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PLANKTON POPULATIONS AND SOME EFFECTS OF MINE DRAINAGE ON PRIMARY PRODUCTIVITY OF THE COEUR D'ALEME RIVER, DELTA AND LAKE

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ABSTRACT

Variations in primary production and physiochemical measurements in the Coeur d'Alene River and Lake contaminated by mine and industrial wastes were examined from May, 1969, to November, 1970. Metal concentrations Md, Cd, Mg, Ca, Pb, Cu, Zn, Fe, Na and K; water quality and phytoplankton composition-density were determined for thirty-five dates during this period. Additional sampling included unpolluted portions of Coeur d'Alene Lake from December, 1969, to November, 1970, and the unaffected St. Joe River during the summers of 1969-70.

Primary production ranged from 17.6 to 1337.9 mg $C/m^2/day$ in the Coeur d'Alene River and 69.3 to 1714.5 mg $C/m^2/day$ in the Coeur d'Alene Lake. Concentrations of zinc (0.1 to 11.2 mg Zn/1) and copper (0.0 to 0.6 mg Cu/1) in the Coeur d'Alene River indicated that heavy metals could be toxic to algae. Diatoms dominated phytoplankton in the Coeur d'Alene River, Lake, and St. Joe River.

Primary production in the southern portion of Coeur d'Alene Lake appeared controlled by discharges from the Coeur d'Alene and St. Joe rivers. Low concentrations of inorganic carbon and moderately high concentrations of nitrate and phosphate in the Coeur d'Alene River, Lake and St. Joe River suggest the importance of carbon in regulating production. The effect of wind on eplimnetic production and poorly developed stratification in the south end of the lake appeared related to decreased depths. Wind action may control eutrophication by suppressing hypolimnetic oxygen depletion and anaerobic regeneration.

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Nannoplankton from Coeur d'Alene Lake were exposed to known concentrations of Cu^{2+} , Cd^{2+} , Zn^{2+} and dilutions of Coeur d'Alene River water under controlled light and temperature. Inhibitory effects of separate and interacting metals on carbon-14 uptake by algae were assessed with factorial designed bioassays and response surfaces. Copper, cadmium, and zinc were acutely and synergistically toxic to carbon uptake by phytoplankton. Concentrations ranged from 0.05 to 0.75 mg Cu/1, 0.1 to 0.3 mg Cd/1, and 0.1 to 1.5 mg Zn/1. Copper caused an overriding effect on two- and three-way interactions of Cu^{2+} , Cd^{2+} , and Zn^{2+} . Dilutions of Coeur d'Alene River water decreased Cu and Zn toxicity. Variable algal community structure, major cations, softwater (<60 mg/1 as CaCO₃), and water quality appeared to affect metal toxicity.

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INTRODUCTION

The Coeur d'Alene River and Lake have received mine tailings and metallic sulfide minerals for over 80 years. Toxicity of the river water to fish and plankton was documented at the mouth of the Coeur d'Alene River in 1932 (Ellis, 1940). Sappington (1970) used unpolluted headwaters of the Coeur d'Alene River and reported that over a 96 hour period that 50% of the cutthroat fingerlings succumbed at 0.09 mg An/1. Savage (1970) noted that deposits of mine wastes limited bottom insect colonization of riffle areas in the Coeur d'Alene River.

The objectives of this study were to (1) compare plankton populations and phytoplankton production in the Coeur d'Alene river, delta, and lake, (2) to relate algae productivity in these areas to principle chemical, physical and biological parameters of the lake and (3) to bioassay certain physical and chemical factors as to their inhibiting effect on productivity. These original objectives were generally satisfied by research carried out by Mr. Bob Minter and Mr. Bob Wissmar. The following report is a compilation of Mr. Minter's thesis and Mr. Wissmar's dissertation. A more detailed account of our research is to be found in the thesis and dissertation, the titles of which are listed at the beginning of this report.

Prior to the study, sparse plankton communities were noted along with high concentrations of zinc, copper and lead, and a minimal pH of 6.4 at the river mouth. Maximum metal concentrations of 3.05 mg Zn/1 and 0.50 mg Cu/1 exceeded the tolerance limits of most phytoplankton (McKee and Wolf, 1963) and suggested inhibition of algal productivity by a synergistic mode of toxicity. Metal synergism usually results from simultaneous cooperation of separate elements which produce an effect greater than of any metal taken alone. Such combined toxic actions of metals are well known for various species of fish (Skidmore, 1964), but little information exists on cultured and <u>in situ</u> algal sensitivities to interacting metals. Fitzgerald (1971) detected no synergism between copper and zinc in tests of hardwater cultured bluegreen and green algae. However, the naturally softwater of the Coeur d'Alene River and the presence of acidic and various metallic wastes increases the probability that synergism reduces phytoplankton and productivity. Heavy metals have been shown to be more toxic to fish (Jones, 1938) and algae (Moyle, 1949) in softwater than in hardwater.

Mine wastes enter the main Coeur d'Alene River from the South Fork some 30 miles upstream from the lake (Figure 1). Contaminants in the South Fork include seepage from old tailing deposits, heavy metals, acids and suspended solids-colloids from electrolytic zinc and antimony plants, milling sufuric-phosphoric acid and fertilizer operations (Mink, 1972).

The Coeur d'Alene and St. Joe Rivers enter the southern end of Coeur d'Alene Lake (Figure 1). The close proximity of the river mouths and differences in environments provide unique opportunities to study the behavior of pollutants. The Coeur d'Alene River has poorly developed aquatic communities with no apparent harvestable crop of fish. Colloidal mill and industrial effluents impart a greenish cast to the river and alter light penetration while tailings sediments cover most substrates. The St. Joe River has a productive sport fishery, but it has been affected by sewage from the town of St. Maries and by farming, logging and boating activities.

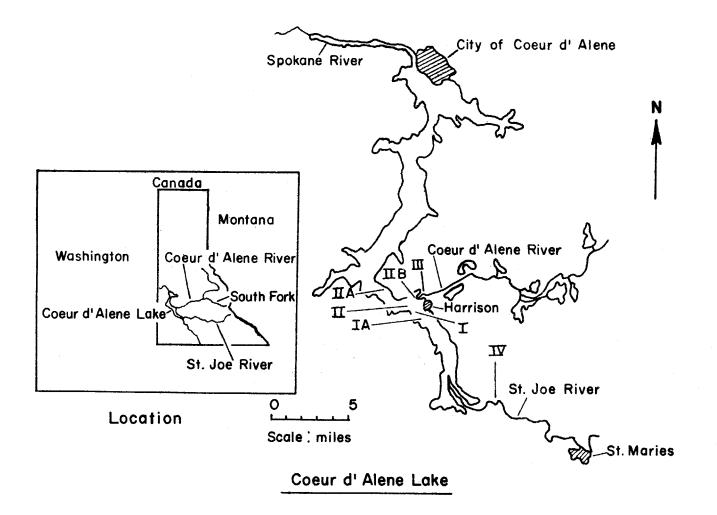


Figure 1. Coeur d'Alene River, Lake, and St. Joe River Station Locations.

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Coeur d'Alene Lake lies in a sunken river valley 23 miles long and drains northwest through the Spokane River near the city of Coeur d'Alene (Figure 1). The lake appears moderately productive with autumnal biological enrichment in developed bays.

Plankton populations, algal production and water chemistry samples were collected at the four stations weekly from May (when they were established) until September and biweekly during October, 1969. Beginning in November, 1969, samples were taken monthly until May, 1970, and biweekly thereafter until November, 1970. Collections were made in the late morning and early afternoon. Sampling was performed by Mr. Wissmar together with Mr. Minter from an outboard motor boat with the aid of a hand-operated winch.

Primary production was measured with the carbon-14 light and dark bottle technique of Goldman (1960). Stock solutions of carbon-14 were prepared for each sampling period from one milliliter serum bottles containing $20\mu c$ of NAH¹⁴CO₃.

Bioassays were conducted in a controlled light and temperature tank at the shore laboratory. The bottles were incubated in a 0.6 m³ stainless steel tank. Tank temperatures were controlled by a separate submerged refrigeration unit and circulated by self-priming centrifugal pumps. Four 500-w incandescent bulbs illuminated the bioassay tank. A submarine photometer measured light at the neck level of submerged incubation bottles. The light source and temperature were regulated to simulate average light and temperature conditions in the lake.

RESULTS AND DISCUSSION

Mine and industrial pollution is the main cause of differences in water quality between the Coeur d'Alene River, the Lake and the St. Joe River. Mine wastes and increased metal concentrations in the river and delta can be related to various milling operations, extraction processes, sulfuric acid and phosphoric acid fertilizer plants. Zinc sulfate and sodium cyanide are used in zinc flotation and processing, soda ash for buffering pH in metallurgy, sodium in leaching associated with electrolytic antimony operations and calcium sulfate in phosphoric acid processes. The sources of low pH, high conductivity, high levels of Zn, Ca, Na, Mn and lower quantities of Cd, Cu, Pb, Fe and F are associated with acidic pond effluents and seepages adjacent to the zinc and phosphoric acid plants. Zinc, F, Cd, Cu and Pb appear to be the major toxic materials in the South Fork. Maximum levels of 21.0 mg Zn/1 (5241 kg/day), 2.3 mg F/1, 0.45 mg Cd/1 (109 kg/day), and 0.1 mg/1 (25 kg/day) of both Cu and Pb have been noted near industrial discharges in the South Fork. The maximum sodium concentrations occur with high conductivity in pond effluents from antimony operations. The metals of Ni, As, Cr and Hg are present but occurred below reported limits of detectability (Mink, et. al., 1971; Mink, 1972).

Tailing sedimentation in the Coeur d'Alene River and delta occurred prior to the 1968 construction of settling ponds when all tailings and wastes were discharged directly into the South Fork. It has been estimated that approximately 500,000 tons were discharged to the river annually (Ellis, 1940). The water of the Coeur d'Alene River and Lake can be characterized as softwater (60 mg as $CaCO_3$). Concentrations of zinc were the only ion that consistently occurred at high levels. If zinc is excluded, the Coeur d'Alene River (0.1 - 11.2 mg Zn/1) and Lake (0.1 - 1.0 mg Zn/1) are comparable to other softwater lakes and rivers. Lake Tahoe, California, produced zinc concentrations of 0.014 mg Zn/1 (Gcldman, 1965) while the Clearwater and Snake Rivers of northern Idaho showed 0.04 mg Zn/1 (Kopp and Kroner, 1968).

Inorganic carbon concentrations were low for regional waters with the Coeur d'Alene River and Lake being less than the St. Joe River. Levels of inorganic carbon were related to the softwaters of the area and could be indicative of the inert geochemical character of the drainage. Bicarbonate and pH of the Coeur d'Alene River and Lake were lower than the St. Joe River and probably resulted from mine wastes. Various acid seepages and inflows are diluted but not effectively neutralized due to the poor buffering capacity of the river. This could be important to the carbon uptake by the algal, predominately diatom, community since HCO_3 ions were the main form of inorganic carbon available. The scarcity of inorganic carbon and the low pH (6.4 and 7.3) in the Coeur d'Alene River and minecontaminated portions of the delta and lake could be associated with a low solubility for CO₂ and its consequent loss to the atmosphere. The nature of the tailing deposits also interfere with CO₂ regeneration from bottom sediments.

Most nutrients were in ample supply and not limiting to algae growth. Nitrates and phosphates were at higher levels in the Coeur d'Alene and St.

Joe Rivers than in the lake. Silica in the Coeur d'Alene River and Lake indicated concentrations of 3.6 to 7.9 mg $\text{SiO}_2/1$. Sulfate levels of 20 to 50 mg $\text{SO}_4/1$ from above the Coeur d'Alene River mouth were reported by Stokes and Ralston (1971).

Ellis (1932) found ample plankton in some of the tributary lakes, and a sparse plankton population in Coeur d'Alene Lake. He also noted a particularly poor plankton composition in the southern end of the lake and none near the mouth or in that portion of the Coeur d'Alene River carrying mine wastes. Kemmerer, et. al., (1923) found similar results in their study of the lake and river during 1911, and noted that plankton counts in the vicinity of the river mouth near Harrison were lower than elsewhere in the lake. At that time they also reported that the suspended matter carried by the waters of the Coeur d'Alene River could be traced well out into the lake. The higher plankton counts recorded during the present investigation are believed to be partially brought about by the decrease in silt load carried by the Coeur d'Alene River following the installation of settling ponds.

Highest phytoplankton and zooplankton counts in the Coeur d'Alene River occurred during May and June and again during early fall. Phytoplankton density was low but diversity was high when compared with the St. Joe River counts. This strongly suggests that drift from the lateral lakes influence the plankton community in the Coeur d'Alene River since few if any reaches of the river below the mining operations are suitable habitat for plankton production. Plankton collections from these lakes have yeilded higher counts than have appeared in the river (Ellis, 1940).

Maximum numbers of plankton in the St. Joe River occurred in August during this investigation. However, the period during peak discharge was not sampled and could not be compared with the Coeur d'Alene River. Davis (1961) reported a June phytoplankton peak occurring in the lower reaches of the St. Joe River and attributed this to the overflow of plankton rich waters from ponds and lakes associated with the backwaters. This peak occurred where the lakes at the southern end of Coeur d'Alene affect the St. Joe River during flood stage. In addition, raw sewage from the town of St. Maries is dumped into the St. Joe River backwater. The fertilizing effect of this sewage would favor zooplankton and phytoplankton production in the lower slackwater.

The higher plankton counts recorded during this investigation in the lower St. Joe River as compared to the lower Coeur d'Alene River may also be attributed to the more vegetated shoreline which exists along the St. Joe River and serves an allochthonous source of energy.

Davis attributed the low plankton numbers in the St. Joe River to softwater, current, water age, lack of associated lentic environments and fluctuations of hydrographic conditions. As all of these factors also act on the lower Coeur d'Alene River, with the exception of the lack of associated lentic environments, it is understandable why river plankton are subject to extreme fluctuations. In the case of the Coeur d'Alene River, the added toxic effects of heavy metals on plankton and fish as found by Ellis (1932) remains the major limiting factor on the biota of that portion of the river carrying mine wastes.

Measurements of physical, chemical and biological features indicate a change from oligotrophic (unproductive) to mesotrophic (mildly enriched) conditions in some bay areas of Coeur d'Alene Lake. The extreme southern

portion of the lake is highly enriched (eutrophic) due to the shallow conditions and increased human activity. This is substantiated by various plankton indicators (Rawson, 1956; Teiling, 1955), lake depth, relatively high temperatures during the summer, decreasing oxygen content near the bottom and a high population of phytoplankton comprised mostly of diatoms. The lake apparently has a high population of phytoplankton in comparison to other large lakes in the northwest studied by Kemmerer, et. al. (1923).

The inhibiting effect of a large influx of warm turbid waters from the Coeur d'Alene River on phytoplankton production was demonstrated by the decline in phytoplankton standing crop in the delta region during June, 1970. Another factor which influenced this decrease was the large volume of plankton-poor river waters displacing or diluting the delta waters. Similar conditions were reported by Stross (1954) during spring discharge of the Clark Fork River into Lake Pend Oreille, Idaho, and by Verduin (1951) in western Lake Erie.

The open waters of the delta region are affected by the increase of spring winds during and after the spring overturn. It is believed that open waters of the lake and delta are enriched with plankton from the more productive bays near the west shore during windy periods. A distinct color from the river waters can be observed to flow along the east shore, north of the river mouth during windy periods. Temperature stratification of the waters did not occur until late August, 1969, due to a cooler spring and windy conditions throughout the first two months of summer. Ruttner (1964) points out that spring winds inhibit stratification until the entire lake is warmed.

The most dominant and fluctuating algae genera present during the fall test period were <u>Melosira</u>, <u>Tabellaria</u>, <u>Mougeotia</u>, and <u>Ulothrix</u> (Figure 2). <u>Melosira</u> was the most abundant during August while <u>Tabellaria</u> was dominant from September to November. Densities of <u>Mougeotia</u> and <u>Ulothrix</u> exceeded <u>Melosira</u> in September and October. <u>Synedra</u> and <u>Aster-</u> <u>ionella</u> counts were highest in August and October.

Primary production of Coeur d'Alene Lake and River over 19 months averaged 476.6 and 269.2 mg $C/m^2/day$ with large fluctuations on a seasonal basis (Figure 3). The annual mean productivities during 1970 (includes December, 1969) for the lake and river were 533.3 and 312.3 mg $C/m^2/day$, respectively. The depth of the trophogenic layer in the lake varied from 5 to 15 m and from 5 to 9 m in the river.

The mean productivities for optimal growth periods during summers and falls of 1969 and 1970 were 418.6 and 727.0 mg $C/m^2/day$ in the lake and 255.6 and 470.0 mg $C/m^2/day$ for the river. The above values were calculated from synchronous dates in 1969 and 1970. The lower areal production of both the lake and river in 1969 as compared to 1970 resulted from shallower trophogenic layers, colder epilimnetic temperatures and greater irregularities in solar radiation.

The third objective of this study was to determine the effect of the Coeur d'Alene River on plankton populations in the southern part of Lake Coeur d'Alene. Zinc, copper and cadmium treatment levels were chosen on the basis of concentrations in the Coeur d'Alene River because of potential zinc toxicity and synergism with copper and cadmium. Water samples were collected from the lake, bottled and the samples were inclubated for about twelve hours in a large stainless steel tank in a laboratory adjacent to the shore.

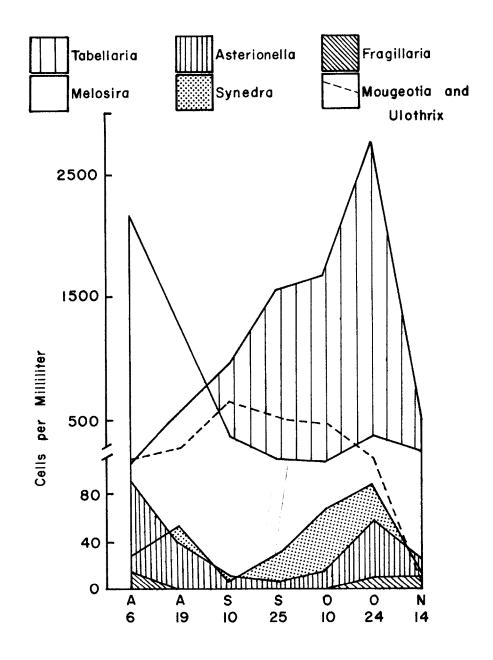


Figure 2. Nannoplankton community structure during test period, August to November, 1970.

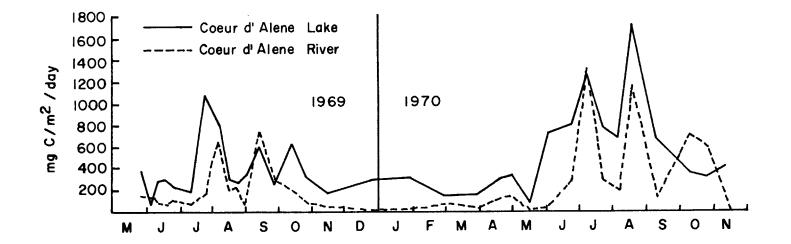


Figure 3. Seasonal variation of primary productivity (mg $C/m^2/day$) in the Coeur d'Alene Lake (Station I) and River (Station III).

The artificial light source and temperature were regulated to simulate average temperature and light readings in the lake during periods of peak plankton growth.

Bioassays indicated that copper was the most toxic metal tested. A marked reduction in phytoplankton photosynthesis occurred when copper concentrations were between 0.10 and 0.30 mg Cu/1. Copper concentrations of 0.75 mg Cu/1 were only slightly more inhibitory than 0.30 mg Cu/1. The toxicity of copper sulphate in these tests can be attributed to its success as an algicide under conditions of both soft and hardwater. Although copper quantities in the Coeur d'Alene River compare closely to those of non-polluted waters, the relatively softwater of the river enhances toxic effects of copper on phytoplankton.

Cadmium in the tests inhibited carbon fixation at 0.1 and 0.3 mg Cd/1. Bringmann and Kühn (1959) in studying <u>Scenedesmus</u> from a river habitat found threshold concentrations for detrimental effects of Cd as chloride as 0.1 mg Cd/1. McKee and Wolf (1963) reported that cadmium acts synergistically with other substances to increase toxicity.

Zinc decreased phytoplankton carbon uptake at 0.1 and 0.5 mg Zn/1. In general, the effect of zinc decreased as the concentration of zinc increased. At. 1.0 mg Zn/1 the amount of carbon fixed was slightly higher than in controls. These results can be explained partly by information from Bachmann (1963). He suggested that algae cells take up Zn as a direct response to concentrations exceeding those ordinarily found in nature, a "luxury" consumption above immediate metabolic needs.

The high concentrations of Zn and Cu and the softwater in the tests explain the observed synergism. Although the levels of Zn and Cu were high, they were within the range of concentrations observed in the Coeur d'Alene River and suggest that a similar action could occur. Concentrations used in these tests indicated that each metal contributed to the toxicity of the mixture in proportion to their individual toxicities. This suggests that the inhibitory effects of the interactions could be estimated by summation of the fractional toxicities of each metal.

The presence of complexing agents such as polypeptides in the Coeur d'Alene River suggests that current levels of Cu, Cd and Zn are less toxic to algae than our tests indicated. Reduced inhibition with increased volumes of river water indicated binding by pollutants or natural materials. The principal arguments against the importance of chelation in the river and delta are the levels of major cations, the high Zn concentrations and evidence of metal toxicity by synergism.

The impact of metals on aquatic life in the Coeur d'Alene drainage cannot be assessed until knowledge of the contribution of tailings deposits to metal concentrations in solution is known. Prior to about 1930 stampmill-jig-table processes put coarse gravity tailings into the river. The tailings could not be economically smelted and therefore carried high concentrations of silver, lead and zinc. The presence of these metallic sulfides in river sediments consitutes a pollution hazard since physical disturbances and oxidation to sulfates increase the rexicity of these elements. The hgih solubility of sulfate can produce sulfuric acid, lower the pH and release metals into solution. Accordingly, tailing deposits could affect the biota in the river valley and lake for many years.

Research on the effect of tailing deposits on metals in solution shows that a pollution problem exists. Studies of mine tailings indicate that the cation exchange capacities werelow as compared to most soils (Toukan, 1971). Tailings had their highest exchange capacity at Ph 10. Equilibrium equations at various pH values indicated that Zn was released from tailings, increasing the concentration of Zn in settling pond effluents. These results demonstrate that tailings deposits in contact with water of pH 7.0 and lower in the Coeur d'Alene River and delta region releases Zn into solution.

Sediment studies in the Coeur d'Alene River delta have revealed the magnitude of metal concentrations in tailings deposits (Maxfield², unpublished data). The mean Zn concentration for approximately 45 cm cores was 4207 mg/kg. The average levels of Mn, Pb, Sb, Cu, Cd and Ag were 211 percent, and 0.3 percent, respectively, of that of zinc. A mercury concentration of 0.4 percent of the preceding zinc value was reported by Sceva³ (unpublished data). The amount of metals associated with core partitions took the order of clay, organic matter, sand and silt. Metal concentration in delta sediments usually increased with distance from the river mouth, indicating transport by fine suspended particles. Equilibrium equations at pH 7.8 and 2.5 indicated zinc concentrations released at 1.8 and 22.0 mg Zn/l, respectively.

Based on the information gathered during this investigation, the following recommendations are presented for future management and research.

²D. Maxfield, Biological, chemical and geological study of the Coeur d'Alene River delta. Student originated studies, NSF, University of Idaho, Moscow, Idaho, 1972.

³Jack E. Sceva, Geologist, FWPCA, Room 501, Pittock Block, Portland, Ore. Mercury in sediment samples from the Coeur d'Alene River Basin, Ida. Apr. 7, 1971.

 The effect of Coeur d'Alene River water and metal ions on primary production should be monitored at low flow periods in the fall by acute bloassay developed in this investigation.

2. Chronic algal bioassays should be conducted so that application factors can be developed which would indicate safe concentrations of metals and wastes in the receiving waters (Report of the Committee on Water Quality Criteria, 1968). The objective would be to establish maximum allowable values. Recommended values should be adequate where more than one adverse factor exists (Zn, Cu and Cd) and be within suitable limits of pH, hardness and temperature.

3. Additional experiments should be conducted to explore the possibility of some river constituents antagonizing heavy metal toxicity and to continue bipassays of the synergistic effects of metals in sediment suspensions and river water. Simultaneous bipassays should be conducted on natural algal communities, isolated populations and recommended indicator organisms. Such tests would define the effects of metal interactions and sensitivities of community components. These studies should be expanded to endemic and harvestable fish of the area. Fish being very susceptible to metal toxicity could provide great sensitivity then algae in multivariate bipassays.

4. The trophic status of regional waters should be continuously surveyed by production-depth profiles and accompanying physiochemical data. Additional information on nutrient, metal and algal biomass-density depth regimes would aid such a program.

CONCLUSIONS

1. Algal bioassays of heavy metals provide acute tests that have possible utility in management of water resources. Factorial designs, carbon-14 uptake and simple restrictions placed upon algae communities make it possible to screen the simultaneous impact of several pollutants on autotrophic production in aquatic systems.

2. Zinc, copper and cadmium were acutely and synergistically toxic to carbon uptake by phytoplankton.

3. Coeur d'Alene River dilutions and treatments of Zn and Cu demonstrate that increased volumes of river water decrease metal toxicity. Variable algal community structure and the presence of major cations, softwater, low pH values and bicarbonate concentrations and possible chelation affected metal toxicity.

4. Low inorganic carbon and moderately high nitrate and phosphate levels in the Coeur d'Alene River, Delta and Lake and St. Joe River show the importance of carbon rather than other nutrients in regulating growth of autotrophic populations.

5. Net phytoplankton was more abundant in the bays and open water of the lake than near the mouth of the Coeur d'Alene River with major peaks occurring during May and October. Nannoplankton standing crops were highest from May through October. Both net phytoplankton and nannoplankton were dominated by the diatoms <u>Melosira</u>, <u>Tabellaria</u>, <u>Asterionella</u> and <u>Synedra</u>.

6. Primary production in the southern end of Coeur d'Alene Lake is under the control of discharges from the Coeur d'Alene and St. Joe Rivers. Thus changes in the water quality of the lake tend to follow the seasonal fluctuations in the rivers.

7. The effect of wind action on epilimnetic production and weak stratification relate to the decreased depth of the southern end of the Coeur d'Alene Lake. Local mixing of lake waters may be impeding eutrophication by suppressing hypolimnetic oxygen depletion and anaerobic nutrient regeneration.

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