creates a concentration of metals which is toxic to algae, however, planktonic growth will be inhibited and the efficiency of this metal-removal mechanism will decrease. Sedimentation rates will decline and fewer metals will be removed from the water column by algae.

The metals loading to Lake Coeur d'Alene has decreased since the 1960's and 1970's. Some aquatic communities on the Coeur d'Alene River have begun to redevelop (Rabe, 1992, verbal communication). Barring the disturbance of tailings upstream, the rate of metals loadings are likely to

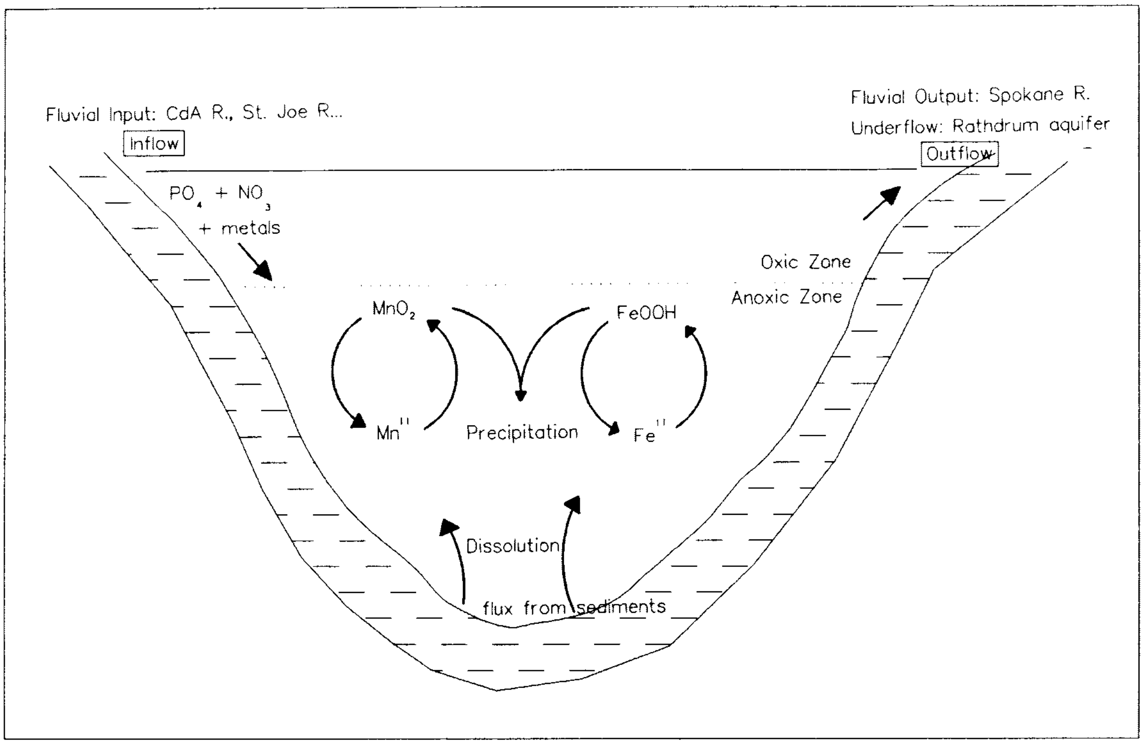


Figure 46. Schematic representation of iron and manganese cycling in a stratified lake.

decrease and planktonic populations in Lake Coeur d'Alene may efficiently regulate the concentration of metals in the water column.

4.3.3 Sulfide Precipitation in a Seasonally Reduced Hypolimnion

The occurrence of trace metals in a highly reduced water column must also be considered. A strongly eutrophic lake has a seasonally or permanently reduced hypolimnion which contains high concentrations of sulfides (Stumm and Baccini, 1978). Trace metals would be expected to form heavy metal sulfides (CuS, Cu_2S, ZnS, CdS, PbS, HgS) under these conditions. The solubility products of these compounds are extremely low. The sulfide complexation of trace metals would effectively convert trace metals back to the inert phase.

The disposal of sulfide-bearing mine tailings under a permanent water column has been proposed as a means of preventing oxidation, sulfide generation and the release of trace metals in mesotrophic to oligrotrphic lakes in Manitoba and British Columbia (Pedersen, Mueller, McNee and Pelletier, 1991). The low ambient oxygen content of natural waters is believed to inhibit the release of metals from the sulfide phase. Mine tailings which have been rapidly deposited in water apparently develop an anoxic sediment column from very near the sediment surface to the depths of the sediment column. A reduced, anoxic environment will prevent the release of metals from the sulfide phase. In one case, an oxic, Fe- and Mn- oxyhydroxide-bearing surface layer appeared to act as a scavenging barrier to the upward diffusion of dissolved metals (Pedersen, Mueller, McNee and Pelletier, 1991).

Considering the current trophic status of Lake Coeur d'Alene, a reduced sulfidic layer is unlikely to develop in the near future. Also, the extremely fine-grained nature of the tailings and the relatively slow transport of metals into the lake have already transformed many of the heavy metals into the oxide phase. Given the low concentration of sulfate in the water column (USGS data, Harenberg, *et al.*, 1991), reduced conditions cause liberation of metals from the oxide phase without the subsequent precipitation as the sulfide phase. Such extremely reduced conditions could enhance metal mobility, but seem unlikely to occur in Lake Coeur d'Alene.

4.3.3 Eutrophication and pH

As discussed in section 3.3.3, biological respiration in the hypolimnion produces CO_2 which leads to a decrease in pH. Although the pH of the lake will probably continue to be buffered by biological processes and by the abiological dissolution of solid calcium carbonate, small decreases in pH can be expected. The slight increase in acidity may be sufficient to liberate Zn, Cu and possibly Cd.

4.4 Selected Case Studies

The water chemistry, biological communities, sediment chemistry, and aquifer permeability make for a unique and complex situation in Lake Coeur d'Alene and the adjacent aquifer. However, Lake Coeur d'Alene in not entirely unique. Heavy metal contamination in glacial sediments and metals cycling in lakes have been observed elsewhere. The following case studies are useful for comparing and predicting conditions in the Coeur d'Alene area.

4.4.1 Glatt River, Zürich, Switzerland

A study area which best resembles the Lake Coeur d'Alene/Rathdrum aquifer recharge system has been the subject of research by scientists in Zürich, Switzerland for several years. The transport of heavy metals from the River Glatt into the adjacent glaciofluvial aquifer has been analyzed in relation to temperature, pH, redox conditions and spatial and temporal trends. The lithology of the unconsolidated aquifer is somewhat similar to that of the Rathdrum Prairie Aquifer: "stones, gravel, sand, silt and clays, and the minerals quartz (30-50%), calcite and dolomite (40-50%), and aluminosilicates (mainly illites, chlorites and feldspars)" (von Gunten, *et al.*, 1988, p.2). The river water which recharges the aquifer may be polluted by heavy metals. As in Lake Coeur d'Alene, redox conditions in the River Glatt are not low enough to liberate ferrous Fe, but Mn peaks have been observed. Photosynthesis and respiration contribute to cyclic pH variations in river water. Diurnal variations in pH were almost completely attenuated within 2.5 meters (8 ft) into the aquifer. Zinc concentrations in groundwater appear to reflect those in river water. Copper and Pb are higher in groundwater during the summer months, probably due to degradation of aquatic biota which contain these trace metals. The concentrations of metals in groundwater were below drinking water limits (von Gunten, *et al.*, 1989). Pronounced Mn^{2+} peaks were observed in groundwater during the summer months, but the dissolved Mn^{2+} concentrations decreased considerably within 7-10 meters (20 to 30 ft) from the river.

These data indicate that, although some metals are carried from the River Glatt into the adjacent aquifer, the metals are attenuated within about 10 meters (35 ft). This situation may not be completely analogous to Lake Coeur d'Alene, however, because of aquifer differences. The glacial outwash of the Rathdrum Prairie Aquifer has been sorted and reworked by the Missoula Floods. As a result, the aquifer has high permeabilities and may require longer distances to attenuate metals.

4.4.2 Ion Cycling in a Seasonally Anoxic Lake

The effects of eutrophication on metals have also been researched. Anderson (1989) studied As, Fe and Mn cycling in the Davis Creek Reservoir, a seasonally anoxic lake in California. The thermocline and oxygen-depleted hypolimnion were well developed by midsummer (July, 1988) and the hypolimnion was completely anoxic in the fall (October, 1988). Anoxia was maintained until the winter turn over, just before December.

Anderson determined that total As increased from July to December and decreased after winter mixing of the entire water column. Arsenate was the dominant species throughout water column prior to the development of thermal layering. As seasonal isolation of the hypolimnion continued into fall anoxia, arsenate in the anoxic layer was reduced to arsenite. Arsenite was also found in epilimnion where it existed at higher concentrations than would be predicted in oxygenated waters from inorganic thermodynamic calculations.

During summer stratification, Fe concentrations were elevated only in the deepest, most anoxic water close to the sediment/water interface. Iron remained in solution at concentrations supersaturated with respect to amorphous iron hydroxide. This suggested a potential for organic ligand complexation of Fe which maintained the solution concentrations.

Manganese cycling was also observed. The hypolimnion was enriched in dissolved Manganese during summer anoxia. With the turnover of the reservoir in the winter, dissolved Mn^{2+} was oxidized and removed with a half life of about 28 days. Reduction of Mn occurred at a higher p*e* than for Fe, and the $Mn^{2+} \rightarrow Mn^{4+}$ oxidation reaction was sluggish oxidation. Anderson determined that equilibrium calculations of Mn and Fe behavior did not adequately describe their behavior in this real system.

5.0 METALS IN THE LAKE/AQUIFER INTERFACE ZONE

5.1 Heavy Metals in Lake Coeur d'Alene

Heavy metals exist in the water column, sediment, and sediment pore water of Lake Coeur d'Alene. The concentrations and distribution of metals in sediments have been discussed in section 4.1.2. Metals in the water column and pore water are discussed below.

5.1.1 Metals in the Water Column

The Coeur d'Alene River is probably still a source for dissolved metals input to Lake Coeur d'Alene. Hornig, Terpening and Bogue (1988) found that although water quality has improved considerably since the 1970's, concentrations of Cd and Zn in water of the South Fork of the Coeur d'Alene River still occur at concentrations which do not meet criteria levels.

More recently, investigations by the U.S. Geological Survey (Harenberg, *et al.*, 1991) revealed that heavy metal concentrations in Lake Coeur d'Alene are generally low. Appendix V gives some of the water quality sampling results, from the summer of 1991, at the following selected locations: Lake Chatcolet; northeast of Blue Point, near Harrison; 1.7 miles northeast of University Point, near Harrison; 0.8 miles southwest of Driftwood Point; Wolf Lodge Bay; and 1.3 miles southeast of Tubbs Hill. Samples were collected from various depths. Arsenic concentrations were consistently less than or equal to 1.0 μg/l. Cadmium concentrations in the water column ranged from <1 to 2 μg/l; Cu from 1 to 15 μg/l; Pb from 2 to 41 μg/l; Hg from <0.1 to 1.8 μg/l. Zinc concentrations ranged from <10 to 390 μg/l. Metal concentrations were generally greater with increasing depth.

5.1.2 Metals in Sediment Pore Water

The results of a USGS study of metal concentrations, phases associations and pH of sediment pore water are forthcoming. Preliminary results indicate that the concentrations of metals are extremely high (Cu as much as 2,000 μg/l) in the reduced zone of the sediment column, and pH values are lower than expected (Woods, 1993, personal communication.)

Several characteristic profiles for reducing conditions and for concentrations of metals in the sediment column and pore water are given in Figure 47. Lake sediments are commonly enriched in Fe and Mn at the anoxic/oxic boundary, and metals concentrations are highest in the pore waters in the anoxic zone and in the solid phase in the oxic zone. The location of the boundary between oxidized and reduced sediments is in part a function of the trophic status of the lake (Figure 48). Lake Coeur d'Alene presently resembles Profile A, which is characteristic of the sediments in oligotrophic to mesotrophic lakes. The upper 10 to 15 cm (4-6 in) of bottom sediments in Lake Coeur d'Alene are oxygenated, with anoxic (reducing) conditions lower in the sediment column (Horowitz, Cook and Elrick, 1992). Under such conditions, Mn is expected to be enriched at the anoxic/oxic boundary because Mn diffuses upward

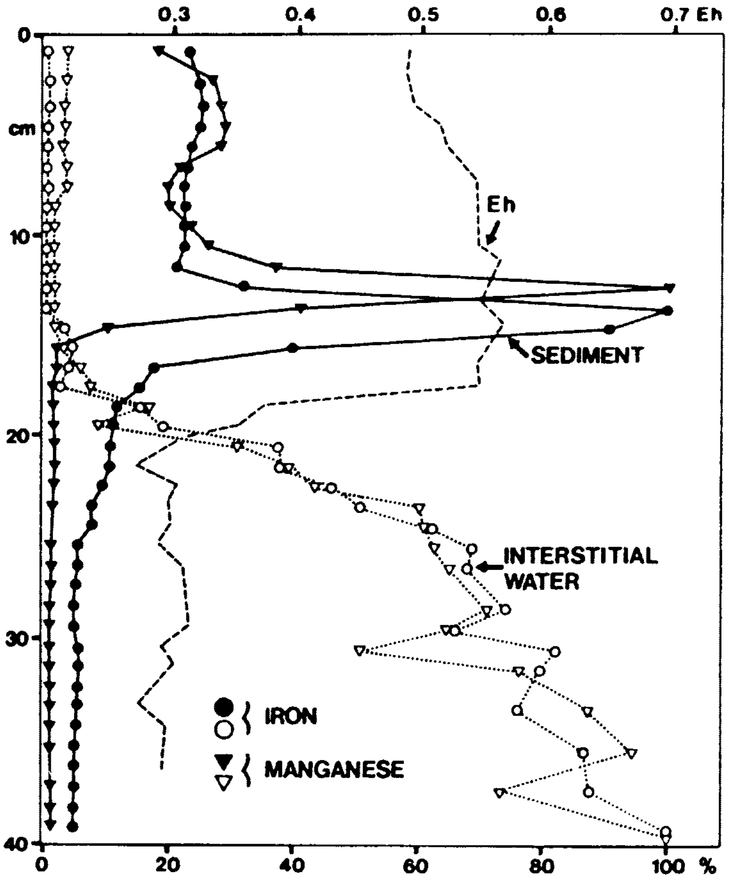


Figure 47. Redistribution of iron and manganese in recent sediments from the Feldsee (West Germany) as functions of Eh and depth (Tessenow and Baynes, 1975).

from the reducing zone and reprecipitates at the anoxic/oxic boundary in the sediment column (Presley and Tefry, 1980).

The zone of Mn (and Fe and phosphorous) enrichment tends to migrate upward as sediments accumulate, because the oxic/anoxic boundary often remains within 10 - 15 cm (4-6 in) of the sediment/water interface. Manganese can also move upward into the oxic layer, because the kinetics of the reprecipitation (oxidation) reaction are slow (Salomons and Forstner, 1984). Eventually, though, Mn does reprecipitate and the result is a band of sediments which are highly enriched in metals.

This situation has been described for sediments in the North Sea, where the concentrations of phosphorous, Fe and Mn were 1,720, 25,900 and 1,230 ppm, respectively, in the oxidized surface layer and 660, 21,120 and 580 ppm in the reduced layer (Salomons and Gerritse, 1981). The adsorption of upwardly migrating trace metals onto the Fe/Mn layer was predicted, indicating that such a layer "may act as a chemical barrier against the upward flow of some trace metals and phosphorous to surface waters" (Salomons and Forstner, 1984, p. 98).

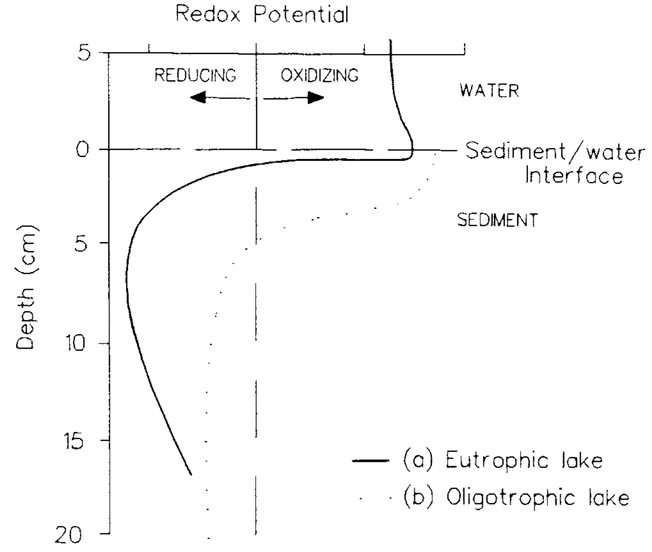


Figure 48. The vertical distribution of oxidized and reduced conditions in lake sediments is determined in part by the trophic status of the lake.

5.1.3 Metals in the Lower Hypolimnion

The effect of an anoxic hypolimnion must also be considered, because of the potential for advanced eutrophication in Lake Coeur d'Alene. Initially, eutrophication may cause temporary reduction of the hypolimnion. Oxygenated conditions can exist in the sediments even when the overlying water is anoxic, because the diffusion of oxygen from sediments is slow. The rate of oxygen diffusion and the thickness of the oxygenated layer depend on grain size, conditions during deposition, amount of organic carbon in the sediments and other factors. Again, the concentrations of metals in pore water will be low in the upper, oxygenated zone and higher in the anoxic, reduced sediment layers. Conversely, the concentration of metals in the solid phase is high in the oxygenated zone and low in the reduced zone (Figure 47). These conditions may cause the upward diffusion of metals in the sediment column, as described above. But if Mn passes through the oxygenated sediment layer and encounters reduced surface waters before the precipitation reaction occurs (the kinetics of the precipitation reaction are slow), Mn^{2+} will be released into the overlying water column. The metal would precipitate when oxygenated water are encountered.

A permanently reduced hypolimnion may develop in a highly eutrophic lake. Under such conditions, the oxygen will eventually completely diffuse out of the sediments, as in Profile B, Figure 48. Manganese cycling may be an ongoing process under these conditions. Section 3.3.2 discussed the processes of manganese-cycling and metals-scavenging in lakes.

5.2 Heavy Metals in Groundwater, Sampling Results

Monitoring wells were installed at the surface water/groundwater interface and were sampled as part of this project. The sampling results must be evaluated in light of current drinking water standards, other ongoing monitoring, and sampling procedures and conditions.

5.2.1 Maximum Contaminant Levels

Groundwater which is used for drinking water is subject to the standards established by law. The Clean Water Act (1977) includes thirteen metals on the list of priority toxic pollutants. Standards and guidelines for the metals in drinking water have been set by the U.S. Environmental Protection Agency (EPA) and by the State of Idaho. The Federal Drinking Water Standards and recommended concentration limits for metals are given in Table 7. The drinking water standards for metals issued by the State of Idaho, as of 1987, are equivalent to federal Maximum Contaminant Levels (MCLs).

5.2.2 Groundwater Monitoring on the Rathdrum Prairie

Twenty seven wells are currently monitored on the Rathdrum Prairie by the Panhandle Health District (Painter, 1991[a]). Operators of public water supply (PWS) systems (those serving greater than 25 residents or five households for more than six weeks per year) are required by the Health District to monitor for nitrates, phosphate, coliform bacteria and other contaminants on a quarterly basis. Groundwater from PWS wells must be monitored for heavy metals at least every five years. Painter (1991[a], p.16) reports that "past analyses for heavy metals have shown that these constituents are not likely to be significant contaminants in the aquifer unless releases are made from an industrial point source into the aquifer."

The U.S. Geological Survey currently maintains a statewide groundwater monitoring network. Water level elevations in seven wells in glaciofluvial gravels in Bonner and Kootenai Counties were measured by the USGS in 1990-91. One well in Kootenai County in 1991 was monitored for heavy metals and other contaminants. The well did not exceed MCLs for metals.

Many businesses and individuals monitor their groundwater on a private basis. Private organizations and individuals may bring samples of their well water or tap water to be tested by the Panhandle Health District for a fee.

5.2.3 Metal Concentrations in Shallow Monitoring Wells

Groundwater samples were collected from monitoring well AIP-2 (Figure 49) as part of this study. Data from three private monitoring wells in the surface water/groundwater interface were also made available for this project. The Hagadone Hospitality Corporation periodically monitors the quality of groundwater in three wells on a private golf course on a voluntary basis (Figure 50). Only five

Substance	MCL mg/ℓ	MCLG mg/ℓ	SMCL mg/ℓ	NRC mg/ℓ	PPCL mg/ℓ
Antimony	---	---	---	---	0.145
Arsenic	0.05	0.05	---	<0.05	0.050
Cadmium	0.010	0.005	---	<0.01	0.010
Chromium	0.05	---	0.12	<0.05	---
Copper	---	---	1.3	1.0	1.0
Lead	0.015	0.02	---	<0.05	0.155, 0.05
Mercury	0.002	0.003	---	---	0.010, 0.002
Nickel	---	---	---	<0.05	0.750
Selenium	0.01	0.045	---	---	0.350, 0.010
Silver	0.05	---	---	---	0.050
Zinc	---	---	5	5	7.500
Iron	---	---	0.3	---	---
Manganese	---	---	0.05	---	---
pH	---	---	6.5-8.5	---	---

Maximum Contaminant Levels (MCLs) are primary drinking water standards which are enforceable and are based on human health considerations, available treatment technologies and cost (40 CFR 141.11 Subpart B, July 1, 1992). **Maximum Contaminant Level Goals (MCLGs)** are non-enforceable health goals that are set at levels which would result in no known or anticipated adverse health effects with an adequate margin of safety (50 FR 46936 - 47002; Nov. 13, 1985). **Secondary Maximum Contaminant Levels (SMCLs)** primarily affect the aesthetic qualities of drinking water, are not federally enforceable but are intended as guidelines for the states (40 CFR 143.3). The **Preliminary Protective Concentration Limits (PPCLs)** are suggested exposure limits at the point of consumption. These values are based on exposure of a 70 kg adult consuming 2 liters of water per day. The PPCLs may be lower or higher than MCLs based on Unit Cancer Index or Average Daily Intake. The standards published by the **National Research Council** in 1977 were endorsed by the National Academy of Sciences, as published in Drinking Water and Health.

Table 7. Federal drinking water standards and recommended concentration limits for metals (from Shields, 1989; Ewers, 1991; US CFR, 1992).

monitoring wells are installed in surface water-groundwater interface zone at the margin of Lake Coeur d'Alene, according to well logs at the Idaho Department of Water Resources. Data from four of these wells, collected in 1989, 1992 and 1993, are presented in Table 8.

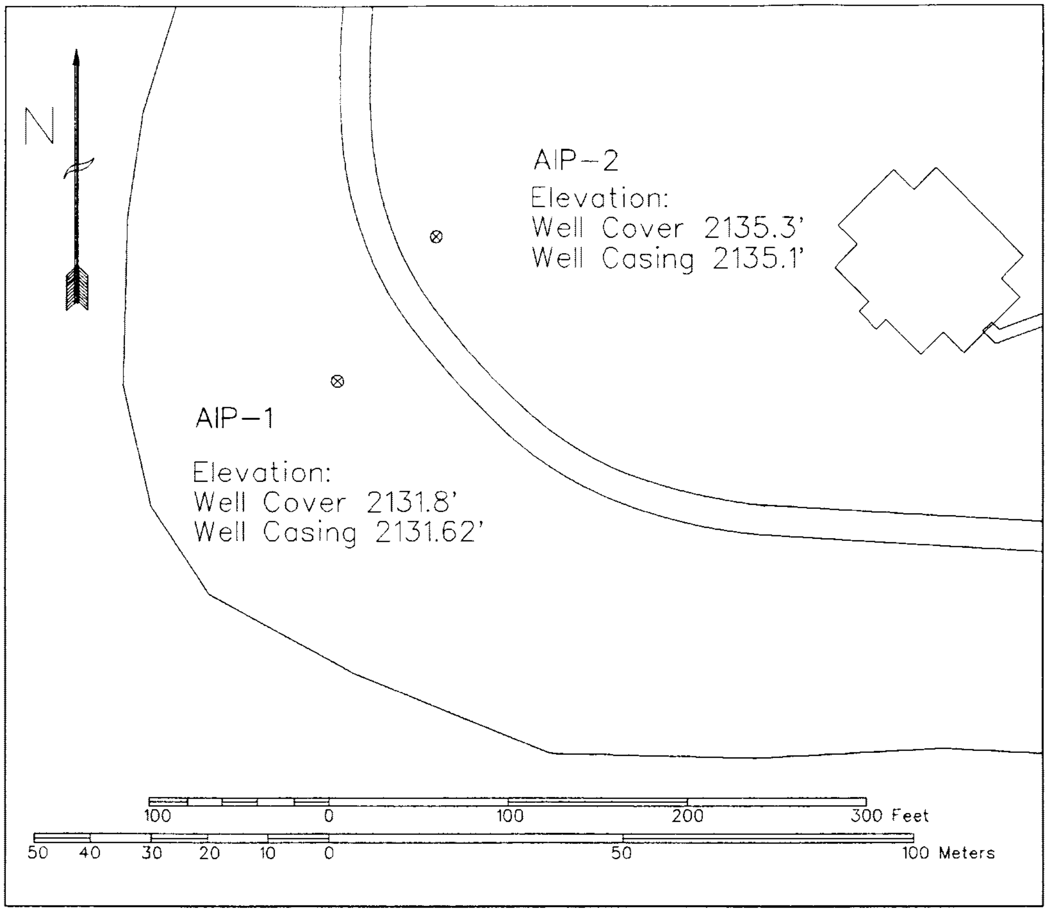


Figure 49. Detailed location map of monitoring wells AIP-1 and AIP-2.

The analyses confirm that metal concentrations in groundwater are generally low, although some elevated concentrations were detected. Concentrations of Fe and Mn exceeded EPA Secondary Maximum Contaminant Levels (SMCLs) in all four wells on the 1989 and 1992 sampling dates. Three wells, P-1, P-2, and P-3, exceeded EPA MCLs for selenium. Well AIP-2 exceeded the EPA MCLs for As, Cd and Pb in December of 1992.

A water sample collected from well AIP-2 in January of 1992 does not show the same elevated levels of metals. Rather, the concentrations of metals are extremely low. The low concentrations are probably a result of oxygenated conditions and the long residence time of water in the well. Customarily, a minimum of three well volumes of water must be purged from a well before a sample is collected, to provide a representative sample of the aquifer. However, the water level in the well was extremely low in January of 1993 because of the drawdown of Lake Coeur d'Alene. The well was purged of water (several quarts) and groundwater slowly moved into the well from the surrounding aquifer. The well yielded just enough water to be filtered for a 10 ml laboratory sample. Admittedly, the poor sampling conditions significantly affected the sampling results. The water had probably been in

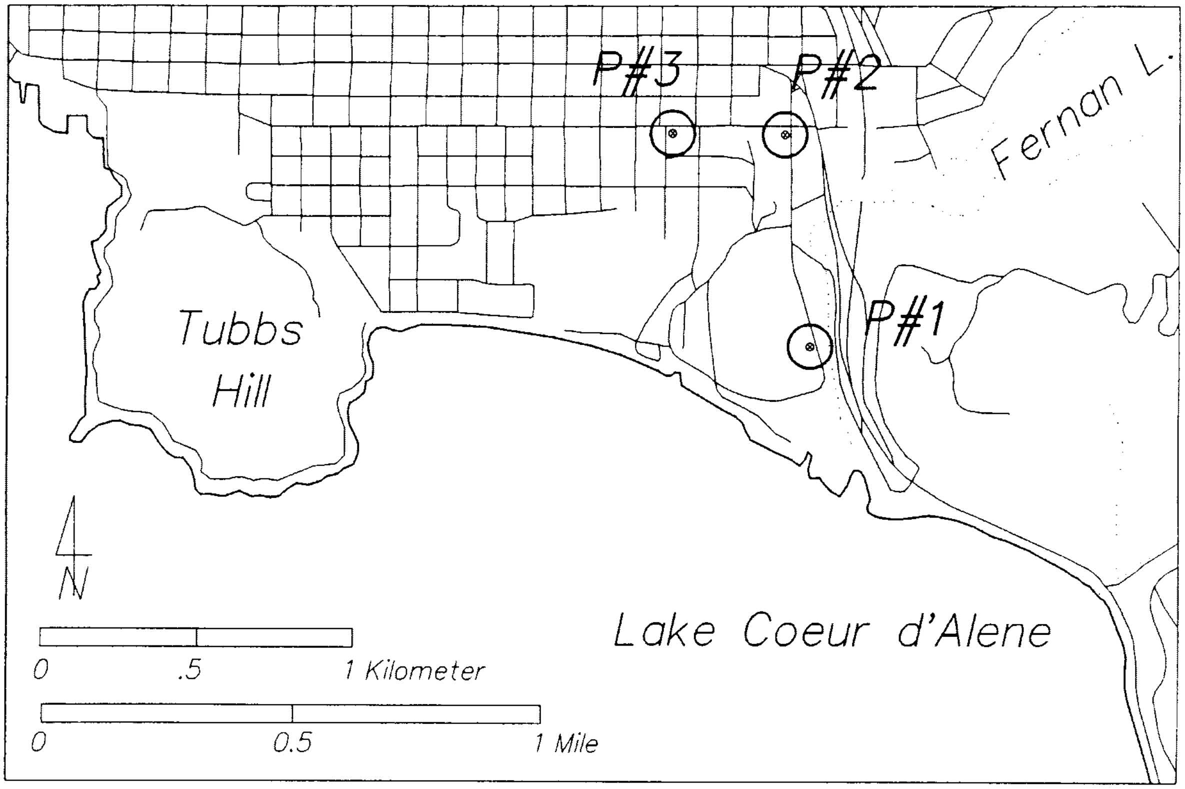


Figure 50. Location of monitoring wells P1, P2, and P3.

contact with the aquifer for an extended period of time. The long residence time, plus the obviously oxygenated conditions at the top of the water table, probably facilitated the precipitation of metals from solution.

It should also be noted that this portion of the study area is not an immediate source of drinking water. Most drinking water is extracted from deeper wells, distant from the surface water/groundwater interface. Public Water Supply (PWS) wells are monitored for heavy metals at least every five years, and no elevated heavy metal concentrations have been reported in public drinking water supplies.

Clay and silt were collected from the filtrate of well AIP-2 in December, 1992. If the adsorptive process dominates the fate of heavy metals which enter the aquifer, the clays should show an enrichment in metals. Table 9 lists the concentrations of metals in the clay/silt samples, compared to background levels for soils (from Bowen [1979] and Merian [1991]). The clay/silt samples from the well are somewhat enriched in As, Co and Cu, but only slightly above average background concentrations in Fe, Mn, Zn, U, and Th. Concentrations in clays are slightly below average background concentrations for Pb, Ni, Sr, V, and Cr. Adsorption onto clays does not appear to have removed metals from the groundwater in that small portion of the recharge zone at that time.

Well	P-1	P-2	P-3	AIP-2	AIP-2	Detection Limit (AIP-2)
Date	12/89	12/89	12/89	12/92	1/93	
Ag (mg/l)	0.010	0.010	0.010	0.01	<0.001	0.001
As (mg/l)	0.040	0.040	0.040	0.10	<0.010	0.01
Cd (mg/l)	0.004	0.004	0.004	0.03	<0.001	0.001
Cr (mg/l)	0.010	0.010	0.010	0.02	<0.002	0.002
Cu (mg/l)	0.015	0.020	0.015	0.07	0.040	0.001
Hg (mg/l)	0.00015	0.00015	0.00015	---	---	---
Ni (mg/l)	---	---	---	0.01	0.006	0.001
Pb (mg/l)	0.030	0.030	0.040	0.10	<.010	0.01
Se (mg/l)	0.050	0.050	0.050	---	---	---
Zn (mg/l)	0.030	0.090	0.050	0.34	<0.001	0.001
Fe (mg/l)	2.770	2.224	14.910	0.4	0.384	0.01
Mn (mg/l)	0.111	0.256	0.753	0.13	0.018	0.01

Notes: Detection limits are given for AIP-2 analyses, but not for Potlatch wells.
--- = Not analyzed.

Table 8. Results of groundwater monitoring in the surface water/groundwater interface.

Element	Background in Soils (from Bowen, 1979 Meriam, 1991)	AIP-2 Clays	Detection Limit
Ag (ppm)		0.1	0.002
As (ppm)	6-7	37.0	0.1
Cd (ppm)		0.4	0.02
Co (ppm)	8	19.0	1.0
Cr (ppm)	70	50.0	1.0
Cu (ppm)	30	71.0	0.02
Ni (ppm)	50	37.0	1.0
Pb (ppm)	35	32.0	0.02
Zn (ppm)	90	128.0	0.1
Fe (ppm)	40000	4.58%	0.01%
Mn (ppm)	1000	1534	1.0

Table 9. Concentration of metals in clay filtrate from well AIP-2.

6.0 CONCLUSIONS

6.1 Hydrogeologic Interpretation

The morphology of the Rathdrum Prairie aquifer is determined by structural controls, such as the Purcell Trench, and ancestral stream drainage patterns. The aquifer is bounded by lacustrine silts and clays of the Latah Formation below and by crystalline basement rocks and basalt along its margins. The aquifer matrix consists of poorly- to moderately-well-sorted glacio-fluvial deposits of Pleistocene age. The deposits were reworked by multiple catastrophic floods, which resulted in extremely high hydraulic conductivities throughout the Rathdrum Prairie Aquifer. The glacial outwash sediments are exceptionally rich in silt and clay in the vicinity of the Lake Coeur d'Alene/Spokane River recharge area. The movement of fine sediments into the coarser aquifer matrix has contributed to the low hydraulic conductivity in this area, relative to the rest of the aquifer. These fine-grained stream sediments form a hydrogeologic barrier or seal which helps to maintain a water level in excess of 2127 feet (648 m) above sea level in Lake Coeur d'Alene.

The Rathdrum Prairie aquifer receives over thirty percent of its recharge from the Coeur d'Alene area, based on calculations by previous authors. Estimates for recharge to the aquifer from Lake Coeur d'Alene and Spokane River above Post Falls range from 225-300 cfs. Most of this water comes from Lake Coeur d'Alene as underflow to the aquifer. The hydraulic gradient is extremely high adjacent to Lake Coeur d'Alene, where the Pleistocene age deposits in the ancestral, v-shaped valley reach 310-340 feet (94-104 m) in thickness.

The Spokane River is the only surface outlet of Lake Coeur d'Alene. The Coeur d'Alene and St. Joe rivers supply almost 94% of the surface water inflow to the lake. The Coeur d'Alene River is a nonpoint source of metals loading to the lake. The St. Joe and other minor streams are sources of nutrient loading.

The upper two cm (0.8 in) of lake bottom sediments are highly enriched in Sb, As, Cd, Cu, Pb, Hg, Ag, and Zn. The thickness of **metal-enriched** sediments ranges from 0 in sheltered bays and the southernmost reaches of the lake to several feet in the delta of the Coeur d'Alene river.

Lake Coeur d'Alene is dimictic: it undergoes two periods of thermal stratification and both a spring and fall overturn. The seasonal stratification is accompanied by vertical gradients in dissolved oxygen, decreased transparency during summer months and variations in nitrogen concentrations due to biological productivity. The northern portion of the lake appears to be oligotrophic; some of the middle and southern regions tend toward mesotrophy and eutrophy. The lake bottom sediments contain an oxic zone which is approximately 10-15 cm (4-6 in) thick, which equates to an oligotrophic to mesotrophic stage in lake evolution. With continued nutrient loading, biological productivity in the epilimnion and biological consumption/respiration in the hypolimnion are expected to contribute to a depletion of dissolved oxygen with depth in the water column. Dissolved oxygen levels as low as 52% at depth have been recorded northeast of Blue Point. Lake Chatcolet, at the southern tip of Lake Coeur d'Alene, has experienced 'complete' oxygen depletion as measured by a standard DO meter. In the event of prolonged oxygen depletion in hypolimnion, the mud surface may become reduced and may release nutrients and other ions back into the water body.

6.2 Hydrochemical Interpretation

The water in Lake Coeur d'Alene and the southeastern Rathdrum Prairie Aquifer is of the calcium carbonate type. The abundance of carbonate minerals in the lake bottom sediments and in the aquifer matrix is expected to contribute to the maintenance of neutral pH in both surface water and groundwater. The pH in the water column of Lake Coeur d'Alene is likely to be high in the epilimnion, particularly during the summer months. The lower portion of the water column is likely to see moderate pH levels (on the order of 6-8) because of acidification from biological respiration and the buffering effect of carbonate species in the system. In the pore water and in the sediments, pH buffering will also tend to stabilize the concentration of the hydronium ion, so that highly acidic conditions are unlikely in Lake Coeur d'Alene.

The redox potential (p*e*) is likely to be highly negative in the epilimnion, where dissolved oxygen will be at or above saturation levels during the productive summer months. Dissolved oxygen will decrease and p*e* will increase in the hypolimnion, as thermal stratification progresses. Oxidizing conditions currently prevail in the upper 4-6 in (10-15 cm) of the lake bottom sediments. Presumably reducing conditions and then neutral conditions will be present deeper in the sediment column. A speciation model of water samples collected from Lake Coeur d'Alene in August, 1991, reflected oxidizing conditions in the water column.

Under prolonged reducing conditions in the hypolimnion, Fe^{3+} and Mn^{4+} will be reduced to Fe^{2+} and Mn^{2+} in the hypolimnion (or may even diffuse upward some distance from the reduced zone of the sediment column through an oxidized water column, due to reaction kinetics). Eventually these mobile species could migrate upward in the water column until they reach the anoxic/oxic boundary. Upon contact with oxygenated waters, Fe and Mn will reprecipitate as oxides (or oxyhydroxides), which scavenge dissolved trace metals from the water column as they settle. This process is likely to maintain relatively low levels of trace metals in the water column. Zinc, Cu, and Cd may be less likely to be scavenged from the water column by oxide/hydroxide coprecipitation, but may be cycled to the bottom sediments will settling biological particles.

6.3 Sampling Results

Despite the low levels of heavy metals which are predicted and which currently exist in the water column, four shallow monitoring wells in the surface water/groundwater interface zone exceeded

EPA Secondary Maximum Contaminant Levels (SMCLs) for Fe and Mn in 1989 and 1992. Three wells exceeded EPA MCLs for selenium in 1989. Well AIP-2 exceeded EPA MCLs for As, Cd, and Pb in December, 1992. The elevated metals concentrations in groundwater may be due, in part, to the migration of particulate matter into the aquifer. The samples from well AIP-2 were filtered through a 0.45 μm filter, indicating that the metals in groundwater were either in an extremely small particulate or colloidal phase or were in solution.

The clay fraction of aquifer material does not appear to be attenuating the migration of metals by ionic adsorption. Laboratory analysis of clays from well AIP-2 indicates that the fine-grained aquifer material is enriched in As, Co and Cu, but only slightly above average background concentrations in Fe, Mn, Zn, U, and Th. Concentrations in clays are slightly below average background concentrations for Pb, Ni, Sr, V, and Cr. Precipitation/coprecipitation reactions are expected to attenuate the migration of metals within tens of meters (30+ feet) of infiltration into the aquifer, based on a case study from near Zürich, Switzerland, where elevated concentrations of manganese and other trace metals were attenuated within 10 meters (30 ft). In the Coeur d'Alene area, however, well AIP-2 is 63 feet (21 m) from the lake and contained elevated Fe, Mn, As, Cd, and Pb. Additional monitoring wells are needed to determine whether natural attenuation is actually occurring.

Most drinking water is extracted from deeper wells, distant from the surface water/groundwater interface. It appears unlikely that municipal or private water supply wells will experience elevated metals concentrations due to the migration of metals from Lake Coeur d'Alene. Zinc may be an exception, due to its mobility in solution within pH 0-7.3. Zinc levels are not expected to exceed federal Maximum Contaminant Levels in public water supply wells. Wells northeast of the city of Coeur d'Alene have reportedly exceeded secondary drinking water standards for Mn and Fe. These wells are far distant from the Lake Coeur d'Alene recharge zone. Dissolution of the aquifer matrix material could be the source of that Mn and Fe, but the subject requires more study. The monitoring wells at the surface water-ground water interface are likely to contain seasonally elevated metals concentrations.

6.4 Recommendations for Further Study

A more complete understanding of the chemical and physical transport processes occurring in this critical aquifer recharge zone may be necessary, in the event that the water quality of Lake Coeur d'Alene is seriously degraded. The following tasks are recommended to achieve the necessary level of understanding:

1. Expand the network of monitoring wells in the surface water-groundwater interface zone, in order to characterize the spatial variability in groundwater quality.

2. Continue to monitor the existing shallow wells on North Idaho College campus. Such analyses should be conducted at regular intervals to determine the temporal variability in groundwater quality and to determine the effects of seasonal changes in lake water quality on the adjacent aquifer.

3. Consistently monitor the pH in wells adjacent to the aquifer, because pH controls the adsorption, precipitation and coprecipitation of trace metals. Seasonal changes in pH should be identified.
4. Determine the redox conditions within the aquifer, either by measuring DO directly (which is difficult to do) or by monitoring pH and temperature and collecting water samples for laboratory analysis. The redox conditions should be calculated from various redox couples, in order to learn more about reaction kinetics within the aquifer. Again, seasonal/temporal variations in redox may be important in light of surface water conditions.
5. Construct a small scale numerical model of the recharge zone, utilizing the conceptual hydrogeologic model presented in this report. Determine whether the published estimates of recharge, groundwater velocity and transmissivity are valid.
6. Continue to monitor lake water quality. Attempt to incorporate physical chemistry and trace metal interactions into the eutrophication model which is currently under construction.

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APPENDIX I

Results of the Grain Size Analysis of Sediments in the Interface Zone, Borehole B

Sample #	Depth Interval (cm)		$\phi5$	$\phi16$	$\phi50$	$\phi84$	$\phi95$	D90	Median ϕ	Mean ϕ	Mean (mm)	Skew (1)	Sorting (2)	Avg. Depth (cm)
1	0	11	-2.85	-1.75	-0.28	1.00	3.20	2.00	-0.28	-0.34	1.27	0.041	1.27	5.5
2	11	19	-3.27	-2.10	-0.57	0.70	2.35	1.10	-0.57	-0.66	1.58	-0.027	1.58	15.0
3	19	29	-3.15	-2.00	-0.57	0.50	1.47	0.84	-0.57	-0.69	1.61	-0.130	1.61	24.0
4	29	40	-3.38	-2.25	-0.77	0.99	1.46	0.83	-0.77	-0.68	1.60	0.004	1.60	34.5
5	40	48	-3.90	-3.12	-1.13	0.42	1.16	0.74	-1.13	-1.28	2.42	-0.110	2.42	44.0
6	48	54	-4.05	-3.40	-1.09	0.67	1.74	0.93	-1.09	-1.27	2.42	-0.079	2.42	51.0
7	54	60	-7.20	-1.20	-1.61	0.18	0.44	0.44	-1.61	-0.88	1.84	0.565	1.84	57.0
8	60	69	-8.35	-1.80	-1.56	0.56	1.70	0.99	-1.56	-0.93	1.91	0.222	1.91	64.5
9	69	73	-8.92	-5.60	-2.25	0.44	1.64	0.69	-2.25	-2.47	5.54	-0.186	5.54	71.0
10	73	79	-9.52	-5.67	-1.85	0.56	1.80	0.82	-1.85	-2.32	4.99	-0.291	4.99	76.0
11	79	84	-10.2	-6.45	-2.72	0.52	1.74	0.78	-2.72	-2.88	7.38	-0.162	7.38	81.5
12	84	88	-9.91	-6.12	-2.41	0.49	1.74	0.72	-2.41	-2.68	6.41	-0.205	6.41	86.0
13	88	94	-9.47	-5.76	-2.00	0.67	1.72	0.89	-2.00	-2.36	5.15	-0.252	5.15	91.0
14	94	99	-11.0	-6.98	-1.80	0.72	1.81	0.97	-1.80	-2.69	6.44	-0.391	6.44	96.5
15	99	105	-6.35	-3.77	-1.01	0.65	1.76	0.83	-1.01	-1.38	2.60	-0.283	2.60	102.0
16	105	114	-9.15	-5.43	-1.70	0.47	1.20	0.54	-1.70	-2.22	4.66	-0.352	4.66	109.5
17	114	123	-7.50	-4.60	-1.40	0.37	1.38	0.65	-1.40	-1.88	3.67	-0.331	3.67	118.5
18	123	131	-3.73	-2.50	-0.91	0.69	2.00	1.10	-0.91	-0.91	1.87	0.009	1.87	127.0
19	131	140	-8.00	-4.92	-1.47	0.69	1.93	1.10	-1.47	-1.90	3.73	-0.273	3.73	135.5
20	140	148	-6.25	-3.98	-1.10	0.57	1.69	0.90	-1.10	-1.50	2.83	-0.282	2.83	144.0
21	148	155	-8.90	-5.75	-1.65	0.69	1.70	1.10	-1.65	-2.24	4.71	-0.321	4.71	151.5
22	155	161	-9.40	-6.23	-2.11	0.48	1.51	0.88	-2.11	-2.62	6.15	-0.282	6.15	158.0
23	161	173	-8.90	-5.75	-1.71	0.62	1.78	1.10	-1.71	-2.28	4.86	-0.308	4.86	167.0
24	173	181	-8.65	-5.37	-1.32	0.40	1.78	0.80	-1.32	-2.10	4.28	-0.405	4.28	177.0
25	181	191	-5.06	-3.35	-1.48	0.81	2.61	1.20	-1.48	-1.34	2.53	0.084	2.53	186.0
26	191	197	-4.95	-3.30	-1.37	0.52	1.69	0.75	-1.37	-1.38	2.61	-0.044	2.61	194.0
27	197	200	-7.52	-4.60	-1.75	0.74	2.22	1.00	-1.75	-1.87	3.66	-0.126	3.66	198.5
28	200	210	-5.65	-2.95	-0.84	0.59	1.98	0.81	-0.84	-1.07	2.09	-0.226	2.09	205.0
29	210	220	-4.40	-1.93	-0.17	0.48	0.93	0.60	-0.17	-0.54	1.45	-0.524	1.45	215.0
30	220	235	-3.30	-1.82	-0.49	0.36	0.97	0.63	-0.49	-0.65	1.57	-0.268	1.57	227.5
31	235	246	-5.35	-2.68	-0.70	0.41	1.59	0.70	-0.70	-0.99	1.99	-0.311	1.99	240.5
32	246	258	-2.50	-1.50	-0.49	0.36	0.93	0.60	-0.49	-0.54	1.46	-0.129	1.46	252.0
33	258	262	-2.76	-1.54	-0.52	0.50	1.42	0.68	-0.52	-0.52	1.43	-0.036	1.43	260.0
34	262	275	-3.27	-1.70	-0.50	0.45	1.42	0.62	-0.50	-0.58	1.50	-0.149	1.50	268.5

Sample #	Depth Interval (cm)		$\phi 5$	$\phi 16$	$\phi 50$	$\phi 84$	$\phi 95$	D90	Median ϕ	Mean ϕ	Mean (mm)	Skew (1)	Sorting (2)	Avg. Depth (cm)
35	275	281	-3.58	-2.21	-0.80	0.04	1.00	0.51	-0.80	-0.99	1.99	-0.235	1.99	278.0
36	281	288	-4.52	-2.80	-0.94	0.40	1.34	0.62	-0.94	-1.11	2.16	-0.192	2.16	284.5
37	288	293	-5.25	-2.95	-0.98	0.15	1.10	0.50	-0.98	-1.26	2.39	-0.308	2.39	290.5
38	293	300	-7.25	-4.25	-1.24	0.20	1.55	0.60	-1.24	-1.76	3.39	-0.359	3.39	296.5
39	300	305	-7.60	-4.12	-0.83	0.25	1.80	0.70	-0.83	-1.57	2.96	-0.473	2.96	302.5
40	305	310	-8.75	-5.07	-1.35	0.35	2.40	0.94	-1.35	-2.02	4.07	-0.350	4.07	307.5
41	310	312	-3.05	-1.40	-0.49	0.38	1.07	0.57	-0.49	-0.50	1.42	-0.133	1.42	311.0
42	312	316	-5.03	-3.11	-1.08	1.39	3.94	2.24	-1.08	-0.93	1.91	0.109	1.91	314.0
43	316	324	-4.79	-2.86	-0.83	1.54	4.17	2.37	-0.83	-0.72	1.64	0.097	1.64	320.0
44	324	326	-6.17	-3.74	-1.34	0.73	3.16	1.10	-1.34	-1.45	2.73	-0.055	2.73	325.0
45	326	332	-8.86	-5.25	-1.67	1.04	3.91	1.84	-1.67	-1.96	3.89	-0.132	3.89	329.0
46	332	334	-7.74	-4.87	-2.02	0.31	2.48	0.60	-2.02	-2.19	4.57	-0.110	4.57	333.0
47	334	344	-5.10	-3.02	-0.98	0.69	3.61	0.95	-0.98	-1.10	2.15	-0.023	2.15	339.0
48	344	349	-4.55	-2.65	-0.85	0.85	4.16	1.34	-0.85	-0.88	1.84	0.061	1.84	346.5
49	349	352	-5.25	-3.16	-1.01	0.50	3.13	0.75	-1.0	-1.22	2.33	-0.093	2.33	350.5

(1) Key to Coefficient of Skew:

$>+0.30$ = strongly fine-skewed
+0.3 to +0.1 = fine-skewed
+0.10 to -0.10 = near- symmetrical
-0.10 to -0.30 = coarse-skewed
>-0.30 = strongly coarse-skewed

(2) Key to Coefficient of Sorting:

<0.35 = very well sorted
0.35-0.5 = well sorted
0.5-0.71 = moderately well sorted
0.71-1.0 = moderately sorted
1.0-2.0 = poorly sorted
>2.0 = very poorly sorted

APPENDIX II

Summary of Geologic Logs From Wells on the Southeastern Rathdrum Prairie.

TOWNSHIP	SECTION	1/4 SECT.	LITHOLOGY	DEPTH (ft)
T50N R4W	Sec 1	SW SW	?	0-216
			sand	216-226
			brown clay	226-244
			medium sand	244-309
		SW SW	pea gravel, sand	0-226
		?	gravel	0-241
T50N R4W	Sec 2	?	sand, gravel	0-18
			sand, gravel	18-51
		SE NW	sand, gravel	0-298
			fine sand, clay	298-300
T50N R4W	Sec 3	SE SE	fine sand	0-?
			gravel	?-191
			coarse gravel	191-193
			sand, gravel	193-200
			boulder	200-201
		SE NE	sand, gravel	0-10
			clay	10-20
			sand, gravel, clay	20-229
			basalt boulder or layer	229-237
		NW NW	gravel, sand	0-310
		?	sand, gravel	0-230
			sand, gravel, clay	230-310
		NW NW	sand, gravel	28-130
			sand, gravel, boulder	130-134
			sand, gravel, clay	134-154
			sand, gravel	154-230
			sand, gravel	230-310
		SE NW	sand, gravel	0-229
			basalt layer or boulder	229-237
		?1/4 NW	sand, gravel	0-164
			fine sand	164-171
			coarse sand, gravel	171-190
			rock	190-193
			fine sand	193-196
			gravel	193-232
			gravel, sand	232-272

TOWNSHIP	SECTION	1/4 SECT.	LITHOLOGY	DEPTH (ft)
T50N R4W	Sec 4	??	fill	254-259
			granite	259-320
T50N R4W	Sec 4	W SE	clay	0-32
			basalt	32-125
			clay	125-205
			basalt	205-250
		NW SW	sand, gravel	0-288
		NW SW	sand, gravel, silt	0-227
		SW SW	sand, gravel	0-98
			sand, clay	98-142
			gravel, clay	142-200
		NW NW	sand, silt gravel	0-352
		SW SE	pea gravel, coarse sand	0-243
		E NE NE	sand, gravel	0-315
			medium sand	315-340
			blue sandy clay	340-350
		SW SW	gravel	0-201
		NW SW	sand, gravel	0-227
		NW SE	brown clay	0-32
			basalt	32-125
			brown clay	125-205
			basalt	205-250
		NW SW	sand, gravel	0-288
		SW SW	sand & gravel, sand & clay, gravel, sand & clay, pea gravel, clay	0-200
		SW SE	gravel, silt, sand	0-243
		SE NE	large gravel, boulders, gravel, sand	0-105
T50N R4W	Sec 5	??	sand, clay lens, sand	0-162
		NW SW	sand, silt	0-190
		NW SW	coarse sand, gravel, cobbles	0-325
		NW SW	fine to coarse sand, wheat/pea gravel	0-350
		NW NW	repaired well "making lots of sand" 350' plugged, recompleted to 308'	

TOWNSHIP	SECTION	1/4 SECT.	LITHOLOGY	DEPTH (ft)
T50N R4W	Sec 5	SW	sand, gravel	0-190
			sand, gravel	90-180
			fine sand	180-204
		SW SW	small boulders at surface	0-?
			sand, gravel	-161
		NW SE	sand	0-226
		SW SE	gravel, sand	0-174
		SE NW	clay, basalt	57-121
			broken basalt	121-123
			clay, sand	123-150
		??	gravel, sand	0-200
		SE SE	coarse sand	0-130
			sand, clay	130-152
			gravel, sand	152-200
			coarse sand, clay	200-212
		NE SE	sand, gravel	0-183
		Post Falls	sand, gravel	0-275
			clay	275-279
T50N R4W	Sec 9	SW NW	sand, gravel	0-28
			clay	28-77
			heavy clay, sand, gravel	77-83
		NE NW	sand, gravel, clay	0-105
			basalt ledge	105-107
			sand, gravel, clay	107-163
		SE NE	decomposed granite?	0-38
			basalt	38-60
			clay, shale	60-550
		SW SW	granite	0-100
		??	clay	0-42
			basalt	42-124
			gray, blue shale	124-132
		SW SW	clay	0-85
			silt	85-121
			granite	121-190

TOWNSHIP	SECTION	1/4 SECT.	LITHOLOGY	DEPTH (ft)
T50N R4W	Sec 9	SW SW	granite	0-250
T50N R4W	Sec 10	??	basalt	0-25
			clay	25-180
			sandy clay, gravel, coarse gravel	180-283
			sand	283-286
			granite	286-595
T50N R4W		SW NE	clay	0-5
			basalt	5-40
			brown clay	40-62
			hardpan	62-70
			basalt	70-81
			hardpan	81-106
			basalt	106-115
			sand	115-120
		SW SW	granite	0-246
T50N R4W	Sec 11	no wells		
T50N R4W	Sec 12	NW SW	gravel, sand	202-225
			fine sand	225-235
			sand, clay	235-260
			fine sand	260-275
			gray clay	275-276
			very fine sand	276-284
			sandy clay	284-295
		SW SW	sand, gravel	4-57
			blue clay	57-60
			hardpan	60-73
			sand, gravel, boulder, sand & gravel	73-250
			fine sand	250-264
			gray clay	264-269
			basalt	269-270
		NW SW	sand, gravel	0-202
		SE SE	soft, decomposed granite	0-37
			granite	37-400
T50N R4W	Sec 13	7th & Wallace	sandy clay, sandy silt, sand, silt, gravel	0-175
			"possible basalt"	175-180
T50N R4W	Sec 14	no wells		

TOWNSHIP	SECTION	1/4 SECT.	LITHOLOGY	DEPTH (ft)
T50N R4W	Sec 15	NE SE	broken basalt, coarse gravel	2-42
			clay	42-50
			broken basalt	50-104
			sandy clay	104-155
			sand	155-180
		SE NE	clay + basalt boulder	0-26
			hard gray basalt	26-31
			basalt + brown clay	31-48
			hard gray basalt	48-54
			basalt + brown clay	54-65
			hard gray basalt	65-70
			basalt + brown clay	70-95
			clay	95-105
			sand	105-120
			dark gray shale	120-160
			brown shale	160-170
			gray shale	170-308
		SE NW	fill	
			cobbles, boulders	
			hardpan clay, sand, gravel	
			yellow clay + sand	26-55
			green blue clay	55-92
			decomposed granite	92-105
			soft granite	105-185
			med granite	185-350
			hard granite	350-393
		NW SE	soft broken basalt	4-50
		NW NE	granite	0-140
		NE SW	clay>coarse-fine sand	0-72
			black basalt	72-87
			clay	87-112
			fine sand, wood	111-121
			clay	121-167
			granite	167-563
		NE SW	sand, gravel	0-100
		NE SW	brown clay	0-46
			granite	46-92
		SE SW	granite	0-275

TOWNSHIP	SECTION	1/4 SECT.	LITHOLOGY	DEPTH (ft)
T50N R4W	Sec 15	NE? NE SW	sand, gravel	0-34
			brown clay	34-143
			fine sand	143-150
			clay	150-192
			decomposed granite	192-354
			granite	345-500
		NE SW	sand, gravel	0-40
			clay	40-73
			gravel, clay	73-76
			clay	76-150
		NW SW	granite	0-90
T50N R4W	Sec 16	NE NW	basalt	150-425
		most other wells/boreholes in Sec 16 are in granite		
T50N R3W	Sec 6	SW NE	sand	0-52
			clay	52-70
			fine gravel	70-75
			brown clay	75-100
			fine gravel	100-104
			shale	104-220
		NW SE	shale	0-75
			slate	75-640
		? SE	sand	0-22
			clay	22-26
			coarse sand	26-42
			sand, gravel, clay	42-140
		? SE	medium sand	0-45
			sand, gravel	45-165
			shale	165-170
		SE NE	clay	0-60
			soft basalt	60-250
			slate	250-300
			very soft basalt	300-540
		NE SE	sand, gravel	0-185
		NE SE	sand, gravel	0-205
		NE SE	gravel	0-175
		NE NE	shale	0-175

TOWNSHIP	SECTION	1/4 SECT.	LITHOLOGY	DEPTH (ft)
50N R3W	Sec 7		most wells in sec 7 all shale	
		SE SE	soil & clay	0-155
			broken basalt	155-160
			brown clay	160-244
			shale	244-475
T50N R3W	Sec 8	NW SE	basalt	0-32
			broken basalt + clay	32-135
			basalt	135-150
			basalt	150-185
			gray clay	185-188
		NW NW	brown clay	2-10
			hard basalt	10-53
			hard clay (white > brown > red > yellow)	53-214
		NE SW	clay, basalt	4-180
			basalt & shale layers	180-165
T50N R3W	Sec 18	SE NE	sand	3-16
			brown clay	16-22
			shale	22-185
			gray clay	185-284
			shale	284-338
			gray clay	338-350
		SE NE	sand	0-14
			brown clay	14-28
			basalt	28-175
			gray clay	175-178
		NE SE	basalt	17?-160
			brown shale	160-200
			gray clay	200-255
			basalt	255-300
		SW NE	coarse sand	0-42
			broken basalt	42-80
			sand	80-83
			broken basalt	83-100

TOWNSHIP	SECTION	1/4 SECT.	LITHOLOGY	DEPTH (ft)
T50N R3W	Sec 18	SE NE	basalt	4-35
			shale	35-92
			gray, black basalt	92-112
			broken black "granite"	112-165
			clay	165-195
			mixed	195-240
		SW SE	sand, gravel	0-140
			sand, gravel, clay	140-290
			quartzite	290-344

APPENDIX III

Water Level Elevations From Wells in the Southeastern Rathdrum Prairie.

USGS Water Level Data:						
LOCATION	ELEV (feet)	DEPTH (feet)	DATE	Depth to Water (ft.)	Water level Elev. (ft.)	*
50N 03W 06AAA1	2360	225	03/15/78	33.27	2326.7	
50N 03W 05BBA1	2320	277	08/15/78	47.35	2272.7	
50N 04W 10ABA1	2182.5	156	08/14/78	137.06	2045.4	
50N 04W 05DDC1	2150	163	08/22/78	123.57	2026.4	
50N 04W 04CCD1	2168	201	08/14/78	118.53	2049.5	
50N 04W 06CCA1	2174.7	205	08/15/78	174.44	2000.3	
50N 04W 05DAC1	2147.9	178	08/18/77	132.69	2015.2	
50N 04W 05DBC1	2175.4	205	08/14/78	162.78	2012.6	
50N 04W 05CAB1	2250	352	08/22/78	241.00	2009.0	r
50N 04W 06BCA1	2362.9	426	03/14/78	372.52	1990.4	r
50N 04W 03ADD1	2203.6	237	08/23/78	161.04	2042.6	
50N 04W 04AAD1	2248.5	350	08/15/78	235.68	2012.8	p
50N 04W 01CCD1	2237.5	226	08/25/78	189.10	2048.4	
50N 04W 03DCB1	2195.8	---	08/15/78	158.17	2037.6	
50N 04W 05CAB2	2250	350	09/21/88	242.80	2007.2	
50N 04W05DCC1	2149.2	---	08/14/78	136.55	2012.7	
50N 04W 07ADD1	2060	110	08/17/78	74.47	1985.5	
50N 04W 12CBB1	2221.3	295	08/25/78	170.49	2050.8	
51N 03W 30ACB1	2280	700	08/24/78	27.92	2252.1	
51N 03W 19CDA1	2600	620	03/17/78	365.83	2234.2	
51N 03W 18BDA1	2350	260	08/24/78	162.93	2187.1	
51N 03W 18BCB1	2295	281	08/23/78	220.99	2074.0	
51N 03W 19BAB1	2292.9	221	06/29/78	137.70	2155.2	
51N 03W 30BDD1	2280	275	08/24/78	142.48	2137.5	

LOCATION	ELEV (feet)	DEPTH (feet)	DATE	Depth to Water (ft.)	Water level Elev. (ft.)	*
51N 04W 34CCC2	2247.5	---	08/25/78	240.12	2007.4	
51N 04W 31DDA1	2342.9	420	08/24/78	349.31	1993.6	
51N 04W 32DAC1	2261.7	343	08/22/78	267.26	1994.4	
51N 04W 33CAB1	2269.3	332	08/24/78	273.64	1995.7	
51N 04W 32ACA1	2271.5	318	08/24/78	277.63	1993.9	
51N 04W 35ABB1	2220	296	08/25/78	250.30	1969.7	
51N 04W 28CAD1	2281.8	348	08/25/78	286.60	1995.2	
51N 04W 28BCA1	2263.3	297	08/24/78	268.45	1994.9	
51N 04W 25BBB1	2250	297	01/11/78	229.54	2020.5	
51N 04W 30CAA1	2240	---	08/24/78	256.51	1983.5	
51N 04W 24CCB1	2259.5	---	08/25/78	249.56	2009.9	
51N 04W 23DCB1	2280	367	03/23/78	269.27	2010.7	
51N 04W 19BDD1	2233.7	295	08/24/78	240.86	1992.8	
51N 04W 20BDA1	2255	315	08/25/78	255.88	1999.1	
51N 04W 14DBB1	2296.3	388	08/25/78	295.98	2000.3	
51N 04W 14ABA1	2305	380	08/10/77	306.35	1998.7	
51N 04W 14AAB1	2304.9	335	08/16/77	301.63	2003.3	
51N 04W 12CAC1	2295	---	08/23/78	293.60	2001.4	
51N 04W 12ABA1	2410	232	08/24/78	68.04	2342.0	
51N 04W 15AAA1	2300.3	348	08/25/78	302.93	1997.4	
51N 04W 22BCA1	2297.4	357	08/25/78	229.59	2067.8	
51N 04W 27DDB1	2274	310	03/13/78	268.82	2005.2	
51N 04W 29DBB1	2232.5	268	08/24/78	238.82	1993.7	
51N 04W 06BAD1	2222.8	256	08/18/78	223.61	1999.2	
51N 04W 23BCC1	2268.6	324	09/22/78	283.66	1984.9	
51N 04W 23DAA1	2275.6	330	08/25/78	262.31	2013.3	
51N 04W 24ABB1	2249.6	217	08/23/78	179.53	2070.1	
51N 04W 26AAA1	2240.3	280	08/24/78	231.31	2009.0	
51N 04W 29DCD1	2269.4	---	09/23/88	277.33	1992.1	

LOCATION	ELEV. (feet)	DEPTH (FEET)	DATE	Depth to Water (ft.)	Water Level Elev. (ft.)	*
51N 04W 33ADC1	2260	335	08/25/78	269.98	1990.0	
51N 04W 35ADB1	2220	228	08/25/78	203.74	2016.3	
51N 04W 35CCC1	2220	250	08/25/78	203.82	2016.2	
Sagstad's Water Level Data:						
50N 4W 01BAB	2230	235	9/75	193.70	2036.3	
50N 4W 01CCD	2238	309	9/75	187.30	2050.7	
50N 4W 03CDA	2202	190	9/75	155.90	2046.1	
50N 4W 03CC	2170	193	4/48	136.00	2034.0	
50N 4W 03DDC	2195	203	62	146.00	2049.0	
50N 4W 04AAD	2243	350	9/75	233.80	2009.2	
50N 4W 04CBC	2205	210	9/75	181.00	2024.0	
50N 4W 04CAC	2230	230	9/75	205.30	2024.7	
50N 4W 04DDD1	2181.7	200	9/75	130.50	2051.2	
50N 4W 04DDD3	2187	215	9/75	136.60	2050.4	
50N 4W 05ADD	2243	360	9/75	233.75	2009.3	
50N 4W 05CBC	2155	325	?	141.00	2014.0	
50N 4W 05CBD	2175	190	9/75	161.20	2013.8	
50N 4W 04DBC	2180	202	9/75	160.00	2020.0	
50N 4W 05CCD	2146	153	9/75	129.20	2016.8	
50N 4W 05CDC	2155	161	9/75	136.50	2018.5	
50N 4W 05CCC	2155	145	9/75	136.30	2018.7	
50N 4W 05CDD	2155	170	9/75	136.00	2019.0	
50N 4W 05DCC	2155	153	9/75	140.70	2014.3	
50N 4W 05DCB1	2155	145	9/75	137.30	2017.7	
50N 4W 05DBD	2155	214	9/75	141.30	2013.7	
50N 4W 05DCD1	2155	161	6/75	136.00	2019.0	
50N 4W 05DDC	2155	163	9/75	125.10	2029.9	
50N 4W 05DDD	2155	135	9/75	113.40	2041.6	

LOCATION	ELEV. (feet)	WELL DEPTH	DATE	Depth to Water (ft.)	Water Level Elev. (ft.)	*
50N 4W 05DCD2	2155	150	9/75	127.50	2027.5	
50N 4W 06BDD	2227	325	9/49	206.40	2020.6	
50N 4W 07BCB	2157	249	9/75	153.50	2003.5	
50N 4W 07DCC	2400	110	71	35.00	2365.0	
50N 4W 08AAB	2155	163	9/75	129.50	2025.5	
50N 4W 08BBB	2145	171	9/75	133.00	2012.0	
50N 4W 08ADA2	2140	135	9/75	78.60	2061.4	
50N 4W 08ADA1	2140	45	9/75	8.00	2132.0	
50N 4W 08BCB	2140	210	9/75	102.00	2038.0	
50N 4W 10AAD	2160	---	9/75	88.90	2071.1	
50N 4W 10AAB	2190	159	9/75	134.60	2055.4	
50N 4W 11BBB	2240	---	9/75	187.50	2052.5	
50N 4W 12CDC	2220	270	9/75	164.50	2055.5	
50N 4W 12CBC	2221	295	9/75	169.10	2051.9	
50N 4W 15ABD	2145	111	6/75	5.50	2139.5	
51N 4W 25CBB	2233	231	9/75	215.80	2017.2	
51N 4W 26ADD	2240	280	74	220.00	2020.0	
51N 4W 26AAD	2250	330	9/75	234.00	2016.0	
51N 4W 26CCC	2265	301	9/75	252.30	2012.7	
51N 4W 28BBD	2270	297	72	260.00	2010.0	
51N 4W 28CDB	2270	348	74	295.00	1975.0	
51N 4W 29BDD	2250	285	74	231.00	2019.0	
51N 4W 31DDD	2340	420	73	352.00	1988.0	
51N 4W 32ACC	2260	318	75	272.00	1988.0	
51N 4W 33ACC	2264	335	9/75	261.20	2002.8	
51N 4W 34CCD1	2245	270	9/75	237.00	2008.0	
51N 4W 35CCC1	2220	250	9/75	196.60	2023.4	

LOCATION	ELEV. (feet)	WELL DEPTH	DATE		Water Level Elev. (ft.)	*
Potlatch Wells:						
50N 3W 19ACB	2136.5	56.5	10/92 ?		2095	
50N 3W 19BAA	2159	110	10/92 ?		2071	
50N 3W 19BAB	2157.5	94.5	10/92 ?		2071	
* Status: p= pumping well, r= recovering well						

APPENDIX IV

Water Levels Elevations in Well AIP-2, 1992 to 1993

Date	Casing Elevation	DTW (feet)	Water Level Elevation (feet)	Water Level Elevation (meters)
7 Oct 92	2135.1 ft.	22.917	2112.18	643.8
17 Oct 92	2135.1 ft.	23.56	2111.54	643.6
4 Nov 92	2135.1 ft.	26.38	2108.72	642.7
25 Nov 92	2135.1 ft.	27.35	2107.75	642.4
2 Dec 92	2135.1 ft.	29.20	2105.9	641.9
9 Dec 92	2135.1 ft.	30.50	2104.6	641.5
16 Dec 92	2135.1 ft.	31.00	2104.1	641.3
23 Dec 92	2135.1 ft.	31.50	2103.6	641.2
6 Jan 93	2135.1 ft.	31.00	2104.1	641.3
13 Jan 93	2135.1 ft.	31.00	2104.1	641.3
20 Jan 93	2135.1 ft.	31.40	2103.7	641.2
27 Jan 93	2135.1 ft.	33.50	2101.6	640.6
3 Feb 93	2135.1 ft.	32.0	2103.1	641.0
...	2135.1 ft.	dry	<2100.8	<640
24 Mar 93	2135.1 ft.	27.4	2107.7	642.4
31 Mar 93	2135.1 ft.	21.3	2113.8	644.3
7 Apr 93	2135.1 ft.	19.55	2115.55	644.8

APPENDIX V

Metal Concentrations in the Waters of Lake Coeur d'Alene, 1991

LOCATION	DATE	Arsenic µg/l	Cadmium µg/l	Copper µg/l	Lead µg/l	Mercury µg/l	Zinc µg/l
Chatcolet	1/15/91	<1	<1	15	3	<0.10	20
Chatcolet	4/15/91	<1	<1	2	3	<0.10	<10
Chatcolet, 1 m	6/5/91	<1	<1	2	3	0.10	<10
Chatcolet, 9 m	6/5/91	<1	<1	4	4	0.30	<10
Chatcolet, 1 m	7/16/91	<1	<1	2	4	0.20	<10
Chatcolet, 9 m	7/16/91	<1	<1	2	3	0.30	20
Chatcolet, 1 m	8/28/91	<1	<1	3	2	<0.10	<10
Chatcolet, 9 m	8/28/91	1	<1	2	2	0.20	<10
NE of Blue Point, near Harrison	4/17/91	<1	<1	2	4	0.10	<10
NE of Blue Point, near Harrison, 15m	4/17/91	<1	<1	2	23	<0.10	40
NE of Blue Point, near Harrison	6/4/91	<1	<1	3	3	0.20	<10
NE of Blue Point, near Harrison, 14m	6/4/91	<1	<1	3	5	<0.10	30
NE of Blue Point, near Harrison	7/16/91	<1	<1	2	5	<0.10	50
NE of Blue Point, near Harrison, 15m	7/16/91	<1	<1	1	5	<0.10	50
NE of Blue Point, near Harrison	8/28/91	<1	<1	2	4	0.20	60
NE of Blue Point, near Harrison, 15m	8/28/91	<1	<1	2	5	<0.10	80
1.7 mi. NE of University Pt., near Harrison	1/15/91	<1	<1	5	9	0.10	160

LOCATION	DATE	Arsenic μg/l	Cadmium μg/l	Copper μg/l	Lead μg/l	Mercury μg/l	Zinc μg/l
1.7 mi. NE of University Pt., 36 m depth	1/15/91	<1	<1	2	10	<0.10	120
1.7 mi. NE of University Pt., near Harrison	4/17/91	1	<1	3	41	0.40	130
1.7 mi. NE of University Pt., 36 m depth	4/17/91	<1	<1	3	16	<0.10	130
1.7 mi. NE of University Pt., near Harrison	6/4/91	<1	<1	3	8	<0.10	70
1.7 mi. NE of University Pt., 38 m depth	6/4/91	<1	<1	3	7	0.10	110
1.7 mi. NE of University Pt., near Harrison	7/16/91	<1	<1	2	8	<0.10	80
1.7 mi. NE of University Pt., 38 m depth	7/16/91	<1	<1	2	8	0.80	110
1.7 mi. NE of University Pt., near Harrison	8/27/91	<1	<1	3	3	<0.10	80
1.7 mi. NE of University Pt., 38 m depth	8/27/91	<1	<1	2	4	<0.10	110
0.8 mi. SW of Driftwood Pt.	1/15/91	<1	<1	3	8	<0.10	120
0.8 mi. SW of Driftwood Pt., 15 meter depth	1/15/91	<1	<1	4	7	0.10	120
0.8 mi. SW of Driftwood Pt.	4/16/91	<1	<1	3	20	0.10	130
0.8 mi. SW of Driftwood Pt., 45 meter depth	4/16/91	<1	<1	4	7	0.40	130
0.8 mi. SW of Driftwood Pt.	6/4/91	<1	1	5	8	<0.10	110

LOCATION	DATE	Arsenic µg/l	Cadmium µg/l	Copper µg/l	Lead µg/l	Mercury µg/l	Zinc µg/l
0.8 mi. SW of Driftwood Pt., 49 meter depth	6/4/91	1	1	3	8	0.20	110
0.8 mi. SW of Driftwood Pt.	7/17/91	<1	<1	2	8	0.30	70
0.8 mi. SW of Driftwood Pt., 50 meter depth	7/17/91	<1	2	11	14	0.30	390
0.8 mi. SW of Driftwood Pt.	8/27/91	<1	<1	2	4	<0.10	70
0.8 mi. SW of Driftwood Pt., 48 meter depth	8/27/91	<1	<1	2	6	0.20	130
Wolf Lodge Bay	1/15/91	<1	<1	3	3	<0.10	110
Wolf Lodge Bay, 25 meters	1/15/91	<1	<1	2	2	<0.10	100
Wolf Lodge Bay	4/16/91	<1	<1	2	3	<0.10	90
Wolf Lodge Bay, 15 meters	4/16/91	<1	<1	3	5	0.20	110
Wolf Lodge Bay	6/4/91	1	<1	2	8	<0.10	70
Wolf Lodge Bay, 26 meters	6/4/91	<1	<1	5	4	0.20	100
Wolf Lodge Bay	7/16/91	<1	<1	2	5	0.40	60
Wolf Lodge Bay, 27 meters	7/16/91	<1	<1	2	10	0.30	110
Wolf Lodge Bay	8/27/91	<1	<1	2	3	<0.10	70
Wolf Lodge Bay, 27 meters	8/27/91	<1	<1	2	5	<0.10	110
1.3 mi. SE of Tubbs Hill	1/16/91	<1	<1	2	5	<0.10	110
1.3 mi. SE of Tubbs Hill, 38m	1/16/91	<1	<1	2	6	<0.10	110
1.3 mi. SE of Tubbs Hill	4/16/91	<1	<1	3	7	0.10	110
1.3 mi. SE of Tubbs Hill, 38m	4/16/91	<1	<1	6	6	<0.10	110
1.3 mi. SE of Tubbs Hill	6/5/91	<1	<1	2	5	<0.10	60

LOCATION	DATE	Arsenic µg/l	Cadmium µg/l	Copper µg/l	Lead µg/l	Mercury µg/l	Zinc µg/l
1.3 mi. SE of Tubbs Hill, 40m	6/5/91	<1	1	3	8	<0.10	70
1.3 mi. SE of Tubbs Hill	7/17/91	<1	<1	1	4	0.30	60
1.3 mi. SE of Tubbs Hill, 40m	7/17/91	<1	<1	1	6	1.8	120
1.3 mi. SE of Tubbs Hill	8/27/91	<1	<1	3	2	<0.10	70
1.3 mi. SE of Tubbs Hill, 40m	8/27/91	<1	<1	3	4	<0.10	140