

Benthic Flux of Metals and Nutrients into the Water Column of Lake Coeur d'Alene, Idaho:

Report of an August, 1999, Pilot Study



Water-Resources Investigations Report 00-4132

U.S. Department of Interior

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By James S. Kuwabara¹, William M. Berelson², Laurie S. Balistrieri³, Paul F. Woods⁴, Brent R.Topping⁵, Douglas J. Steding⁶, and David P. Krabbenhoft⁷.

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Executive Summary

A field study was conducted between August 16 – 27, 1999, to provide the first direct measurements of the benthic flux of dissolved (0.2-micron filtered) solutes between the bottom sediment and water column at two sites in Lake Coeur d'Alene, Idaho, (Background, Fig. 1, Field Schedule: Table 1). Trace metals (namely, cadmium, copper, manganese, mercury species, and zinc) and nutrients (namely, ammonia, nitrate plus nitrite, oxygen, orthophosphate and silica) were solutes of primary interest. Benthic flux (sometimes referred to as internal recycling) represents the transport of dissolved chemical species between the water column and the underlying sediment.

With a variety of remedial strategies under consideration for the Coeur d'Alene River basin, the primary question posed in this pilot study was, "Is the magnitude of the benthic flux of metals and nutrients in Lake Coeur d'Alene significant relative to riverine inputs?" The question was motivated by a number of factors. First, a significant mass of metal has accumulated in bottom lake sediments downgradient of long-term (decadal time scales) mining activities (Horowitz and others, 1995). One might therefore question whether some fraction of these sediment-associated solutes may become remobilized for transport to the overlying water. Second, initial diffusive-flux calculations (Balistrieri, 1998) indicated that benthic flux of certain dissolved metals, like zinc and lead, may be significant at certain lake locations (i.e., the concentration gradient at the sediment-water interface, as described above, was large enough to drive significant transport). Third, water-column gradients for all metals and nutrients (except manganese) have exhibited increases near the bottom sediment as one might expect when a benthic source is dissipated upwards and horizontally. Fourth, changes in oxidizing or reducing (redox) conditions and nutrient availability near the sediment-water interface can dramatically alter the mobility of metals and ligands associated with the bottom sediment of the lake (La Force and others, 1998). Ligands are anions or molecules that form complexes with metals. Finally, there is a growing body of evidence from other aquatic systems that benthic flux or internal recycling of contaminants and nutrients is an important process to consider in developing appropriate water-quality models (Berelson and others, 1982; Flegal and others, 1991; Kuwabara and others, 1999). The question posed in this pilot study may therefore affect our fundamental view of contaminant transport in Lake Coeur d'Alene.

This report is formatted unconventionally in the fashion of a pyramid in an effort to effectively serve the diverse group of people that want to access the information in various levels of detail (<u>Appendix 1</u>). Using hyperlinks to supporting figures and tables, and an electronically linked Table of Contents, the report enables quick transitions between the initial summary

information (figuratively at the top of the pyramid) and later details of methods or results (that is, figuratively towards the base).

Both sampling sites for this study were in Lake Coeur d'Alene down gradient of the mouth of the Coeur d'Alene River: one in the main channel 7 km down gradient of the mouth of the river (33 m depth), and the other in an embayment, Mica Bay, 17 km down gradient of the mouth (27 m depth). At each site, water-column samples were collected to observe any vertical water-quality gradients. An *in situ* flux chamber, hereafter referred to as a lander, automated to sample chamber water 6 times during an incubation period, was deployed multiple times at each site (i.e., four times in Mica Bay and three times at the main channel site; <u>Table 1</u>) to determine dissolved nutrient, oxygen, radon, metal and bromide (tracer) fluxes (<u>Fig. 2</u>). Sediment cores were also collected for incubation experiments to provide complementary flux estimates and benthic biological characterizations (<u>Fig. 3</u>). These benthic flux measurements were often similar in magnitude to areally averaged riverine fluxes. The following major observations from interdependent physical, biological and chemical data were made:

Physical Data

- 1. The surficial substrate at both embayment (Mica Bay) and main-channel (near mouth of Coeur d'Alene River) sites was characterized by high porosity (~ 90%) at the sediment-water interface. This is consistent with direct observations of unconsolidated surficial material in incubated cores (Table 2; Methods).
- 2. Composition of the surficial material was quite different at the sites, with Mica Bay exhibiting detrital and macroinvertebrate-associated material, while the main-channel surficial material was dominated by inorganic particles coated with an orange, ferric hydroxide-like material (Fig. 4). Analysis of the coating mineralogy is proceeding. It should be noted that if the coating was primarily ferric hydroxide, the neutral pH of the water column would provide conditions favorable for adsorption of metals and certain ligands (e.g., orthophosphate) onto these coatings, thereby affecting the mobility of these solutes.

Biological Data

- 1. The biological data reflected an oligotrophic system where taxonomic analyses revealed very few if any living macroinvertebrates even at Mica Bay where only remnant material from macroinvertebrates were abundant (Table 3).
- 2. Chlorophyll-*a* concentrations were consistently below 5 micrograms per square centimeter (Table 4).
- 3. Benthic bacterial concentrations were of the order of 10^8 10^9 cells per gram-surficial sediment (<u>Table 5</u>). These concentrations fall within a wide range of published concentrations for lake sediments from approximately $10^6 10^7$ cells per dry gram lake sediment using plate-counting techniques (Hayes and Anthony, 1959; Young, 1978; Ehrlich, 1981) to 10^6 10^{10} cells per dry gram lake sediment using direct counts ((Jones and others, 1979, Harrington and others, 1998a). These microbial communities may be critical in establishing the redox gradients that regulate the

remobilization, transformation and subsequent transport of sediment-associated contaminants

<u>Chemical Data</u> - Multiple lines of evidence indicate that benthic flux at both lake sites was diffusion dominated during our pilot study in August. Because of the broad scope of chemical parameters determined in this study, the observations are organized with parameters of similar behavior. Unless otherwise specified, the concentrations discussed in this section operationally refer to dissolved (i.e., 0.2 micron-filtered) samples.

- 1. Dissolved oxygen, radon and injected bromide Dissolved oxygen was measured during lander deployments as an indicator of microbial respiration of carbon, and oxidation of reduced metals. Bromide and radon were used as tracers of hydrologic transport between chamber water and sediment pore water. Dissolved oxygen was measured in cores to confirm contrasting overlying-water conditions during coreincubation experiments (Table 6).
 - a. Dissolved oxygen Oxygen consumption measured during lander deployments was similar between stations and deployments (combined range of 6.0 to 9.5 millimoles O₂ per square meter per day; <u>Table 7</u>). This range is consistent with the low biological activity reflected in the macrofaunal and benthic chlorophyll-*a* analyses. There was no spatial pattern to the oxygen flux data with respect to Mica Bay or the main-channel station near Rockford Bay (Oxygen discussion).
 - b. Bromide The temporal loss of injected bromide during lander deployments for all sites indicated that diffusion was the primary transport process occurring on the lake bottom during the pilot study. There is enough uncertainty in the Br data and the diffusion model to allow for some small amount of bio-irrigation, but the system is predominantly diffusive (Bromide discussion).
 - c. Radon-222 Diffusive flux of radon, predicted from sediment radium measurements, is consistent with the measured fluxes of radon. This provides another line of evidence that diffusion is the primary transport mechanism for exchange of dissolved chemical species across the sediment-water interface (<u>Radon discussion</u>).
- 2. Water-column gradients Concentrations for all nutrients and metals, except dissolved manganese, indicate a vertical gradient at both sampling sites with elevated concentrations of dissolved chemical species near the sediment-water interface relative to shallower depths (<u>Table 8</u>). This may be generated by an upward benthic source, a settling of detrital material from the euphotic zone that becomes remineralized, a density-driven horizontal source, or a combination of the three (Fig. 5; Water-column discussion).

3. Nutrients (nitrogen species, orthophosphate and silica) – With the exception of dissolved silica, benthic flux of macronutrients determined from both lander deployments and core incubations were consistently significant (that is of equivalent or greater order of magnitude) relative to riverine sources. Although the results of this pilot study do not provide estimates of temporal variability of these fluxes and only first-order estimates of spatial variability, initial determinations would strongly suggest that benthic nutrient sources should not be neglected in nutrient-cycling models that affect water-quality management decisions.

Benthic flux ratios of total dissolved nitrogen to orthophosphate, derived from Lander results, suggest that the sediments act as effective traps for biogenically derived P. (Nutrient discussion)

Silica benthic flux determined from lander deployments provides a fourth line of supporting evidence of diffusion-control benthic flux at both sampling sites during the pilot study. By comparison, core incubations generated silica benthic fluxes that were consistently three to four times higher than observed in lander deployments. These methodological differences in diffusive transport may help explain differences in metal benthic flux estimates derived from the two approaches (See <u>discrepancies</u> below; <u>Nutrient discussion</u>)

4. Benthic flux of metals – Flux estimates from both lander deployments and coreincubations, when averaged over the affected lake area, were of similar magnitude as the dissolved-metal flux from the Coeur d'Alene and St. Joe Rivers even with oxygenated bottom waters in the lake (<u>Table 9</u>; <u>Metals discussion</u>). This is consistent with previous diffusive flux calculations determined from pore-water concentrations gradients (Balistrieri, 1998), and with the potential remobilization of sediment-associated metals that have been widely distributed at elevated concentrations on the lake bottom (Horowitz and others, 1995). Although core-incubations were designed to bracket the dissolved-oxygen conditions in the lake, discrepancies between the lander and core-incubation results suggest that the perturbations involved in the latter design, namely bubbling rather than magnetically stirring the overlying water of incubated cores, may have resuspended and altered chemical gradients at the sediment-water interface significantly.

Like the nutrients, some metals exhibited a positive flux that primarily occurred during the initial hours of incubation or deployment. Flux estimates presented in the tables indicate how nonlinearities generate lower flux estimates and coefficients of determination when data from the entire deployment or incubation were used relative to the initial hours (Core fluxes: <u>Table 10</u>, Lander fluxes: <u>Table 11</u>). This behavior suggests that for certain metals and nutrients a chemical equilibrium between the pore water and overlying water in the core or chamber was reached rapidly relative to the entire period of incubation or deployment.

With the possible exception of dissolved lead, no consistent trends between aerated and argon-purged cores were evident.

In the development of future remediation strategies for the watershed, it would seem unwise at this point to discount the importance of metal remobilization from the sediment, because measured benthic fluxes were significant in magnitude relative to riverine inputs.

5. Mercury - The first estimates of the benthic flux of dissolved mercury (total and methylated forms) for Lake Coeur d'Alene were determined. The total mercury and methyl-mercury flux from the sediment into the water column were of the order of 0.1 and 0.001 micrograms per square centimeter per year, respectively. This is orders of magnitude lower than the benthic flux of other metals, but similar to values determined elsewhere (Mercury discussion, Fig. 7). Consistent with previous studies, methyl-mercury flux in aerated cores was lower than in purged cores. Because this represents the first dissolved mercury study for the lake using ultra-clean sampling and analytical techniques, no comparative riverine-flux estimate is available.

With highly collaborative efforts between scientists, managers and stakeholders in general, initial steps are being taken to build process-integrated solute-transport models for the lake that may ultimately represent a critical management tool for the watershed. Recent benthic flux studies have only begun to address questions related to the importance of this process, and formidable challenges remain. Because redox sensitive zones in contaminated aquatic systems are so common, there is strong motivation to methodically overcome those challenges and find relevant answers.

RECOMMENDATIONS

- 1. As initially proposed, implement a sampling design that would provide spatial and temporal resolution of the variability of benthic fluxes for dissolved chemical species of environmental concern to determine if the fluxes as spatially similar as observed between Mica Bay and the main channel site in August, 1999, and to determine the magnitude and direction of fluxes across the sediment-water interface if the benthic community is as dense as observed by Ruud (1996).
- 2. Run one set of core-incubations without bubbling (using conventional magnetic stirring) in coordination with a lander deployment to determine whether comparable flux estimates are thereby generated.
- 3. Because the lake hypolimnion was oxic during the pilot study, it would be useful in future deployments to determine the benthic flux of dissolved species when the overlying water in the lander chamber is allowed to go anoxic.
- 4. As a test of the diffusive model, inject a microbial inhibitor into the lander chamber to observe any effects on benthic flux. Molybdate may be injected as an inhibitor of sulfate reduction so that the contribution of the sulfate-reducing bacteria to methylmercury production could be quantified.
- 5. Microbial studies in coordination with benthic flux experiments and measurements of carbon and nitrogen species would determine the temporal and spatial importance of denitrification as a component of nitrogen cycling in the lake.
- 6. Microbial studies are needed to quantify manganese reduction rates.
- 7. With such consistently high manganese benthic fluxes, why is there no water-column gradient for dissolved manganese? Does dissolved manganese (0.2 micron filtered) precipitate over time scales longer than our experiment. A simple field test could be performed to determine if manganese precipitated or aggregated to a filterable size in the water-column samples while being stored.
- 8. Pore-water studies with sediment chemistry that are coordinated with direct benthic flux measurements would provide critical information to interpret and develop quantitative models for processes regulating contaminant distribution in the lake.

BACKGROUND - What is benthic flux and why should it be considered?

Many fundamental processes affect the transport of dissolved chemical species (either a nutrient or a toxic substance; metal or ligand) through and within a lake. A conceptual model of these processes (Fig. 6) illustrates some familiar physically based processes that have been examined and carefully quantified for several years (e.g., advective transport and point source inputs).

Conversely, there are flux terms in the conceptual model that have received little attention. A prime example is the benthic flux term where no direct measurements have heretofore been available for Lake Coeur d'Alene. Benthic flux (sometimes referred to as internal recycling) represents the transport of dissolved chemical species between the water column and the underlying sediment. This flux can be either positive (that is, out of the sediment into the water column) or negative (consumed by the sediment). It can be variable over multiple temporal and spatial scales.

As a result of physical, chemical and biological changes in the vertical cross section, geochemical gradients take on a variety of forms (Fig. 8). The simplest case is when there is no gradient (That is, the concentrations of a substance above and below the sediment-water interface are equivalent.) In this case, there is no net transfer of that substance across the interface; **no benthic flux**. In contrast, concentrations of a dissolved substance may decrease in the water column and continue to decrease in the bottom sediment until that concentration is negligible. This would be typical of a negative benthic flux where the sediment **consumes** a substance, represented by dissolved oxygen where microbial respiration may create a sediment demand for oxygen.

Other vertical concentrations gradients near the sediment-water interface may show water-column concentration increasing near the sediment-water interface and continuing to increase in the sediment pore waters. This gradient can physically drive the **release** of dissolved chemical species from the sediment to the overlying water, generating a positive benthic flux. This might be represent by the diffusive flux of a metal or ligand that is remobilized in the sediment due to biotic and abiotic repartitioning reactions.

As with most processes in nature, confounding factors may regulate the benthic flux of biologically reactive substances. The vertical gradient for one dissolved species may be dependent on the gradient of another chemical species. For example, an **attenutated release** may occur when solute concentrations increase below the sediment-water interface only when another solute is depleted. Dissolved iron often falls within this category as suboxic conditions increase its solubility as it reduces from ferric to ferrous forms. Additionally, macroscopic invertebrates can biologically enhance the benthic flux by irrigating, or perturbing surficial sediment layers (**bioirrigation or bioturbation**). Certain productive benthic communities can enhance diffusive flux by orders of magnitude. In summary, vertical chemical gradients generated by a variety of interdependent processes induce the movement of a dissolved chemical species across the sediment-water interface.

In many aquatic environments, scientists and water-quality managers are only beginning to appreciate the importance of benthic flux. In recent years (that is within the past decade or two) people have gradually realized that there are non-hydrologic processes like benthic flux that must be incorporated into water-quality models to generate physically meaningful modeling results. The USGS has been involved in studies at lake Coeur d'Alene for about a decade, but as with many other environments, benthic-flux studies began only recently, in this case pore-water studies were done in 1992 and benthic flux calculations were done in 1998 (Balistrieri, 1998). Relative to other flux terms, quantifying benthic flux is instrument and manpower intensive.

As described in the Executive Summary, the primary question posed in this pilot study was, "Is the magnitude of the benthic flux of metals and nutrients significant relative to riverine inputs?" Although the technical rationale for posing that question is multifaceted (introductory comments), a major objective of the pilot study is to offer some help and scientific basis for directing regulatory strategies for the watershed by providing the first comparisons of direct benthic-flux measurements to riverine fluxes. For substances of potential environmental concern like mercury, where there has been little or no prior speciation studies, the first benthic flux measurements for the lake are provided. These initial measurements may be critical in developing a basin-wide understanding of the transport processes that regulate the distribution of nutrient and toxic solutes (that is, a budget for environmentally significant chemical species).

RESULTS AND DISCUSSION

<u>Physical Data</u> – Please refer to porosity table (<u>Table 2</u>).

Biological Data

1. Macroinvertebrates – Three striking differences were observed between the cores from within Mica Bay and from the main channel. First, Mica Bay cores contained many empty invertebrate cases (exoskeletons) compared to virtually none in main-channel cores. Whether the empty invertebrate cases in Mica-Bay cores originated at the site or were transported to the site is unknown. Higher frequency temporal sampling would probably determine whether there is an active benthic invertebrate community at these sites. Second, Mica Bay cores contained more organic detritus. Finally, cores from the main channel contained predominately large inorganic particles (Methods, Table 12)

A compilation of results from benthic lake studies indicates that the benthic community sampled during the pilot study was sparse at both sites relative to other oligotrophic or mesotrophic lakes (Fig. 9). Although this scarcity of macroinvertebrates (0-130 individuals per square meter) is consistent with preliminary samples taken in October, 1998, Ruud (1996) observed macroinvertebrate abundances two orders of magnitude greater in deep-lake sediments (water-column depths of 20 and 40 meters) in October, 1995. He reported a range of 10,000 to 98, 695 individuals per square meter from Ekman Bottom Dredge grab samples. The variability in macroinvertebrate abundance between and within studies indicates that the diffusion-dominance of benthic flux observed in this study may not always hold (Table 3).

- 2. Chlorophyll-a Please refer directly to table summaries (<u>Table 4</u>).
- 3. Benthic bacteria Previous microbial studies of Lake Coeur d'Alene sediments have consistently described the importance of the microbial community at establishing gradients in oxidation-reduction potential that facilitate changes in the chemical structure, mobility and biological availability of contaminants, particularly arsenic, in the lake (Harrington and others, 1998b; Cummings and others, 1999). Harrington and others (1998a) reported total microbial abundance in Lake Coeur d'Alene surficial sediments of ~10⁸ cells per gram wet weight by direct epifluorescent counts. Given the high porosity of surficial sediments (Table 2) this range converts to ~10⁹ cells per gram dry weight; a range consistent with the direct epifluorescent determinations of this study (Table 5). Estimated sulfate-reducing bacteria concentrations as high as 10⁶ cells per gram wet weight are among the highest reported (Harrington and others, 1998b). Given the benthic chlorophyll and macroinvertebrate results from this pilot study, one might logically question where the carbon source is that supports such impressive microbial abundances.

<u>Chemical Data</u> – For consistency with previous geochemical studies of Lake Coeur d'Alene, concentrations and flux estimates are provided in mass units. However, in the discussion of these results, especially with biologically related uptake or release that occur on a molecular basis, mass units are much less meaningful than molar units. Therefore the discussion of dissolved chemical species, particularly with regard to nutrient fluxes and flux ratios are presented in molar units with equivalent mass units parenthetically provided.

- 1. Dissolved oxygen Consistent with the low benthic chlorophyll-a concentrations (< 5 micrograms per square centimeter), oxygen-consumption rates are reflective of low benthic biological activity. Cornwell and Kipphut (1992) determined similar oxygen fluxes into Toolik Lake sediments that averaged 7.6 millimoles O₂ (240 milligrams) per square meter per day and described them as "extremely low rates of benthic oxygen consumption for a lake environment." This is consistent with lake data compiled by Hutchinson (1957) and Hayes and MacAulay (1959) indicating a range of benthic oxygen consumption from 2-33 millimoles O_2 (64 – 1100 milligrams) per square meter per day. Hargrave (1969) compiled oxygen results from various aquatic environments and determined that much of the variability in the data ($r^2 = 0.72$) could be explained by bottom-water temperature. His empirical expression: ln(Y) =1.74ln(T) - 1.30, where Y is sediment oxygen consumption in milliliters O₂ per square meter per hour, and T is temperature in degrees centigrade, may be applied to Lake Coeur d'Alene (bottom-water temperature of 7°C at time of sampling). The modeled oxygen-consumption rate would be within the range of measured values (~8 millimoles O₂ (260 micrograms) per square meter per day). This suggests a possible link between microbially mediated sediment-oxygen demand and bottom-water temperature that could be tested in future studies.
- 2. Bromide Multiple approaches were used to confirm that benthic flux from lake sediments during the pilot study was diffusion dominated. First and most directly, there simply was not enough biota to generate biologically enhanced advection through bioirrigation or bioturbation (Table 12). Secondly the time series of injected bromide consistently indicated a loss of bromide into the sediment that is consistent with diffusive rates (Table 13, Fig. 10). Finally, radon emanation measurements also indicate a flux from the sediments into the water column that is diffusion dominated (Table 7). So the conceptual model for benthic flux would be somewhat simplified, because the benthic community exerted negligible effect on flux due to bioirrigation or bioturbation. This is contrary to many other aquatic systems where the benthic biota can enhance the flux by orders of magnitude. It should also be noted that macroinvertebrate abundances measured at other sites in Lake Coeur d'Alene in October, 1995 by Ruud (1996) suggests that there is dramatic spatial and temporal variability in benthic-macroinvertebrate abundance, and so this simplification may not always hold.

In addition to measurements of bromide loss to the sediment, the initial bromide concentration after injection was used to determine the overlying water-column heights in the lander's flux chamber which were approximately 7.6 and 10.0 centimeters for the second and fourth Mica Bay deployments, and 11.4, 13.1 and 12.8 centimeters for the three main-channel deployments, respectively. The first

deployment at Mica Bay overpenetrated the sediment and the chamber height of the third Mica Bay deployment was apparently (based on dissolved-oxygen chamber data) modified twice during the incubation by public tampering.

3. Radon-222 – Consistent radon flux from lander deployments and predicted sediment flux from radium measurements indicated that diffusion is the primary transport mechanism for exchange of dissolved chemical species across the sediment-water interface. The virtual absence of a macroinvertebrate community to enhance advective transport by bioturbation corroborates this conclusion.

Radon fluxes from the chambers were determined to range from 99-242 atoms per square meter per second, with all but one of the chamber fluxes between 99-128 atoms per square meter per second. The one site with the high radon flux value cannot be easily interpreted as a site of high bio-irrigation as the Br data do not support this interpretation. It is possible that the distribution of Ra in lake sediments is patchy. The flux values reported are 10-20% greater than fluxes established by excluding bottom water from the model fit. However, including the radon in bottom water value to the model fit adds constraint to the flux by significantly increasing the number of data points modeled. The flux values are reported using both approaches (Table 7).

The diffusive flux of radon at the Mica Bay and main-channel sites were determined to be approximately 110 and 133 atoms per square meter per second, respectively.

That the diffusive flux of radon, predicted from the sediment radium measurements, agrees so well with the measured fluxes of radon is clear indication that diffusion is the primary transport mechanism for exchange of dissolved species between the bottom sediment and overlying water column. The bromide and radon data show good agreement on this point.

Few other measurements of lake sediment radon emanation rate are published, but they indicate that radon fluxes in Lake Coeur d'Alene are 2-4 times greater than typical lake sediments (Imboden and Joller, 1984; Emerson, 1974). This relatively high flux of radon from Lake Coeur d'Alene sediments indicates that the sediments of the lake have scavenged a large amount of radium. Mn-oxides are known to be effective at scavenging Ra and thus the oxides present in lake sediments are likely the source of the large radon fluxes measured.

4. Water-column gradients – With the exception of dissolved manganese, water-column concentrations for all nutrients and metals were elevated near the sediment water interface relative to the shallower depths (Fig. 5; Table 8). As indicated in the Background Section (Fig. 8), this trend is one indication that remobilization and accumulation of a chemical species in pore waters can result in a release of those solutes into the overlying water, generating a positive benthic flux. It should be noted, however, that elevated bottom-water concentrations may also be generated by a settling of detrital material from the euphotic zone that becomes remineralized, or by a density-driven, horizontal, riverine source. Given that elevated trace-metal

concentrations in bottom lake waters were also observed in October, 1998, when Chlorophyll-a concentrations are not typically elevated, it seems less likely that the settling of planktonic material caused the observed water-column gradients (Woods and Beckwith, 1997). Furthermore, the density driven horizontal source is unlikely because such thermal stratification, generated by colder riverine water relative to shallow lake water only occurs during winter months (Woods, unpublished data). Conclusive identification of the dominant process that generated elevated bottomwater concentrations is beyond the scope of this pilot study, but circumstantial evidence would emphasize a benthic source to the overlying water.

5. Nutrients - Oxygen uptake is likely partitioned into two major reactions, oxidation of organic carbon and oxidation of reduced metals. As the flux of reduced Fe and Mn is positive, out of the sediments, it could be assumed that the oxygen uptake rate measured by the chamber is primarily the result of carbon oxidation. The molar ratio of oxygen uptake to carbon oxidation is typically assigned a value of 1.2 (that is, the inverse of the respiratory quotient). Thus it could also be assumed that between 6 and 7 millimoles C (72 to 84 milligrams) per square meter per day were being consumed on the lake floor. If a system is in steady state, this value of benthic carbon oxidation must represent the minimum value for lake primary productivity.

The ratio between carbon oxidation and ammonia release is dependent on the carbon to nitrogen ratio in the organic matter undergoing degradation. Freshwater algae have a molar carbon to nitrogen ratio of approximately 6.7 (5.7 mass ratio, Wetzel, 1983). The expected efflux of N, either as ammonium or nitrate would be about 1 millimole N (14 milligrams) per square meter per day (That is, oxygen uptake divided by 1.2 and by 6.7). The measured efflux of fixed N is 0.4-0.6 millimoles N (5.6 to 8.4 milligrams) per square meter per day. This indicates that: (a) the molar carbon to nitrogen ratio of lake algae is closer to 14 than 6.7, or (b) sedimentary nitrification and denitrification are responsible for transferring roughly 50% of the fixed N into N_2 , thereby removing it from the nutrient pool of the lake, or (c) some combination of both explanations is true.

With the exception of dissolved silica, estimates of macronutrient benthic flux from lander deployments and core-incubations were consistently similar to or greater than areally averaged riverine flux (Table 9). In an oligotrophic aquatic system, the concept of a limiting nutrient is a fragile one, because typically the concentrations of dissolved substances are balanced in such a way that minimal changes in concentration of one chemical species can alter nutrient limitation. The mechanism of zinc toxicity to aquatic primary producers is an interference with phosphorylation reactions (Bates and others, 1982; Kuwabara, 1985). So as zinc bioavailability increases, phosphate assimilation is retarded. Conversely, when phosphate bioavailability increases, zinc toxicity effects are mitigated. Because orthophosphate has a high affinity to adsorb onto metal-oxide surfaces under oxic, pH-neutral conditions (Kuwabara, 1992), the molar nitrogen to phosphorus (N:P) flux ratios for Lake Coeur d'Alene have particular significance. The molar N:P flux ratio into benthic chambers is 33 for Mica Bay and 70 for the Rockford site (Fig. 11). By comparison, the molar N:P Redfield Ratio is only 16 (7 by mass ratio). That is, on

average, approximately 16 moles of nitrogen (220 grams) is taken up for every mole of phosphorus (31 grams) to generate freshwater algal tissue . The higher benthic flux ratio of nitrogen to phosphorus for both sites suggests that the lake sediments act as effective traps for biogenically derived P, and could significantly affect orthophosphate availability, and hence zinc toxicity, in the water-column by sorption/desorption reactions. The molar N:P riverine flux in 1999 was approximately 32, also much higher than the Redfield Ratio.

Dissolved silica fluxes complement bromide injections as a natural tracer of physical and biologically enhanced solute transport across the sediment-water interface. Previous benthic studies have focused on bacterial and macroinvertebrate communites (Ruud, 1996; Cummings and others, 1999), and very little is known about the structure of the benthic algal community. However, based on the fact that diatoms consistently dominate the phytoplankton community structure (Woods and Beckwith, 1997), it is reasonable to speculate that diatoms also represent a significant component of the benthic algal community. Assuming that the silica flux results from dissolution of biogenic material (e.g., diatom frustules) as it does in other aquatic systems, a stoichiometric relationship similar to a Redfield Ratio can be used to estimate a silica flux (Si:N molar ratios of approximately 0.8 to 1.2; Brezeninski, 1985). Using calculations analogous to those for total nitrogen above, one might expect silica fluxes to be approximately the (oxygen uptake)/(1.2*6.7*(N:Si)) or 0.6 to 1.4 millimoles of silica per square meter per day (600 to 1500 micrograms silica per square centimeter per year). This is consistent with the measured silica fluxes from the lander deployments (1148 to 1866 micrograms silica per square centimeter per year; (Table 14: Si)). In contrast, elevated dissolved silica fluxes were determined from core incubations (2897 to 6164 micrograms silica per square centimeter per year; (Table 14: Si)) relative to: (1) estimates derived above based on biogenic dissolution, (2) measured fluxes from lander deployments, and (3) diffusive silicaflux estimates based on reported interstial-water concentrations in the vicinity of our sampling sites (i.e., data from Vahalla and East Point; Balistrieri, 1998). The elevated dissolved silica fluxes during core incubations is consistent with the idea that excessive mixing of the overlying water in the cores may have disrupted the chemical gradients at the sediment-water interface (See Dissolved Zn and Cd)

Time series of dissolved nutrients from incubated core indicated that concentration increases in the overlying water primarily occurred in the initial hours of the incubation. However, even if data over the entire incubation are used in the flux calculation, the benthic flux of orthophosphate and nitrogen species are still significant relative to areally averaged riverine fluxes (<u>Table 9</u>). For example, the average orthophosphate fluxes from Mica Bay and main-channel cores were 100 and 120 micrograms phosphorus per square centimeter per year, respectively, compared with a riverine flux of approximately 60 micrograms per square centimeter per year from the St. Joe and Coeur d'Alene Rivers in 1999 (Woods and Beckwith, unpublished data; <u>Table 9</u>). Ammonia benthic flux averaged approximately 730 and 300 micrograms nitrogen per square centimeter per year from Mica Bay and mainchannel cores. This is within the same order of magnitude of total nitrogen flux from

the St. Joe and Coeur d'Alene Rivers in 1999 (approximately 560 micrograms per square centimeter per year).

<u>Trace Metals</u> (General observations) - The magnitude of the flux varied among metals over orders of magnitude (<u>Fig. 12</u>). Measured flux was not always positive or out of the sediment. Negative fluxes represent solute transport into the sediment from the overlying water. For each of the metals the magnitudes of the the fluxes, whether positive or negative, are significant relative to areally averaged riverine fluxes (<u>Table 9</u>). Data from 1999 monitoring efforts indicate that riverine inputs of metals are predominantly from the Coeur d'Alene River.

- 6. Copper, iron and mercury species. These solutes, like the nutrients, exhibited a positive flux that primarily occurred during the initial hours of incubation or deployment. Calculations provided in the tables indicate how nonlinearities generate lower flux estimates and coefficients of determination when data from the entire deployment or incubation was used relative to the initial hours (Table 15; Fig. 7, Fig. 13, Fig. 14). This behavior suggests that for certain solutes a chemical equilibrium between the pore water and overlying water in the core or chamber was reached rapidly relative to the entire period of incubation or deployment. Alternatively, the initially positioning of the lander may have disturbed the sediment-water interface, temporarily increasing the flux, then returned to steady state.
- 7. Dissolved organic carbon (DOC) Dissolved organic carbon (DOC) DOC concentrations serve as a model for the abundance of organic ligands that can complex and enhance the solubility of metals. In many aquatic systems, certain dissolved metals predominantly exist as organic complexes (Mantoura and others, 1978; McKnight and others, 1983). Although DOC water-column gradients were not measured in this study, preliminary samples taken in October, 1998 near the main channel indicated an elevated bottom-water concentration (1.17 + 0.01 milligram)carbon per liter) relative to the surface (1.07 + 0.04 milligrams carbon per liter). It is therefore not surprising that DOC benthic flux was consistently positive (out of the sediment). However, in contrast to many of the dissolved inorganic substances, DOC concentrations showed a generally linear increase throughout the 12-hour coreincubation period (9 of 12 cores with coefficients of determination >0.6; Table 16). The longer time-scales of linearity for DOC flux relative to nutrient and metal flux suggest that complexation of metals with organic substances did not control the speciation of metals near the sediment-water interface in the cores. Although DOC flux differences between sites were not statistically significant, given the higher detrital composition of the surficial sediment at Mica Bay (Fig. 4), it is curious that the mean flux from Mica Bay cores (approximately 1800 micrograms carbon per square centimeter per year) was less than the mean from the main-channel cores (approximately 2700 micrograms carbon per square centimeter per year). No measurements of riverine-DOC loads are currently available for comparison.
- 8. Dissolved lead (Pb) As with the dissolved chemical species mentioned in item 3 above, Pb flux primarily occurred in the initial hours. Purged cores had an initially elevated Pb concentration, but flux was generally lower than aerated cores (<u>Table 10</u>).

Because purged cores were conditioned and incubated under a positive argon pressure (Coring methods), but not in a glove bag, Pb may have been mobilized in the purged cores during set up for incubations (i.e., when the overlying water for conditioning was replaced to begin the incubation). It is somewhat surprising that differences between aerated and purged cores are not more evident, especially for the other metals and nutrients. Although benthic flux measurements from purged cores and lander deployments were lower than riverine inputs estimated for 1999, fluxes from aerated cores were similar to riverine flux (Table 9).

9. Dissolved zinc (Zn) and cadmium (Cd) – As one might expect from preliminary porewater data and flux estimates (Balistrieri, 1998), the lander data indicated a fairly consistent positive flux of Zn and Cd from the sediments of magnitudes similar to riverine fluxes (Fig. 15, Fig. 16). As with the other metals, nonlinearities in the concentration time series caused the magnitude of these fluxes to be dependent on the window of incubation time that was used in the calculation.

In contrast, the core-incubations indicated a fairly consistent negative flux, that is, a flux of dissolved zinc and cadmium into the sediment. Before and during incubation, the overlying water in each core was bubbled with either compressed air or ultrahigh-purity argon to maintain either oxygen-saturated or suboxic conditions (Table 6). Typically, a magnetic stirrer is used less vigorously to keep the overlying water from stratifying (Fig. 17). Although the purpose of this modification in the core incubations was to bracket the natural conditions sampled during the lander deployments, the overlying water in the incubated cores may have been so vigorously bubbled that the sediment-water interface and its associated gradients were disturbed. Flooding events in the Lake Coeur d'Alene watershed have been hypothesized to result in: (1) enhanced mobility of contaminants due to changing availability of nutrients to benthic microbes and (2) shifts in vertical redox gradients that promote precipitation of certain metal sulfides (La Force and others, 1998). If this hypothesis is true, then the difference depicted between lander and core-incubation results may represent a range of potential flux over extremely different hydrodynamic conditions; that is, conditions when there is little mixing and physical perturbation of the surficial sediment, to events where there is greater turbulence and advective transport near the bottom sediment. Irrespective of those differences, the magnitude of benthic flux from both lander and core-incubations are similar to riverine inputs (Fig. 12).

10. Mercury – The dissolved-mercury flux (Fig. 7) was orders of magnitude lower than the flux of other dissolved metals (Fig. 12), because the magnitudes of the concentrations and the gradients were orders of magnitude lower (Table 15). Furthermore, the benthic flux of methyl-mercury, the biologically reactive form of the element, was approximately two orders of magnitude lower than the flux for total mercury. Because the mechanisms of toxicity for different metals are different, and methylated mercury accumulates in tissues of organisms where trophic transfer can be fairly efficient, the relatively low benthic flux estimates for mercury species does not imply that this flux should be disregarded as environmentally insignificant.

Methyl-mercury fluxes in cores from both sites were lower in aerated cores than in argon-purged cores. This is consistent with previous studies indicating that mercury methylation may be constrained in the presence of oxidized surficial sediments, and that methyl mercury may be retained by ferric-oxide surfaces and released in reduced sediments (Gagnon and others, 1996; Gagnon and others, 1997).

These are the first measurements of mercury benthic flux in the lake, so comparative results for this lake or others in the vicinity are not available. Furthermore, very few mercury studies in lakes have included determinations of benthic flux. Working at Pallette Lake in Wisconsin, a pristine, ground-water flow-through lake, Krabbenhoft and others (1998) estimated that maximal methyl-mercury benthic flux occurred in littoral sediments during the spring. Spring, high-flow periods may enhance methylation rates by increasing the availability of nutrients that stimulate microbial activity near the sediment-water interface (Kelly and others, 1997; La Force and others, 1998). The flux was dominated by pore-water (or ground-water) advection and ranged from 0.16 to 2.25 nanograms per square centimeter per year. This range for methyl-mercury benthic flux from Pallette Lake's littoral zone, predominantly driven by advective flux, brackets the initial determinations presented herein for Lake Coeur d'Alene, dominated by diffusive flux (0.2 to 1.7 nanograms per square centimeter per year). In contrast to the pristine setting of Pallette Lake, Gill and others (1999) measured mercury benthic fluxes in Lavaca Bay, a secondary embayment on the Texas Gulf Coast that received mercury discharge between 1966 and 1979 from a chlor-alkali facility. They estimated methyl-mercury diffusive fluxes from 15 sites that ranged from 0.01 to 55 nanograms per square centimeter per year, as well as a direct chamber measurement from one site of 0.6 nanograms per square centimeter per year. Mindful of the major differences between these aquatic environments, it is interesting to note that the range for methyl-mercury flux in this study (0.2 to 1.7 nanograms per square centimeter per year) tightly brackets their direct measurement and is bracketed by the overall range for their spatial network. As mentioned in the Executive Summary, this represents the first dissolved mercury study for the lake using ultra-clean sampling and analytical techniques. No comparative riverine-flux estimate is therefore available.

STUDY DESIGN AND METHODS

The protocol described in this section focuses on method applications in this pilot study. Details (e.g., quality control specifications) for each analysis has been previously documented (Woods and others, 1999).

Physical Data

<u>Sediment Porosity</u> – After core-incubations, approximately 10 milliliters of surficial sediment was collected from each core, then bottled, and refrigerated in darkness. Wet weight and dry weight after lyophilization was measured to calculate porosity (<u>Table 2</u>).

Biological Data

- 1. <u>Benthic Macrofauna</u> After core incubations, each core was sieved (500-micron mesh). The sieved samples were fixed with 10% buffered formalin, picked, sorted and taxonomically analyzed (Fig. 18).
- 2. <u>Benthic Chlorophyll-a</u> Each incubated core was sampled in triplicate for benthic chlorophyll-a. Surficial sediment was collected on a glass-fiber filter and buffered with magnesium carbonate. Samples were then frozen in darkness until spectrophotometrically analyzed (Thompson and others, 1981; Franson, 1985) (<u>Fig. 19</u>).
- 3. <u>Benthic Bacteria</u> After core incubations, each core was sub-sampled using a syringe corer. Approximately 10 milliliters of surficial sediment was collected and fixed with 0.5 milliliters of 37% formalin. Samples were then refrigerated in darkness. Benthic bacterial concentrations were determined by direct epifluorescent counts using acridine-orange preparations.

Chemical Parameters

1. <u>Lander deployments</u> – An *in-situ* benthic-flux chamber (lander) specifically designed for trace-element studies was deployed multiple times at each of the two lake sites from the research vessel Second Chance (Fig. 2). The device was set down with the help of EPA divers so that a rectangular acrylic chamber on the bottom of this device would penetrate the sediment but still retain some overlying water. This overlying water was isolated from the ambient lake water by closure of a lid, which initiated the incubation of approximately 1500 square centimeters of lake-bottom sediment surface. The deployments ranged from about a half day to two days, and were iteratively adjusted based on oxygen consumption data observed in previous lander deployments. Before each deployment, the lander was programmed to sample the overlying water within the chamber at 6 specified times during the chamber incubation. For trace-element and nutrient analyses, sampled water was stored in fluoroethylene polymer columns until the lander was retrieved. The time-series of

- solute concentrations from a deployment was used to determine an estimate of benthic flux. At the beginning of each deployment, bromide was injected into the chamber as a tracer of physical mixing processes (i.e., diffusion, advection).
- 2. Water-column gradients Prior to coring at both lake sites, water-column samples were collected for analysis of macronutrients by automated spectrophotometry, trace metals primarily by inductively coupled plasma mass spectrometry, and mercury species by cold-vapor atomic fluorescence spectroscopy. Samples were pumped from three depths (2 meters below the surface, mid-depth, and 2 meters above the bottom) using a high-displacement peristaltic pump and a tethered length of rigid fluoroethylene polymer tubing.
- 3. Coring operation At each of the two lake-sampling sites, eight cores were taken using a coring device fabricated from non-metallic parts (Savillex Corporation, Minnetonka, MN). To avoid sample contamination, wetted surfaces of the coring device and core tubes were acid-washed polypropylene or fluoroethylene polymer. Four of the eight cores from each site were aerated and the other four argon-purged overnight to condition wetted surfaces before the incubation period (Fig. 3, Fig. 17). Three of the four aerated and argon-purged cores were selected for incubation based on visual determination of any disturbances of the sediment-water interface. Water overlying the sediments in the six cores per site was sampled at four intervals during a 12-hour incubation. Trace element and nutrient samples were processed in a Class-100 laminar-flow hood. As with lander samples, the concentration time series was used to determine the benthic flux from each of the 12 incubated cores.
- 4. Riverine Flux Estimates Areally averaged riverine fluxes were based on two estimates: (1) annual riverine loads determined in 1999 as part of a lake monitoring program (Woods, 2000), and (2) the estimated affected lake area (108.2 square kilometers; Horowitz and others, 1995). Alternatively, a mass flux to match riverine-load units (mass per unit time) could have been estimated from benthic flux measurements. However, for consistency and comparison with previous diffusive-flux estimates (Balistrieri, 1998), the benthic and riverine fluxes were represented in units of micrograms per square centimeter per year (Table 9).
- 5. Dissolved oxygen In lander deployments, dissolved oxygen fluxes were measured within the lander using a pulsed electrode mounted inside the chamber. A second electrode positioned outside the chamber tracks oxygen tension in the ambient lake water. For core incubations, dissolved oxygen in the overlying water and replacement water was determined by micro-Winkler titrations (Broenkow and Cline, 1969; Redden, written communication, 1999]. In core-incubation experiments, dissolved oxygen was measured to confirm contrasting overlying-water conditions during incubations (i.e., suboxic versus oxygen-saturated conditions) (Table 6). Detectable dissolved-oxygen concentrations were routinely observed in the overlying water of argon-purged cores despite vigorous bubbling (100 150 milliliters per minute) during the incubation. Oxygen diffusion through the fluorethylene-polymer core walls could conceivably have maintained residual concentrations in the overlying water, but the measured oxygen may also represent a lower limit in the

analysis of small water-sample volumes (approximately 10 milliliters) transferred from the cores. Use of a glove bag for processing dissolved-oxygen samples may be tested to lower that limit

6. Bromide (Br) – Bromide and radon were used as tracers of hydrologic transport between chamber water and sediment pore water. Bromide is a purposeful tracer, injected as a CsBr solution (of a known concentration and volume) into a chamber at the beginning of a lander deployment. The initial dilution of Br within chamber water provides a measure of the volume of incubated water trapped and the rate of Br loss from the chamber is diagnostic of exchange processes across the sediment-water interface. Br behaves as a conservative tracer of water transport and thus the change in Br concentration with time is indicative of the exchange rate between pore water and the overlying chamber water. The rate of Br disappearance from the chamber follows a nearly exponential pattern. Bromide loss from the chamber water after a certain period of time can be predicted on the basis of known rates of Br diffusivity. This value can be compared to the observed data. As samples were removed, bottom water flowed into the chamber. Knowing the bottom-water bromide concentration, and the volume of the chamber and water withdrawn, the sample bromide concentrations can be dilution corrected. The initial bromide concentration after injection was used to determine the overlying water-column heights which were approximately 7.6 and 10.0 centimeters for the second and fourth Mica Bay deployments, and 11.4, 13.1 and 12.8 centimeters for the three main-channel deployments. The first deployment at Mica Bay overpenetrated the sediment and the chamber height of the third Mica Bay deployment was apparently modified twice during the incubation by public tampering.

Dissolved bromide concentration of filtered samples was determined by flow-injection colorimetery (Fig. 20).

- 7. Radon-222 Radon is a naturally occurring radioisotope (3.85 day half-life) produced by radium-226 decay within the sediments. In addition to flux determinations from samples taken during lander deployments, radon flux was also estimated following the determination of radon emanation strength of lake sediments. Emanation rate was established by incubating a few tens of milliliters of lake sediment in a jar filled with lake water. The sediment was incubated long enough for the radon to reestablish equilibrium with the radium contained within the sediment. Radon diffusive flux was then estimated according to procedures described by Berelson and others (1982).
- 8. Nutrients (nitrogen species and orthophosphate) Dissolved nutrients from water-column sampling, lander deployments and core incubations were filtered with 0.2 micron polycarbonate filters. The filtered samples were immediately refrigerated in darkness, but unlike trace metal samples, were not acidified. Nutrient analyses were performed by automated spectrophotometry (Fig. 21).
- 9. Dissolved metals by Inductively Coupled Plasma Mass Spectrometry Dissolved trace-metal samples from water-column sampling, lander deployments, and core

incubations were filtered with 0.2 micron polycarbonate filters. Filtered samples were acidified with quartz-distilled nitric acid to 0.03N, then refrigerated in darkness until their analyses. Aliquots of lander samples were diluted (by approximately a factor of 10) due to sample-volume constraints. Metal analyses were performed by direct-injection inductively coupled plasma mass spectrometry using external standardization (Fig. 22).

- 10. Dissolved iron by graphite-furnace atomic absorption spectrophotometry (GFAAS) This method was used only for dissolved iron from undiluted lander samples because the dilution of sample aliquots resulted in dissolved-iron concentrations near ICP-MS detection limits. There was insufficient volume of undiluted lander samples to analyze by ICP-MS (Fig. 23).
- 11. Mercury speciation by cold-vapor atomic fluorescence spectroscopy (CVAFS) Total dissolved mercury was determined in filtered aqueous samples by CVAFS after evolved elemental mercury was purge and trapped onto gold-coated sand columns. Methyl-mercury also analyzed by CVAFS, but after a distillation and aqueous-phase ethylation method (Fig. 24).
- 12. Dissolved organic carbon (DOC) Dissolved organic carbon was determined by high-temperature non-catalytic combustion (Qian and Mopper, 1997). Sodium phthalate were used as standards. Low-DOC water (blanks <40 micrograms-organic C per liter) was generated from a double-deionization unit with additional ultraviolet treatment (Milli-Q UV Millipore Corporation) (Fig. 25).

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Product names are provided for identification purposes only and do not constitute endorsement by the U.S. Geological Survey.

Appendix 1: Comments on the Report Structure

A major objective of this electronic document is to provide a structure that is easily accessible to a potentially wide range of interests in this work. Agency reports in the form of electronically linked products are a fairly recent alternative, but pathways within this document have been constructed to be both logical and intuitive. In addition to hyperlinks within the document to supporting figures and tables, Appendices 2 and 3 provide a quick way to directly review and examine all figures and tables.

Although hard copies of this report are available on request, the advantages of the electronic version relative to the hard copy are substantial in many respects, but particularly in speed of information access at multiple levels of detail.

Your comments about how to improve this evolving type of product are most welcome and may be directed to any of the email addresses provided in the title page, but we request that at least a copy of all comments about the report be addressed to the major author (kuwabara@usgs.gov) so that they may be compiled for future revisions and reports.

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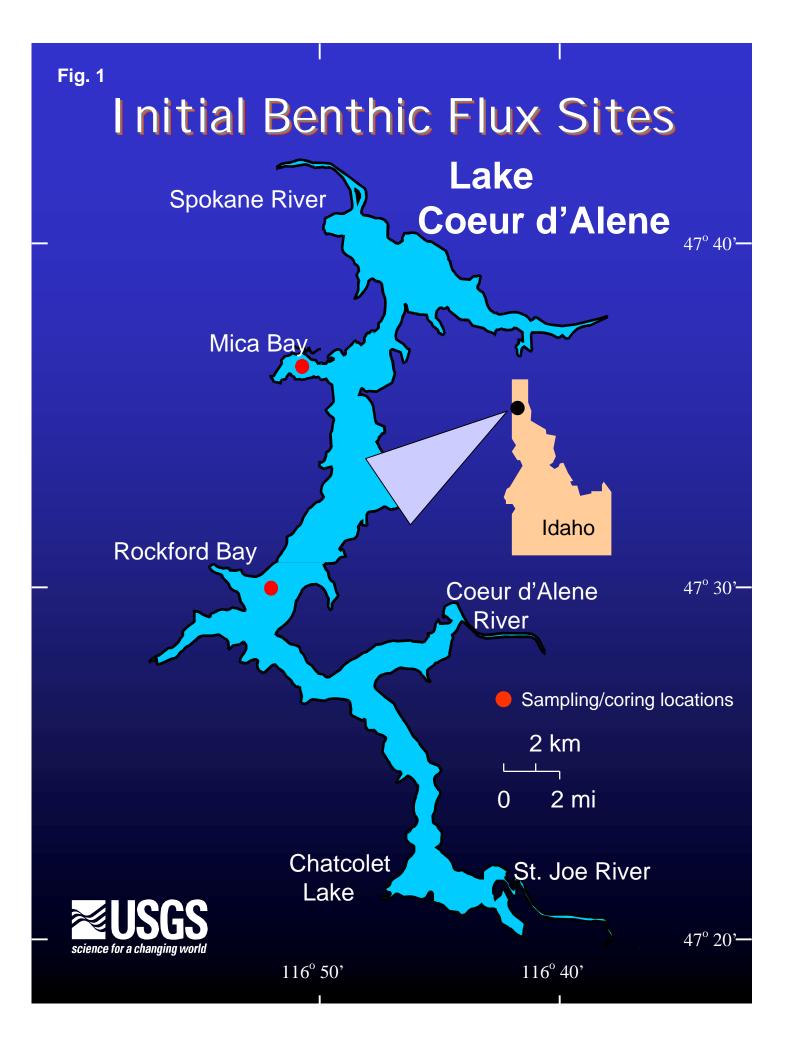
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^a Where applicable, error bars in the figures represent standard error about the mean.

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In situ Flux Chamber (Lander)





Coring Operation







Release

Retrieval

Removal



Mica Bay Benthos





Sieved (500 micron) benthic samples from Mica Bay collected: (A) on October 14, 1998 (rose bengal stained), and (B) on August 17, 1999. Although the living macroinvertebrates in these samples were nearly absent, the relative abundance of invertebrate tubes and detrital material presents a distinct contrast to the benthic material within the main channel of the Lake (Figure 2 below). Differences in the hue and brightness between photomicrographs taken from the two collection dates are due to camera and lighting changes.

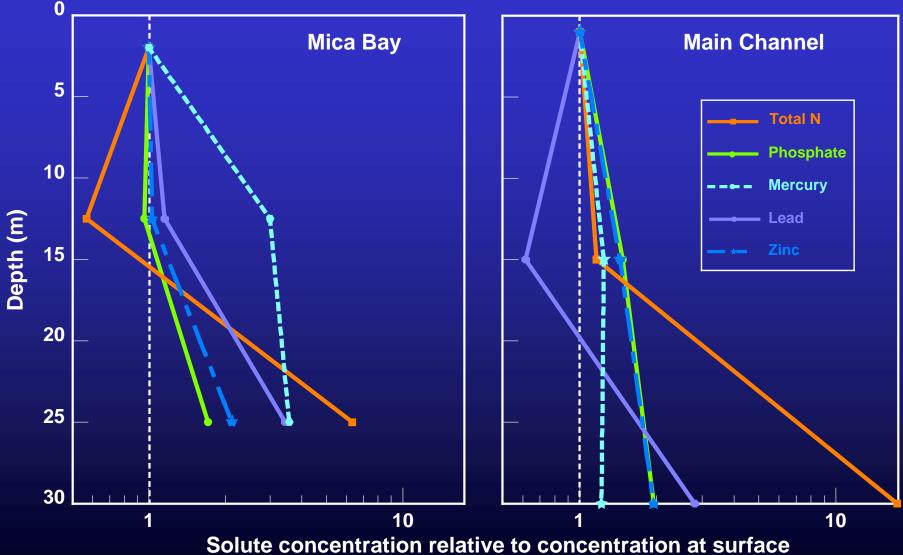
Main Channel





Benthic samples from the main channel of Lake Coeur d'Alene near the mouth of the Coeur d'Alene River collected: (A) on October 15, 1998 (A), and (B) on August 23, 1999. The consistent predominance of inorganically coated particles (presumably by ferric-oxyhydroxide) contrasts with the benthic samples from Mica Bay above. Differences in the hue and brightness between photomicrographs taken from the two collection dates are due to camera and lighting changes.







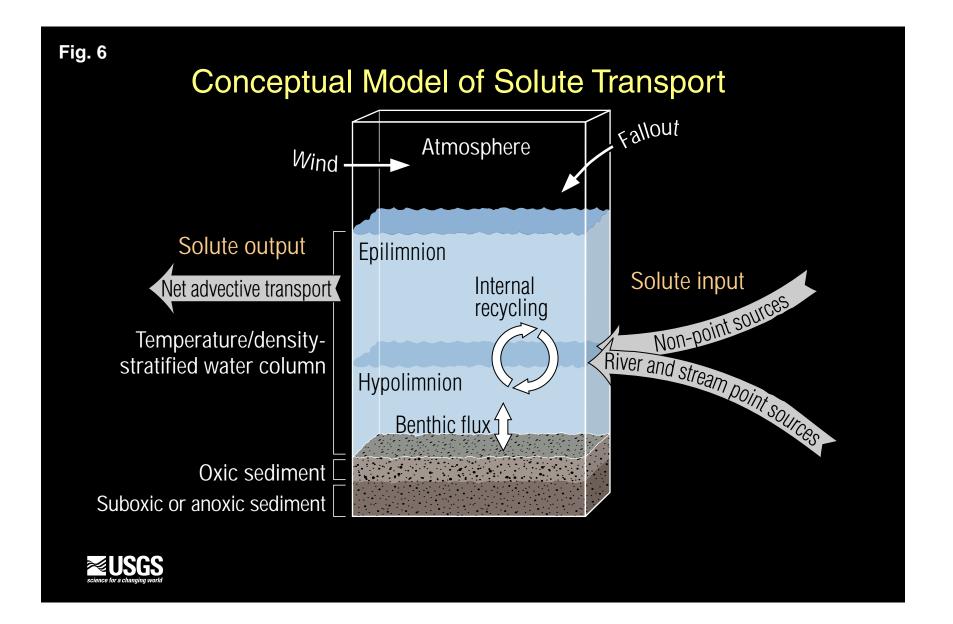


Fig. 7

Mercury

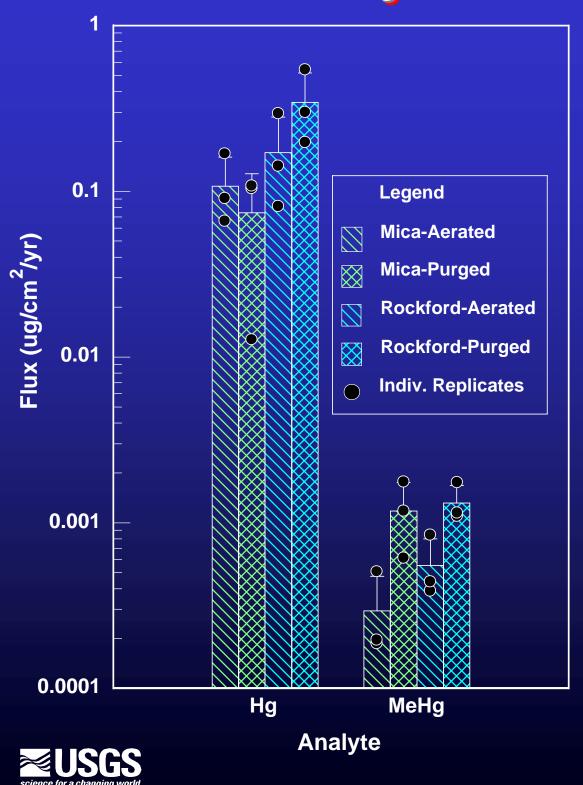


Fig. 8

Processes Regulating Benthic Flux

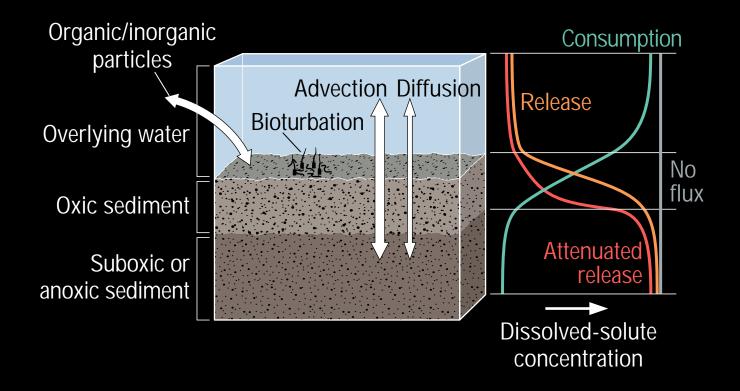




Fig. 9

Comparison of Benthic Indices

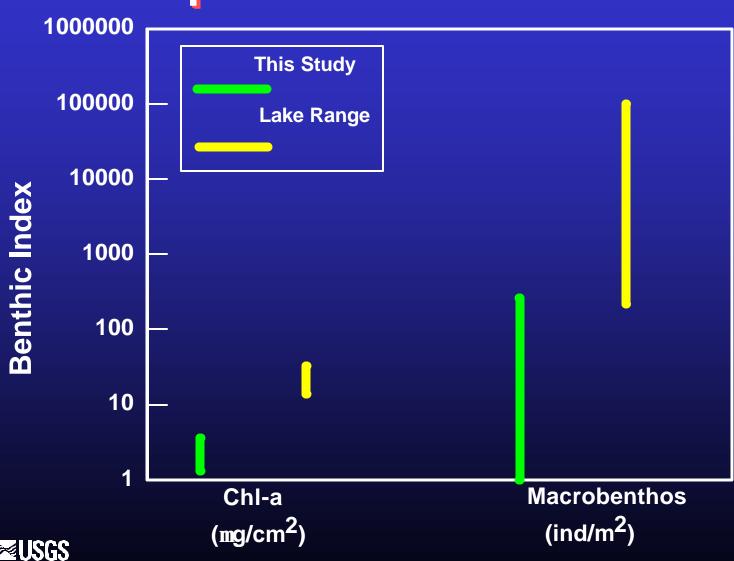


Fig. 10
I njected Bromide during Lander Deployments

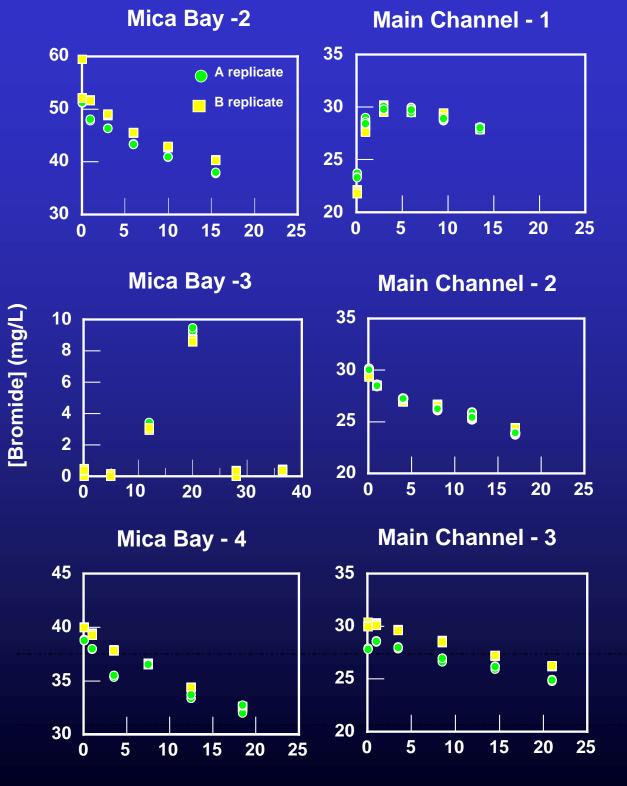




Fig. 11

Nitrogen to Phosphorus Ratio

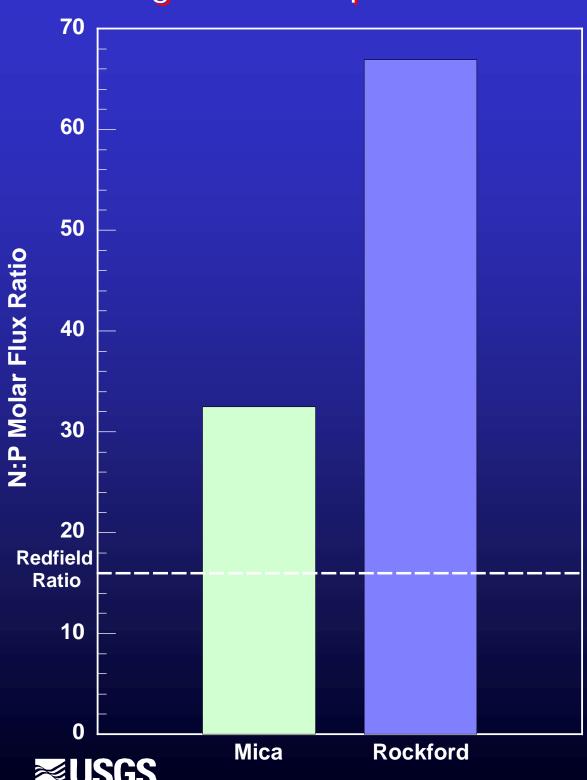
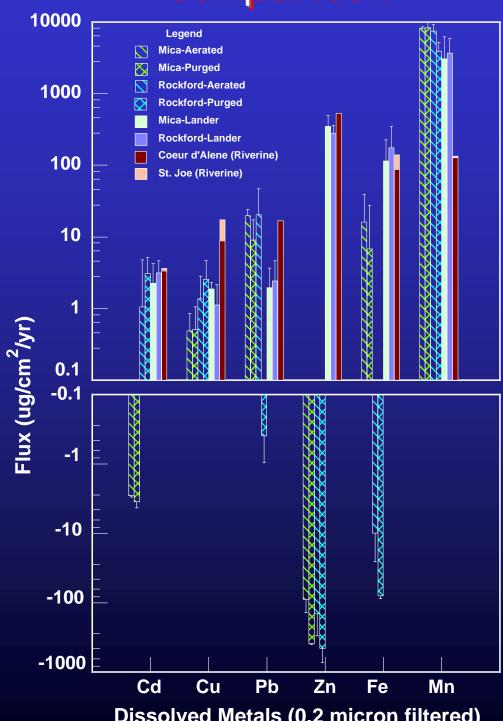
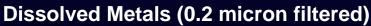


Fig. 12

Benthic vs. Riverine Flux Comparison







Copper

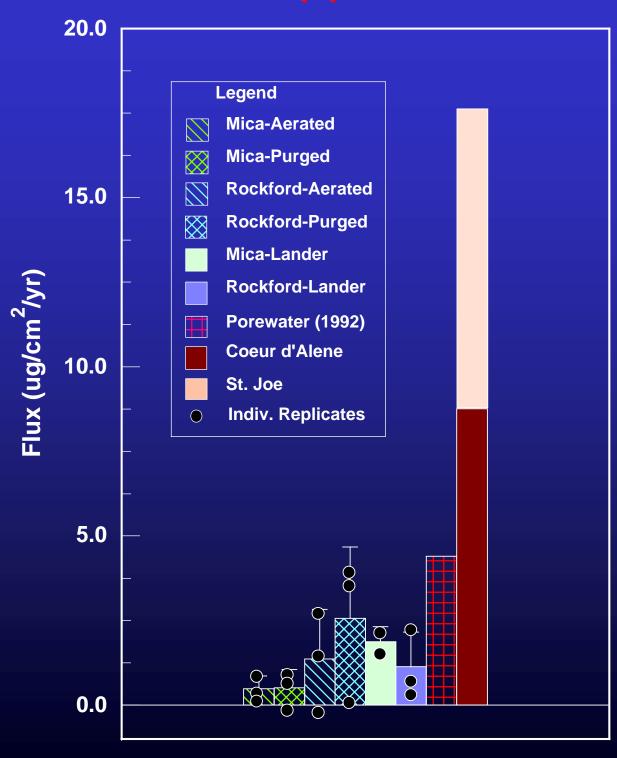




Fig. 14

Iron

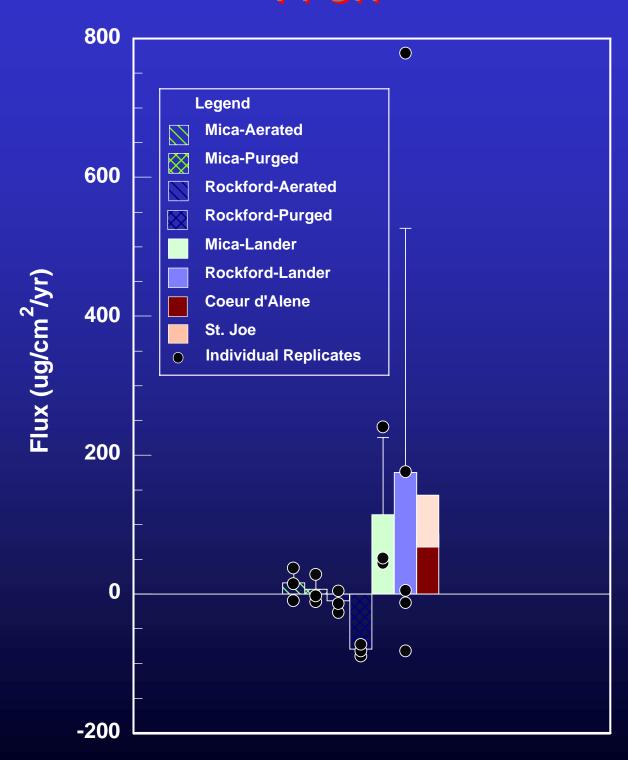
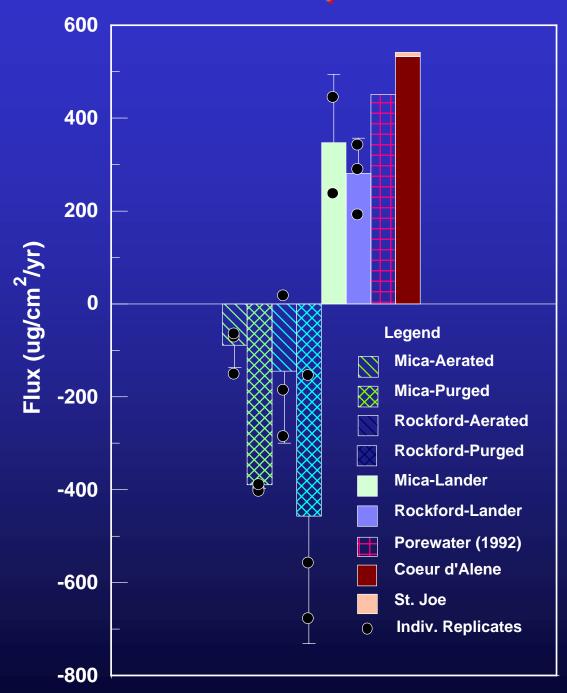




Fig. 15

Zinc Comparison





Cadmium

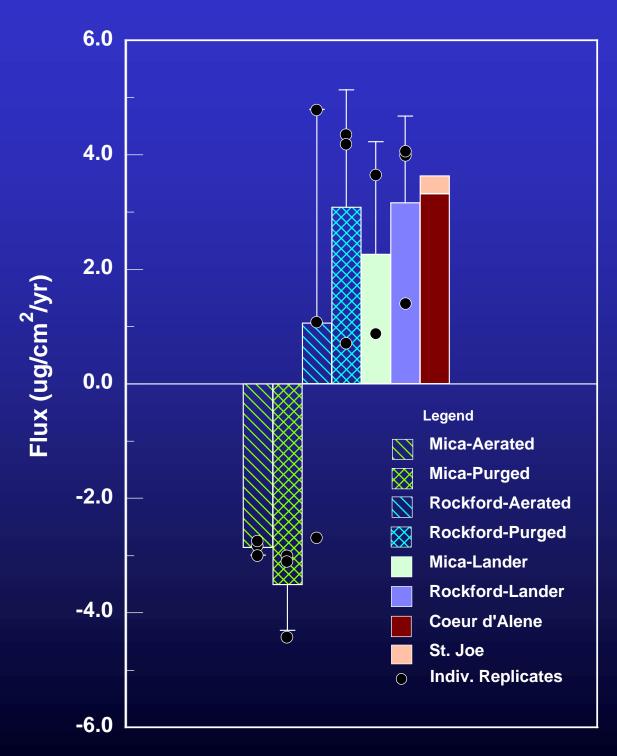
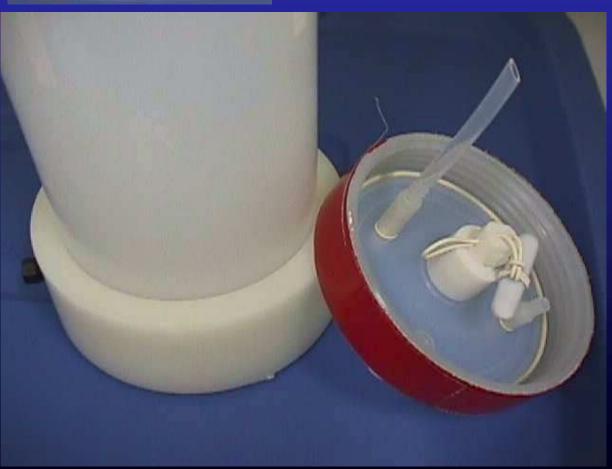




Fig. 17



Incubation Core Design



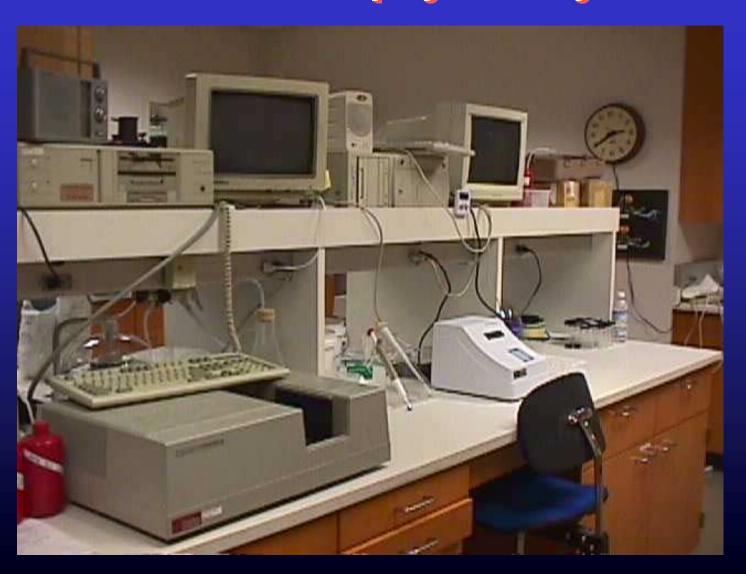


Benthic Macroinvertebrate Taxonomy





Benthic Chlorophyll Analyses





Colorimetric Bromide Analyses





Fig. 21

Spectrophotometric Nutrient Analyses





Dissolved-metal Analyses by ICP-MS





Dissolved-iron Analyses by GFAAS





Dissolved-mercury Speciation by CVAFS





Dissolved Organic Carbon (DOC) Analyses





Table 1. Experimental Schedule for Benthic Flux Pilot Study Lake Coeur d'Alene, August 16 - 27, 1999

Date(s) in			
August '99	Station	Index	Activity (hrs of incubation)
17	Mica Bay		Water-column sampling and coring
17 - 18	Mica Bay	MB-1	Lander deployment (15.5)
18	Mica Bay		6 Core Incubations (12.0)
18 - 19	Mica Bay	MB-2	Lander deployment (14.5)
19 - 21	Mica Bay	MB-3	Lander deployment (36.5)
21 - 22	Main Channel	St4-1	Lander deployment (13.5)
22 - 23	Main Channel	St4-2	Lander deployment (17.0)
23	Main Channel		Water-column sampling and coring
23 - 24	Main Channel	St4-3	Lander deployment (21.0)
24	Main Channel		6 Core Incubations (12.0)
24 - 25	Mica Bay	MB-4	Lander deployment (18.5)

Table 2. Surficial-sediment Porosities (Benthic Flux Experiments - August 18 and 24, 1999)

8/18/99				
Mica Bay	y			
			Bulk Density	Wet/dry
Core #	Treatment	Porosity	(g-dry/cm ³ -sed)	weight
1	Aerated	0.94	0.27	4.54
3	Aerated	0.97	0.29	4.37
4	Aerated	0.95	0.25	4.75
2	Ar-Purged	0.97	0.28	4.51
5	Ar-Purged	0.93	0.29	4.17
7	Ar-Purged	0.97	0.28	4.51

8/24/99				
Main Ch	annel			
			Bulk Density	Wet/dry
Core #	Treatment	Porosity	(g-dry/cm ³ -sed)	weight
9	Aerated	0.94	0.27	4.50
10	Aerated	0.96	0.28	4.41
11	Aerated	0.92	0.26	4.47
12	Ar-Purged	0.91	0.27	4.36
13	Ar-Purged	0.90	0.26	4.41
16	Ar-Purged	0.95	0.21	5.49

Replicate volume = $3 * 3.2 = 9.6 \text{ cm}^3$

Table 3. Benthic-biological Indices for Lakes

Index	Value	Range	Units	Lake	Lake Type	Reference ^a
Chl-a		14 - 33	ug/cm ²	Lake Erken,	mesotrophic	
				Sweden		Goedkoop and Johnson (1996)
		1.3-3.6	ug/cm ²	Lake Coeur	oligotrophic-	
				d'Alene	mesotrophic	This study
		1.0-5.5	Ash-free g-dry	Lake Ontario	mesotrophic	
			weight/m ²			Johnson and Brinkhurst, 1971
Macroinvertebrates	3.36	CI=0.25	g-dry weight/m ²	Lake	mesotrophic	
				Memphremagog,		
				Quebec		Dermott, et al., 1977
Macroinvertebrates		214-829	individuals/m ²	4 British	oligotrpohic -	
				Columbia Lakes	mesotrophic	Ricker, 1952
Macroinvertebrates		893-4671	individuals/m ²	Lakes in Convict	oligotrophic	
				Creek Basin		Reimers et al., 1955
Chironomids		320-720	individuals/m ²	Lake Erken,	mesotrophic	
				Sweden		Goedkoop and Johnson (1996)
Macroinvertebrates		22431 -	individuals/m ²	Lake Myvatn,	eutrophic	
		99947		Iceland		Lindegaard and Jonasson, 1979
Chironomids		21739-40000	individuals/m ²	Priest Lake	oligotrophic	
						Rudd (1996)
Macroinvertebrates		29565 -	individuals/m ²	Priest Lake	oligotrophic	
		60869				Rudd (1996)
Chironomids		0-76956	individuals/m ²	Lake Coeur	oligotrophic-	
				d'Alene ^b	mesotrophic	Rudd (1996)
Macroinvertebrates		10000 -	individuals/m ²	Lake Coeur	oligotrophic-	\/
		98695		d'Alene ^b	mesotrophic	Rudd (1996)
Macroinvertebrates		0-130	individuals/m ²	Lake Coeur	oligotrophic-	, ,
				d'Alene	mesotrophic	This study

^a References:

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^b Data from eutrophic Chacolet Lake not included.

Table 4. Benthic Chlorophyll (Benthic Flux Experiments - August 18 and 24, 1999)

Mica Bay

Core # Treatment Reps^a chl

Main Channel

Core # Treatment Reps^a chl

OOIC #	Treatment	rtcps	Cili	OOIC #	Treatment	rtcps	Citi
			(ug/cm ²)				(ug/cm ²)
1	Aerated	Α	-5.4	9	Aerated	Α	1.5
	Aerated	В	2.0		Aerated	В	2.7
	Aerated	С	2.2		Aerated	С	1.8
2	Aerated	Α	1.3	10	Aerated	Α	2.0
	Aerated	В	3.1		Aerated	В	1.7
	Aerated	С	1.1		Aerated	С	0.8
3	Aerated	Α	1.7	11	Aerated	Α	1.1
	Aerated	В	1.4		Aerated	В	1.2
	Aerated	С	2.6		Aerated	С	1.8
4	Ar-Purged	Α	3.6	12	Ar-Purged	Α	1.4
	Ar-Purged		2.2		Ar-Purged	В	1.3
	Ar-Purged	С	2.8		Ar-Purged	С	2.0
5	Ar-Purged	Α	1.9	13	Ar-Purged	Α	1.1
	Ar-Purged	В	1.1		Ar-Purged	В	1.8
	Ar-Purged	С	2.9		Ar-Purged	С	1.0
7	Ar-Purged		1.8	16	Ar-Purged	Α	1.2
	Ar-Purged	В	2.6		Ar-Purged	В	1.5
	Ar-Purged	С	1.4		Ar-Purged	С	0.8

^a Replicates are indicative of spatial variability within each core.

Cores were numbered to facilitate sample identification.

The omission of a number in series denotes that the core tube was not selected for the coring operation.

Table 5. Surficial Benthic-bacteria Concentrations (After core incubations - August 18 and 24, 1999)

Mica Ba	Mica Bay													
Core #	Cells/g-core	Std. Error	95% CI	Treatment	n									
1	8.4E+08 +/-	2.5E+08	7.3E+07	Aerated	48									
3	8.8E+08 +/-	3.0E+08	8.6E+07	Aerated	48									
4	1.0E+09 +/-	3.3E+08	9.5E+07	Aerated	48									
2	7.6E+08 +/-	2.7E+08	7.7E+07	Ar-Purged	48									
5	6.3E+08 +/-	2.2E+08	6.2E+07	Ar-Purged	48									
7	7.2E+08 +/-	2.8E+08	8.0E+07	Ar-Purged	48									

Main Cl	Main Channel												
Core #	Cells/g-core	Std. Error	95% CI	Treatment	r								
9	8.6E+08 +	/- 3.2E+08	9.2E+07	Aerated	48								
10	6.8E+08 +	/- 2.2E+08	6.4E+07	Aerated	48								
11	6.3E+08 +	/- 2.0E+08	5.8E+07	Aerated	48								
12	3.9E+08 +	/- 1.6E+08	3 4.5E+07	Ar-Purged	48								
13	3.8E+08 +	/- 1.4E+08	3 4.1E+07	Ar-Purged	48								
16	5.1E+08 +	/- 2.0E+08	5.7E+07	Ar-Purged	48								

Table 6. Dissolved Oxygen in Incubated Cores (Benthic Flux Experiments - August 18 and 24, 1999)

Core#	Location	Treatment	Hour	DO (uM)
1	Mica	Aerated	0	237
	Mica	Aerated	2	220
	Mica	Aerated	6	232
	Mica	Aerated	12	256
3	Mica	Aerated	0	205
	Mica	Aerated	2	199
	Mica	Aerated	6	255
	Mica	Aerated	12	255
4	Mica	Aerated	0	152
	Mica	Aerated	2	213
	Mica	Aerated	6	258
	Mica	Aerated	12	266
Overlying	Mica	Aerated	0	193
	Mica	Aerated	12	198

Core#	Location	Treatment	Hour	DO (uM)
	9 Main Channel	Aerated	0	202
	Main Channel	Aerated	2	168
	Main Channel	Aerated	6	173
	Main Channel	Aerated	12	127
1	0 Main Channel	Aerated	0	135
	Main Channel	Aerated	2	179
	Main Channel	Aerated	6	166
	Main Channel	Aerated	12	123
1	1 Main Channel	Aerated	0	183
	Main Channel	Aerated	2	218
	Main Channel	Aerated	6	190
	Main Channel	Aerated	12	152
Overlying	Main Channel	Aerated	0	183
	Main Channel	Aerated	12	177

Core#	Location	Treatment	Hour	DO (uM)
	2 Mica	Ar-Purged	0	62
	Mica	Ar-Purged	2	29
	Mica	Ar-Purged	6	44
	Mica	Ar-Purged	12	16
	5 Mica	Ar-Purged	0	52
	Mica	Ar-Purged	2	31
	Mica	Ar-Purged	6	43
	Mica	Ar-Purged	12	21
-	7 Mica	Ar-Purged	0	59
	Mica	Ar-Purged	2	31
	Mica	Ar-Purged	6	50
	Mica	Ar-Purged	12	21
Overlying	Mica	Ar-Purged	0	56
	Mica	Ar-Purged	12	142

Core#		Location	Treatment	Hour	DO (uM)
	12	Main Channel	Ar-Purged	0	49
		Main Channel	Ar-Purged	2	32
		Main Channel	Ar-Purged	6	34
		Main Channel	Ar-Purged	12	22
	13	Main Channel	Ar-Purged	0	33
		Main Channel	Ar-Purged	2	33
		Main Channel	Ar-Purged	6	32
		Main Channel	Ar-Purged	12	n/a
	16	Main Channel	Ar-Purged	0	41
		Main Channel	Ar-Purged	2	30
		Main Channel	Ar-Purged	6	33
		Main Channel	Ar-Purged	12	14
Overlyi	ng	Main Channel	Ar-Purged	0	32
		Main Channel	Ar-Purged	12	17

 Table 7. Dissolved Oxygen, Radon-222, and Bromide from Lander Deployments (August 16 - 27,1999)

		Estimated Chamber	Initial Bromide	Rador (atoms/		Estimated			Estimated
	Chamber	Ht. Uncert.	Conc.	Including	Excluding	Radon Flux	DO Cons	umption	DO Consumption
Station - Deployment	Ht. (cm) ^a	(<u>+</u> %)	mg/L ^b	BWc	BW ^c	Uncert. (<u>+</u> %)	(mmol/m²/d)	(mg/cm ² /yr)	Uncert. (<u>+</u> %)
Mica Bay - 2	7.6	10	53	128	105	20	-9.5	-11.1	10 - 15
Mica Bay - 4	10.0	10	40	99	85	20	-7.2	-8.4	10 - 15
Main Channel - 1	11.4	20	35	103	84	30	-8.8	-10.3	20 - 25
Main Channel - 2	13.1	10	30	105	83	20	-6.0	-7.0	10 - 15
Main Channel - 3	12.8	10	31	242	214	20	-7.4	-8.6	10 - 15

^a Chamber heights for each deploment were determined from the initial bromide concentration after tracer injection.

^b Initial bromide concentrations were used to determine chamber heights. During the lander incubation bromide concentrations decreased approximately 20%.

^c BW=Bottom Water (either included in or excluded from calculation)

Table 8. Dissolved Chemical Species in the Water Column (Water Column Sampling - August 18 and 24, 1999)

Mica Bay Water Column

		95% Conf.			Total N ^b	Phosphate ^b										
Depth (m)	Zn ppb	Interval	Cu ppb	Interval	Cd ppb	Interval	Pb ppb	Interval	Fe ppb	Interval	Mn ppb	Interval	Hg ppt	Std Error ^a	ppb	ppb
2.0	37.5	0.4	0.359	0.004	0.199	0.002	0.096	0.001	13.1	0.2	1.132	0.003	0.58	0.79	12.03	0.66
12.5	38.5	0.2	0.344	0.003	0.205	0.000	0.111	0.000	13.3	0.4	0.375	0.000	1.75	0.50	6.82	0.63
25.0	79.5	0.5	0.458	0.009	0.333	0.000	0.332	0.005	22.5	0.1	0.524	0.004	2.08	0.01	76.05	1.12

Main Channel Water Column

		95% Conf.			Total N ^b	Phosphate ^b										
Depth (m)	Zn ppb	Interval	Cu ppb	Interval	Cd ppb	Interval	Pb ppb	Interval	Fe ppb	Interval	Mn ppb	Interval	Hg ppt	Std Error ^a	ppb	ppb
2.0	40.8	0.2	0.328	0.029	0.233	0.000	0.140	0.002	12.7	0.1	0.782	0.004	1.77	n/a	5.23	0.46
16.0	58.6	0.6	0.376	0.009	0.239	0.001	0.086	0.003	11.6	0.1	0.581	0.004	2.20	0.65	6.09	0.68
31.0	79.2	0.2	0.429	0.003	0.344	0.002	0.396	0.003	25.8	0.2	0.576	0.002	2.15	0.18	90.64	0.90

^a Only two replicates were analyzed for Hg samples due to volume constraints. Thus, the standard error is given instead of the 95% confidence interval

^b Only one replicate was analyzed for total N and phosphate due to volume constraints. The unit describes micrograms of nitrogen (or phosphorus) per liter.

Table 9. Comparison between Riverine and Measured Benthic Flux

	Areall	y Average	ed			Core Ir	ncubation	Flux ^b (ug/cr	n²/yr)								
Dissolved	Riverine F	lux (ug/cı	m²/yr) ^a		Mica	Bay			Main C	hannel		Lan	der Deploy	men	ts Flux ^c (ug/	/cm²/yr)	
Solute	CDA River	St. Joe	Sum	Aera	ted	Ar-Pu	rged	Aera	ited	Ar-Pu	rged		Mica Bay		Mai	n Channel	
				Average	Std error	Average	Std error	Average	Std error	Average	Std error	Average	Std error	n	Average	Std error	n
Ortho-P	9	9	18	50	30	150	10	90	30	140	120	20	20	2	7	2	3
NO ₃ +NO ₂	n/a	n/a	n/a	230	340	-370	70	140	100	60	70	210	100	2	160	30	3
NH_4^+	n/a	n/a	n/a	740	100	710	100	380	130	210	110	110	110	2	60	10	3
Total N	168	46	214	970	350	340	150	530	40	270	160	320	210	2	220	16	3
DOC	n/a	n/a	n/a	2022	361	1568	238	2763	1001	2583	521	n/a	n/a		n/a	n/a	
Si	23050	26410	49460	5530	540	5980	160	5660	410	4520	1400	1410	370	2	1579	249	3
Cd	3.0	0.3	3.3	-2.9	0.1	-3.5	0.8	1.1	3.7	3.1	2.1	2.3	2.0	2	3.1	1.5	3
Cu (1992) ^d	9.0	9.0	18.0	0.5	0.4	0.5	0.5	1.4	1.5	2.6	2.1	1.9	0.4	2	1.1	1.0	3
Pb	17	0	17	20	5	9	8	20	26	0	1	2	3	3	2	6	5
Zn	532	4	536	-90	50	-390	7	-150	150	-460	270	350	150	2	280	80	3
Fe	87	53	140	16	24	7	21	-10	16	-79	9	114	111	3	175	352	5
Mn	128	5	133	8180	390	8230	1500	7440	1730	3920	1320	3050	3180	2	3680	2240	3
HgTot (All)	n/a	n/a	n/a	0.11	0.05	0.07	0.05	0.17	0.11	0.34	0.18	n/a	n/a		n/a	n/a	
MeHg (All)	n/a	n/a	n/a	0.0003	0.0002	0.0012	0.0006	0.0006	0.0002	0.0013	0.0004	n/a	n/a		n/a	n/a	
HgTot (Init.)	n/a	n/a	n/a	0.84	n/a	0.56	n/a	5.45	n/a	2.05	n/a	n/a	n/a		n/a	n/a	
MeHg (Init.)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.0104	n/a	0.0036	n/a	n/a	n/a		n/a	n/a	

^a Riverine loads were determined as part of a lake monitoring program (Woods, P.F., 2000, Loads and concentrations of cadmium, lead, zinc and nutrients during the 1999 water year for the Spokane River Basin, Idaho and Washington: U.S. Geological Survey Open File Report 00-XXXX, XX p. plus appendices [U.S.G.S. publication approval expected prior to December, 2000])

The affected Lake surface area for calculations (km²) = 108.2 (Horowitz and others, 1995)

Fluxes are presented in units of micrograms solute per square centimeter per year (ug/cm²/yr).

b All core incubation data were derived from three cores for each site and treatment. Standard errors rather than 95% confidence intervals about flux determinations for the site are tabulated.

^c The number of benthic flux estimates used to determine the average and standard deviation for each solute at each location was not constant, as it was in the core incubations. This was due to variable number of deployments at each site, and non-linearities in the concentration time series during lander incubations.

n/a Not available

^d Copper loading estimates were not performed in 1999, thus 1992 data is used.

Table 10. Metals-flux from Core Incubations (Benthic Flux Experiments - August 18 and 24, 1999) Mass fluxes are presented in units of micrograms solute per square centimeter per year (ug/cm²/yr). Coefficients of determination (r²) are tabulated for the time-series regressions used to determine benthic flux.

(All 12 hours of incubation data used)

Cadmi	um Flux Summa								
Core #	Sta. No.*	Cd Flux	(ug/cm ² -yr)	Cd Flux (nr	moles/m ² -h)	r ²	Treatment	n	Comments
1	Mica	-2.7	+/- 0.4	-27.9 -	+/- 4.1	0.60	Aerated	15	
3	Mica	-2.8	+/- 0.5	-28.7 -	+/- 4.9	0.53	Aerated	15	
4	Mica	-3.0	+/- 0.5	-30.5 -	+/- 5.3	0.52	Aerated	15	
2	Mica	-3.1	+/- 0.6	-31.5 -	+/- 5.7	0.50	Ar-Purged	15	
5	Mica	-3.0	+/- 0.5	-30.5 -	+/- 5.4	0.47	Ar-Purged	16	
7	Mica	-4.4	+/- 0.7	-45.0 -	+/- 6.9	0.58	Ar-Purged	15	
									-
Core #	Sta. No.*	Cd Flux	(ug/cm ² -yr)	Cd Flux (nr	moles/m²-h)	r ²	Treatment	n	Comments
9	Main Channel	-2.7	+/- 0.6	-27.3 -	+/- 6.0	0.40	Aerated	15	Immediate Cd depletion
10	Main Channel	1.1	+/- 1.2	11.0 -	+/- 12.0	0.04	Aerated	13	Initial flux dominated
11	Main Channel	4.8	+/- 0.7	48.5 -	+/- 6.8	0.63	Aerated	15	
12	Main Channel	4.2	+/- 1.0	42.4 -	+/- 9.7	0.47	Ar-Purged	13	
13	Main Channel	4.4	+/- 0.6	44.2 -	+/- 6.0	0.64	Ar-Purged	15	
16	Main Channel	0.7	+/- 0.7	7.2 -	+/- 7.6	0.03	Ar-Purged	14	Initial flux dominated
Coppe	r Flux Summary	,	(All 12 h		bation data	•			-
Core #	Sta. No.*	Cu Flux	(ug/cm ² -yr)	Cu Flux (nr	moles/m²-h)	r ²	Treatment	n	Comments
1	Mica	0.4	+/- 0.2	7.2 -	+/- 3.1	0.17	Aerated	14	Initial flux dominated
3	Mica	0.2	+/- 0.2	3.0 -	+/- 3.5	0.02	Aerated	17	Initial flux dominated
4	Mica	0.9	+/- 0.1	16.1 -	+/- 1.5	0.85	Aerated	13	

COIC #	Sta. No.	Cu riux	(ug/cm -yr)	Cu Flux (nmoies/m -n _/	I	rreatment	- 11	Comments
1	Mica	0.4	+/- 0.2	7.2	+/- 3.	0.17	Aerated	14	Initial flux dominated
3	Mica	0.2	+/- 0.2	3.0	+/- 3.9	0.02	Aerated	17	Initial flux dominated
4	Mica	0.9	+/- 0.1	16.1	+/- 1.5	0.85	Aerated	13	
2	Mica	0.7	+/- 0.1	12.4	+/- 1.3	0.73	Ar-Purged	16	
5	Mica	-0.1	+/- 0.1	-1.8	+/- 2.	0.03	Ar-Purged	13	Initial flux dominated
7	Mica	0.9	+/- 0.0	17.0	+/- 0.0	0.96	Ar-Purged	15	
	· -	_		-		<u>-</u>	<u>-</u>		•
									-
Core #	Sta. No.*	Cu Flux	(ug/cm ² -yr)	Cu Flux (nmoles/m²-h)	r ²	Treatment	n	Comments
-	Sta. No.* Main Channel	Cu Flux	, , ,	,	nmoles/m ² -h) +/- 0.3				Comments Odd - No distinctive trend
9		-0.2	, ,	-3.1	+/- 0.3	0.69	Aerated		Odd - No distinctive trend
9 10	Main Channel	-0.2 1.5	+/- 0.0	-3.1 3 26.9	+/- 0.3 +/- 5.8	0.69 0.45	Aerated Aerated	16	Odd - No distinctive trend
9 10 11	Main Channel Main Channel	-0.2 1.5 2.8	+/- 0.0 +/- 0.3	-3.1 3 26.9 2 49.5	+/- 0.3 +/- 5.8 +/- 4.0	0.69 0.45 0 0.81	Aerated Aerated Aerated	16 14 16	Odd - No distinctive trend
9 10 11 12	Main Channel Main Channel Main Channel	-0.2 1.5 2.8 3.6	+/- 0.0 +/- 0.3 +/- 0.2	-3.1 3 26.9 2 49.5 64.2	+/- 0.3 +/- 5.8 +/- 4.0 +/- 7.4	0.69 0.45 0 0.81 4 0.65	Aerated Aerated Aerated Ar-Purged	16 14 16	Odd - No distinctive trend

Lead Flux Summary

(All 12 hours of incubation data used)

- ··	la		, 2 ,		, 2.,	2			la .
	Sta. No.*		ug/cm²-yr)	Pb Flux (nmol		r-	Treatment		Comments
1	Mica	24.6	⊦/- 4.6	135.5 +/-	25.2	0.57	Aerated	13	Initial flux dominated
3	Mica	15.3 +	⊦/- 5.8	84.5 +/-	32.0	0.21	Aerated	14	Initial flux dominated
4	Mica	19.2	⊦/- 6.7	106.1 +/-	36.9	0.19	Aerated	16	Initial flux dominated
2	Mica	18.5	⊦/- 5.1	102.0 +/-	28.1	0.43	9	12	Initial flux dominated
5	Mica	4.7 ⊣	⊦/- 4.5	25.7 +/-	25.0	0.04	Ar-Purged	14	Initial flux dominated
7	Mica	4.0 -	⊦ /- 5.9	21.8 +/-	32.6	0.02	Ar-Purged	13	Initial flux dominated
									_
Core #	Sta. No.*	Pb Flux (ı	ug/cm ² -yr)	Pb Flux (nmol	es/m²-h)	r ²	Treatment	n	Comments
9	Main Channel	50.7 →	⊦/- 7.6	279.6 +/-	41.8	0.59	Aerated	15	Initial flux dominated
10	Main Channel	6.3 -	⊦/- 3.7	34.9 +/-	20.5	0.09	Aerated	15	Initial flux dominated
11	Main Channel	3.9 +	⊦/- 3.7	21.6 +/-	20.3	0.03	Aerated	17	Initial flux dominated
	Main Channel	-0.8	⊦/- 0.3	-4.1 +/-	1.7	0.11	Ar-Purged		Only T3 change
13	Main Channel	-0.7 +	⊦/- 0.6	-3.7 +/-	3.6	0.03	Ar-Purged	15	Initial flux dominated
16	Main Channel	0.2 -	⊦/- 1.8	1.3 +/-	9.8	0.00	Ar-Purged	13	Initial flux dominated

Zinc Flux Summary

(All 12 hours of incubation data used)

Γ_	1		2 .			. 2	2			l _
Core #	Sta. No.*	Zn Flux	(ug/cm ² -yr)	Zn Flux (r	nmoles/	m²-h)	r ²	Treatment	n	Comments
1	Mica	-65.1	+/- 28.0	-1137	+/-	489	0.24	Aerated	12	
3	Mica	-144.9	+/- 49.0	-2530	+/-	856	0.34	Aerated	12	
4	Mica	-58.2	+/- 8.5	-1016	+/-	148	0.59	Aerated	16	
	Mica	-391.0			+/-	250	0.97	Ar-Purged	13	
5	Mica	-396.9	+/- 14.6	-6927	+/-	254	0.97	Ar-Purged	13	
7	Mica	-382.6	+/- 19.6	-6679	+/-	343	0.91	Ar-Purged	16	
Core #	Sta. No.*	Zn Flux	(ug/cm ² -yr)	Zn Flux (r	nmoles/	/m²-h)	r ²	Treatment	n	Comments
9	Main Channel	-179.4	+/- 59.5	-3131	+/-	1038	0.34	Aerated	12	
10	Main Channel	-279.6	+/- 6.3	-4880	+/-	109	0.99	Aerated	12	
11	Main Channel	23.7	+/- 18.4	413	+/-	321	0.07	Aerated	13	Initial flux dominated
12	Main Channel	-551.9	+/- 46.4	-9633	+/-	809	0.87	Ar-Purged	13	
13	Main Channel	-147.9	+/- 16.7	-2582	+/-	292	0.75	Ar-Purged	14	Initial flux dominated
16	Main Channel	-671.3	+/- 88.6	-11718	+/-	1546	0.77	Ar-Purged	12	

Iron Flux Summary

(All 12 hours of incubation data used)

										_
Core #	Sta. No.*	Fe Flux	(ug/c	m ² -yr)	Fe Flux (nmole	s/m²-h)	r ²	Treatment	n	Comments
1	Mica	39.2	+/-	8.2	802 +/-	167	0.52	Aerated	13	Initial flux dominated
3	Mica	-7.7	+/-	8.2	-157 +/-	168	0.03	Aerated	14	Initial flux dominated
4	Mica	16.9	+/-	22.5	346 +/-	461	0.02	Aerated	14	Initial flux dominated
2	Mica	30.3	+/-	14.3	620 +/-	293	0.17	Ar-Purged	13	Initial flux dominated
5	Mica	-0.7	+/-	13.0	-13 +/-	267	0.00	Ar-Purged	13	Initial flux dominated
7	Mica	-9.3	+/-	9.7	-190 +/-	198	0.02	Ar-Purged	17	Initial flux dominated
Core #	Sta No *	E . El		2						
	Sta. INO.	re riux	(ug/c	m ² -yr)	Fe Flux (nmole	s/m²-h)	r^2	Treatment	n	Comments
9	Main Channel	6.3	` _	:m²-yr) 1.3	,	s/m ² -h) 26	r ² 0.45			Comments Initial flux dominated
			+/-	• ,	,		r ² 0.45 0.25		15	
10	Main Channel	6.3	+/-	1.3	129 +/-	26		Aerated	15 13	Initial flux dominated
10 11	Main Channel Main Channel	6.3 -11.8	+/- +/- +/-	1.3 4.4	129 +/- -241 +/- -500 +/- -1439 +/-	26 90	0.25	Aerated Aerated Aerated	15 13 13	Initial flux dominated Initial flux dominated
10 11 12	Main Channel Main Channel Main Channel	6.3 -11.8 -24.4	+/- +/- +/- +/-	1.3 4.4 10.4	129 +/- -241 +/- -500 +/-	26 90 212	0.25 0.21	Aerated Aerated Aerated Ar-Purged	15 13 13 15	Initial flux dominated Initial flux dominated Initial flux dominated

Manganese Flux Summary

(All 12 hours of incubation data used)

							-		-
Core #	Sta. No.*	Mn Flux	(ug/cm ² -yr)	Mn Flux (nmol	es/m²-h)	r ²	Treatment	n	Comments
1	Mica	8372	+/- 1135	174087 +/-	23598	0.68	Aerated	14	Initial flux dominated
3	Mica	8420	+/- 681	175080 +/-	14152	0.79	Aerated	17	Initial flux dominated
4	Mica	7737	+/- 1492	160884 +/-	31025	0.52	Aerated	14	Initial flux dominated
2	Mica	9769	+/- 1243	203140 +/-	25846	0.70	Ar-Purged	14	Initial flux dominated
5	Mica	8058	+/- 1250	167544 +/-	25990	0.62	Ar-Purged	14	Initial flux dominated
7	Mica	6840	+/- 1543	142235 +/-	32094	0.47	Ar-Purged	13	Initial flux dominated
									_
Core #	Sta. No.*	Mn Flux	(ug/cm ² -yr)	Mn Flux (nmol	es/m²-h)	r ²	Treatment	n	Comments
	Sta. No.* Main Channel	Mn Flux 8006	· · · · · ·		es/m ² -h) 24909	r ²	Treatment Aerated		Comments Initial flux dominated
9			+/- 1198	166470 +/-	•	r ² 0.52 0.67		17	
9 10	Main Channel	8006	+/- 1198 +/- 996	166470 +/- 182716 +/-	24909		Aerated	17 17	Initial flux dominated
9 10 11	Main Channel Main Channel	8006 8787	+/- 1198 +/- 996 +/- 1241	166470 +/- 182716 +/- 114851 +/-	24909 20708	0.67	Aerated Aerated Aerated Ar-Purged	17 17 13	Initial flux dominated Initial flux dominated
9 10 11 12	Main Channel Main Channel Main Channel	8006 8787 5523	+/- 1198 +/- 996 +/- 1241 +/- 714	166470 +/- 182716 +/- 114851 +/- 101618 +/-	24909 20708 25798	0.67 0.47	Aerated Aerated Aerated Ar-Purged	17 17 13 14	Initial flux dominated Initial flux dominated Initial flux dominated

Table 11. Metal-flux from Lander Deployments (August 16-27, 1999)

Mass fluxes are presented in units of micrograms solute per square centimeter per year (ug/cm²/yr).

Cadmium Flux Summary

Deploy #	Sta. No.*	Cd Flux (ug/cm²/yr	·)	Comments
2	Mica	3.6 +/-	0.7	
4	Mica	0.9 +/-	0.3	
	Main Channel	4.0 +/-	1.0	
2	Main Channel	1.4 +/-	0.4	
3	Main Channel	4.1 +/-	0.5	

Copper Flux Summary

Deploy #	Sta. No.*	Cu Flux (ug/cm²/yr)		Comments
2	Mica	2.2 +/-	1.2	
4	Mica	1.6 +/-	0.6	
1 .				
1	Main Channel	0.4 +/-	1.5	
2	Main Channel	0.8 +/-	0.3	
3	Main Channel	2.3 +/-	0.4	

Lead Flux Summary

Deploy #	Sta. No.*	Pb Flux (ug/cm²/yr)	Comments
2	Mica	0.4 +/-	1.1	Non-linear; Time series estimate #1
	Mica	5.1 +/-	3.3	Non-linear; Time series estimate #2
4	Mica	0.3 +/-	0.5	
1	Main Channel	- 5.1 +/-	4.5	
2	Main Channel	10.3 +/-	4.2	Non-linear; Time series estimate #1
	Main Channel	2.0 +/-	0.3	Non-linear; Time series estimate #2
3	Main Channel	4.6 +/-	5.8	Non-linear; Time series estimate #1
	Main Channel	0.3 +/-	0.2	Non-linear; Time series estimate #2

Zinc Flux Summary

Deploy #	Sta. No.*	Zn Flux (ug/cı	m²/yr)	Comments
2	Mica	451.0 +/-	100.2	
4	Mica	243.4 +/-	33.4	
1	Main Channel	348.4 +/-	71.6	
2	Main Channel	198.1 +/-	28.6	
3	Main Channel	295.9 +/-	45.3	

Iron Flux Summary

Deploy #	Sta. No.*	Fe Flux (ug/cm ²	/yr)	Comments
2	Mica	53.8 +/-	46.7	Non-linear; Time series estimate #1
	Mica	242.6 +/-	142.7	Non-linear; Time series estimate #2
4	Mica	46.3 +/-	12.6	
1	Main Channel	- 79.9 +/-	79.9	
2	Main Channel	780.7 +/-	101.9	Non-linear; Time series estimate #1
	Main Channel	7.1 +/-	30.2	Non-linear; Time series estimate #2
3	Main Channel	178.2 +/-	77.3	Non-linear; Time series estimate #1
	Main Channel	-10.4 +/-	21.2	Non-linear; Time series estimate #2

Manganese Flux Summary

Deploy #	Sta. No.*	Mn Flu	X (ug/c	m²/yr)	Comments
2	Mica	5294	+/-	1003	
4	Mica	802	+/-	140	
2	Main Channel Main Channel Main Channel	5575 1203 4271	+/-	1003 241 802	

Table 12. Macroinvertebrate Taxonomy (Benthic Flux Experiment - August 18 and 24, 1999) Lake Coeur d'Alene 8/16-27/99

Objective and Scope: The objective of the investigation was to determine the macroinvertebrate composition of sediments collected from Lake Coeur d'Alene, Idaho. Sediments were collected with a 77 cm2 coring device from two locations; Mica Bay and a main channel site near the mouth of the Coeur d'Alene River. Six cores were collected from each site. Collections were made at Mica Bay on August 17, 1999 and from a main channel site on August 23, 1999. After incubtion, each core was sieved in the field using a 500 m mesh sieve. Material retained on the sieve was preserved with 10% buffered formalin. The retained material from each core was rinsed of preservative and remaining fine sediment in the laboratory using a 425 m mesh sieve. All macroinvertebrates were sorted using 10X magnification. Sorted macroinvertebrates were identified to the lowest practicable taxonomic level and stored in either 70% ethanol or slide mounted.

General Comments: The three most striking differences between the cores from the two locations were:

- 1) Mica Bay cores contained many empty invertebrate cases,
- 2) Mica Bay cores contained more organic detritus, and

8/18/99

Mica Bay

3) Cores from the main channel contained predominately large inorganic particles. Whether the empty invertebrate cases originated at the site or were transported to the site is unknown. Higher frequency temporal sampling would probably determine whether there is an active benthic invertebrate community at these sites.

Core # Sta. No.*	Treatment	Taxonomic Observations
1 Mica	Aerated	Largely composed of many empty invertebrate cases. We assume they are chironomid cases.
3 Mica	Aerated	Only contained empty cases.
4 Mica	Aerated	Only contained empty cases.
2 Mica	Purged	Similar to core 1 and was composed of empty invertebrate cases but contained one unidentifiable chironomid head capsule.
5 Mica	Purged	Contained empty cases and 16 chironomid head capsules.
7 Mica	Purged	Contained empty cases and 1 chironomid head capsule.
Main Channel	8/24/99	
Core # Sta. No.*	Treatment	Taxonomic Observations
9 Rockford	Aerated	Contained far fewer empty cases than cores from Mica bay. Also found were 2 chironomid head capsules and 2 bryozoan statoblasts, probably from Pectinatella.
9 Rockford 10 Rockford	Aerated Aerated	were 2 chironomid head capsules and 2 bryozoan statoblasts,
		were 2 chironomid head capsules and 2 bryozoan statoblasts, probably from Pectinatella. Contained a few empty invertebrate cases, 1 unidentifiable chironomid
10 Rockford	Aerated	were 2 chironomid head capsules and 2 bryozoan statoblasts, probably from Pectinatella. Contained a few empty invertebrate cases, 1 unidentifiable chironomid (Tribe: Chironomini), and a mite, Hygrobates. Contained a few empty cases, one mite, one chironomid, and the valve
10 Rockford 11 Rockford	Aerated Aerated	were 2 chironomid head capsules and 2 bryozoan statoblasts, probably from Pectinatella. Contained a few empty invertebrate cases, 1 unidentifiable chironomid (Tribe: Chironomini), and a mite, Hygrobates. Contained a few empty cases, one mite, one chironomid, and the valve of a pelecypod; none of which were identifiable. Contained a few empty cases, 2 empty chironomid head capsules, 2 statoblasts from Pectinatella, and one Procladius, a chironomid in

Table 13. Injected-bromide concentrations during lander deployments

All Samples drew 400 ml

	Station ID	Sample	Elapsed ^a	[Bromide-A] ^b	[Bromide-B]	
_	and Dates	Draw #	hours	(mg/L)	(mg/L)	Deployment Notes
Ī	Mica Bay-2	1	0.08	51.2	54.0	Wooden skids added to chamber
		2	1	47.9	51.7	Oxygen and radon data look good
	Aug 18-19	3	3	46.3	48.9	4A large air bubble
		4	6	43.3	45.5	
		5	10	40.9	42.8	
		6	15.5	37.9	40.3	

	Station ID	Sample	Elapsed ^a	[Bromide-A] ^b	[Bromide-B]	
-	and Dates	Draw #	hours	(mg/L)	(mg/L)	Deployment Notes
	Mica Bay-3	1	0.08	0.0	0.3	All sample (A's) have sediment, 5 and 6 have the least sediment
		2	5	0.0	0.0	All the A samples have air bubbles
	Aug 19-21	3	12	3.4	3.0	This chamber never was properly seated, perhaps due to disturbance,
		4	20	9.3	8.7	clearly a disturbance occured after draw 4 such that the chamber appears
		5	28	0.1	0.1	to be operational during draws 5 and 6, however, chamber height is <<10 cm.
		6	36.5	0.3	0.4	The chamber was partially sealed through draw 4, but did leak enough to
						allow oxygen equilibration.

	Station ID	Sample	Elapsed ^a	[Bromide-A] ^b	[Bromide-B]	
	and Dates	Draw #	hours	(mg/L)	(mg/L)	Deployment Notes
Ī	Mica Bay-4	1	0.08	38.8	40.0	Good deployment although radon in Draw 4 looks low
		2	1	38.0	39.3	Bubbles in 5A and 6A, 4A ok, others not checked
	Aug 24-25	3	3.5	35.4	37.8	Longer skids added to chamber
		4	7.5	36.5	36.6	
		5	12.5	33.5	34.4	
		6	18.5	32.5	32.5	

	Station ID	Sample	Elapsed ^a	[Bromide-A] ^s	[Bromide-B]	
_	and Dates	Draw #	hours	(mg/L)	(mg/L)	Deployment Notes
	Main Channel -1	1	0.08	23.5	22.0	Good deployment
		2	1	28.7	28.0	Teflon tape on 2A, 4A and 6A
	Aug 21-22	3	3	29.9	29.9	2A med bubble, 3B med bubble, 4A med-large bubble, 6A med bubble
		4	6	29.8	29.6	
		5	9.5	28.8	29.2	
		6	13.5	28.0	27.9	

Station ID and Dates	Sample Draw #	Elapsed ^a hours	[Bromide-A] ^b (mg/L)	[Bromide-B] (mg/L)	Deployment Notes
	4				1 /
Main Channel -2	1	0.08	30.1	29.4	Good deployment, deployed without divers
	2	1	28.5	28.5	2A med bubble, 4A med-large bubble, 6A med-large bubble
Aug 22-23	3	4	27.2	27.0	
	4	8	26.2	26.6	
	5	12	25.4	25.4	
	6	17	23.9	24.4	

Station ID	Sample	Elapseda	[Bromide-A] ^b	[Bromide-B]	
and Dates	Draw #	hours	(mg/L)	(mg/L)	Deployment Notes
Main Channel -3	1	0.08	27.9	30.1	Good deployment
	2	1	28.6	30.2	3A, 4A, 5A, 6A all had medium bubbles upon recovery
Aug 23-24	3	3.5	27.9	29.6	
	4	8.5	26.8	28.5	
	5	14.5	26.1	27.2	
	6	21	24.9	26.2	

 ^a Elapsed hours counted following closure of lander lid.
 ^b Sample designations A and B represent successive sample replicates after automated rinsing of the sampling bellows.

Table 14. Benthic Flux of Dissolved Nutrients (Lake Coeur d'Alene Pilot Study - August 16 - 27, 1999) Mass fluxes are presented in units of micrograms solute per square centimeter per year (ug/cm²/yr).

Results from Incubated Cores

NITRATE PLUS NITRITE

Core #	Sta. No.*	NO3 Flu	ıx (uç	g/cm²/yr)	NO3 Flux	(umc	oles/m2/h)	r ²	Treatment	n
1	Mica	37	+/-	223	3	+/-	18	0.15	Aerated	4
3	Mica	22	+/-	143	2	+/-	12	0.14	Aerated	4
4	Mica	626	+/-	986	51	+/-	80	0.72	Aerated	4
2	Mica	-377	+/-	946	-31	+/-	77	0.51	Ar-Purged	4
5	Mica	-427	+/-	1003	-35	+/-	82	0.54	Ar-Purged	4
7	Mica	-298	+/-	281	-24	+/-	23	0.88	Ar-Purged	4

Core #	Sta. No.*	NO3 Flux (ug	/cm ² /yr)	NO3 Flux	(umo	les/m2/h)	r ²	Treatment	n
9	Main Channel	54 +/-	63	4	+/-	5	0.82	Aerated	4
10	Main Channel	129 +/-	213	11	+/-	17	0.70	Aerated	4
11	Main Channel	244 +/-	232	20	+/-	19	0.88	Aerated	4
12	Main Channel	25 +/-	116	2	+/-	9	0.24	Ar-Purged	4
13	Main Channel	141 +/-	224	11	+/-	18	0.72	Ar-Purged	4
16	Main Channel	6 +/-	95	1	+/-	8	0.03	Ar-Purged	4

AMMONIA

Core #	Sta. No.*	NH4+ Flu	ıx (ug/	/cm ² /yr)	NH4+ Flux	(umc	oles/m2-h)	r^2	Treatment	n	
1	Mica	646	+/-	1410	53	+/-	115	0.57	Aerated	4	
3	Mica	849	+/-	1187	69	+/-	97	0.77	Aerated	4	
4	Mica	737	+/-	1777	60	+/-	145	0.54	Aerated	4	İ
2	Mica	796	+/-	1261	65	+/-	103	0.72	Ar-Purged	4	İ
5	Mica	594	+/-	1426	48	+/-	116	0.53	Ar-Purged	4	
7	Mica	739	+/-	1554	60	+/-	127	0.59	Ar-Purged	4	

Core #	Sta. No.*	NH4+ Flu	ıx (ug	/cm ² /yr)	NH4+ Flux	(umo	oles/m2-h)	r ²	Treatment	n	
9	Main Channel	517	+/-	914	42	+/-	75	0.67	Aerated	4	
10	Main Channel	366	+/-	716	30	+/-	58	0.63	Aerated	4	
11	Main Channel	267	+/-	672	22	+/-	55	0.50	Aerated	4	
12	Main Channel	284	+/-	433	23	+/-	35	0.73	Ar-Purged	4	
13	Main Channel	257	+/-	315	21	+/-	26	0.81	Ar-Purged	4	
16	Main Channel	87	+/-	366	7	+/-	30	0.27	Ar-Purged	4	

ORTHOPHOSPHATE

Core #	Sta. No.*	PO4 Flu	x (ug/cr	m²/yr)	PO4 Flux (umoles	/m2-h)	r ²	Treatment	n
1	Mica	15	+/-	167	1 +/-	6	0.05	Aerated	4
3	Mica	50	+/-	125	2 +/-	5	0.51	Aerated	4
4	Mica	71	+/-	57	3 +/-	2	0.91	Aerated	4
2	Mica	130	+/-	264	5 +/-	10	0.61	Ar-Purged	4
5	Mica	155	+/-	263	6 +/-	10	0.69	Ar-Purged	4
7	Mica	154	+/-	245	6 +/-	9	0.72	Ar-Purged	4

Core #	Sta. No.*	PO4 Flux (ug/o	cm ² /yr)	PO4 Flux (umoles/	/m2-h)	r ²	Treatment	n	
9	Main Channel	109 +/-	256	4 +/-	9	0.54	Aerated	4	
10	Main Channel	101 +/-	197	4 +/-	7	0.63	Aerated	4	
11	Main Channel	63 +/-	158	2 +/-	6	0.50	Aerated	4	
12	Main Channel	285 +/-	433	10 +/-	16	0.73	Ar-Purged	4	
13	Main Channel	58 +/-	97	2 +/-	4	0.70	Ar-Purged	4	
16	Main Channel	88 +/-	79	3 +/-	3	0.89	Ar-Purged	4	

SILICA

Core #	Sta. No.*	Si Flux	(ug/c	:m ² /yr)	Si Flux (ı	umole	es/m2-h)	r ²	Treatment	n
1	Mica	5842	+/-	6803	237	+/-	277	0.83	Aerated	4
3	Mica	5846	+/-	4209	238	+/-	171	0.93	Aerated	4
4	Mica	4907	+/-	10297	199	+/-	419	0.59	Aerated	4
2	Mica	5892	+/-	6683	239	+/-	272	0.83	Ar-Purged	4
5	Mica	5869	+/-	6595	239	+/-	268	0.84	Ar-Purged	4
7	Mica	6164	+/-	6535	251	+/-	266	0.85	Ar-Purged	4

Core #	Sta. No.*	Si Flux (u	g/cm ² /yr)	Si Flux (u	ımole	es/m2-h)	r ²	Treatment	n	
9	Main Channel	6076 +/	/- 7538	247	+/-	306	0.81	Aerated	4	
10	Main Channel	5265 +/	/- 5969	214	+/-	243	0.83	Aerated	4	
11	Main Channel	5633 +/	/- 6296	229	+/-	256	0.84	Aerated	4	
12	Main Channel	5357 +/	/- 5402	218	+/-	220	0.86	Ar-Purged	4	
13	Main Channel	5290 +/	/- 3945	215	+/-	160	0.92	Ar-Purged	4	
16	Main Channel	2897 +/	/- 4835	118	+/-	197	0.70	Ar-Purged	4	Predominant initial flux.

Results from Lander Deployments NITRATE PLUS NITRITE

Deploy #	Sta. No.*	NO3 Flux (ug/cm ² /	yr)	
2	Mica	279 +/-	50	
4	Mica	141 +/-	16	
	l	,		
1	Main Channel	175 +/-	50	
2	Main Channel	177 +/-	21	
3	Main Channel	124 +/-	14	

AMMONIA

Deploy #	Sta. No.*	NH4+ Flux (ug/cm²/	/yr)
2	Mica	187 +/-	33
4	Mica	25 +/-	11
2	Main Channel Main Channel Main Channel	53 +/- 47 +/- 75 +/-	35 23 14

ORTHOPHOSPHATE

	Deploy #	Sta. No.*	PO4 Flux (ug/cm²/yr)	
	2	Mica	36 +/-	9
	4	Mica	7 +/-	6
	1	Main Channel	6 +/-	8
	2	Main Channel	7 +/- 1	0
	3	Main Channel	9 +/-	6
,				

SILICA

Deploy #	Sta. No.*	Si Flux (ug/cm²/yr)	
2	Mica	1671 +/- 246	
4	Mica	1148 +/- 287	
1	Main Channel	1866 +/- 369	
2	Main Channel	1425 +/- 256	
3	Main Channel	1445 +/- 246	

Table 15. Benthic Flux of Mercury Species (August 16-27, 1999)

Mass fluxes are presented in units of nanograms solute per square centimeter per year (ng/cm²/yr).

Mercury Flux Summary

(All 12 hours of incubation data used)

Core #	Sta. No.*	Hg-T Flu	x (ng/cm ² -yr)	Hg-T Flux	(nmoles/m2-h)	r ²	Treatment
1	Mica	65	+/- 341	0.4	+/- 1.9	0.19	Aerated
3	Mica	167	+/- 255	1.0	+/- 1.5	0.73	Aerated
4	Mica	90	+/- 281	0.5	+/- 1.6	0.40	Aerated
2	Mica	107	+/- 171	0.6	+/- 1.0	0.71	Ar-Purged
5	Mica	103	+/- 186	0.6	+/- 1.1	0.66	Ar-Purged
7	Mica	13	+/- 236	0.1	+/- 1.3	0.02	Ar-Purged

Core #	Sta. No.*	Hg-T Flux (ng	/cm ² -yr)	Hg-T Flux	(nmo	les/m2-h)	r ²	Treatment
9	Main Channel	292 +/-	3240	1.7	+/-	18.4	0.05	Aerated
10	Main Channel	80 +/-	1544	0.5	+/-	8.8	0.02	Aerated
11	Main Channel	141 +/-	1591	0.8	+/-	9.1	0.05	Aerated
12	Main Channel	537 +/-	1028	3.1	+/-	5.9	0.64	Ar-Purged
13	Main Channel	195 +/-	809	1.1	+/-	4.6	0.27	Ar-Purged
16	Main Channel	296 +/-	755	1.7	+/-	4.3	0.50	Ar-Purged

(Only first 2 hours of incubation data used)

Core #	Sta. No.*	Hg-T Flux (ng/cm ² -yr)	Hg-T Flux (nmoles/m2-h)	r ²	Treatment
1	Mica	926	5.3	1.00	Aerated
3	Mica	803	4.6	1.00	Aerated
4	Mica	799	4.5	1.00	Aerated
2	Mica	531	3.0	1.00	Ar-Purged
5	Mica	539	3.1	1.00	Ar-Purged
7	Mica	610	3.5	1.00	Ar-Purged

Core #	Sta. No.*	Hg-T Flux (ng/cm ² -yr)	Hg-T Flux (nmoles/m2-h)	r ²	Treatment
9	Main Channel	8241	46.9	1.00	Aerated
10	Main Channel	3967	22.6	1.00	Aerated
11	Main Channel	4138	23.5	1.00	Aerated
12	Main Channel	2137	12.2	1.00	Ar-Purged
13	Main Channel	1941	11.0	1.00	Ar-Purged
16	Main Channel	2084	11.9	1.00	Ar-Purged

Methyl-Mercury Flux Summary

(All 12 hours of incubation data used)

Core #	Sta. No.*	Me-Hg Flux (ng/cm²-yr)	Me-Hg Flux (pmoles/m2-h)	r ²	Treatment
1	Mica	0.5	2.9	1.00	Aerated
3	Mica	0.2	1.1	1.00	Aerated I
4	Mica	0.2	1.1	1.00	Aerated
2	Mica	1.2	6.6	1.00	Ar-Purged
5	Mica	1.7	9.9	1.00	Ar-Purged
7	Mica	0.6	3.4	1.00	Ar-Purged

Not significant relative to detection limit

Core #	Sta. No.*	Me-Hg Flux (ng/cm ² -yr)	Me-Hg Flux (pm	oles/m2-h)	r ²	Treatment
9	Main Channel	0.8	4.8 +/-	43.5	0.07	Aerated
10	Main Channel	0.4	2.2 +/-	15.4	0.11	Aerated
11	Main Channel	0.4	2.5 +/-	9.2	0.32	Aerated
12	Main Channel	1.1	6.5 +/-	6.1	0.88	Ar-Purged
13	Main Channel	1.7	9.9 +/-	13.4	0.91	Ar-Purged
16	Main Channel	1.1	6.2 +/-	8.0	0.79	Ar-Purged

(Initial 2 hours of incubation data used)

Core #	Sta. No.*	Me-Hg Flux (ng/cm ² -yr)	Me-Hg Flux (pmoles/m2-h)	r ²	Treatment
9	Main Channel	20.2	114.7	1.00	Aerated
10	Main Channel	6.8	38.6	1.00	Aerated
11	Main Channel	4.2	23.7	1.00	Aerated
12	Main Channel	1.9	11.1	1.00	Ar-Purged
13	Main Channel	4.1	23.2	1.00	Ar-Purged
16	Main Channel	4.6	26.4	1.00	Ar-Purged

Table 16. Dissolved Organic Carbon flux from Core Incubations (Benthic Flux Experiments - August 18 and 24, 1999) Coefficients of determination (r²) are tabulated for the time-series regressions used to determine benthic flux.

Dissolved Organic Carbon Flux Summary (All 12 hours of incubation data used)

Core #	Sta. No.*	DOC Flux (ug/o	cm ² -yr)	DOC Flux	(umc	oles/m²-h)	r ²	Treatment	n	Comments
1	Mica	2439 +/-	138	231.8	+/-	13.1	0.92	Aerated	14	
3	Mica	1808 +/-	65	171.9	+/-	6.2	0.97	Aerated	14	
4	Mica	1819 +/-	9	172.9	+/-	0.9	1.00	Aerated	12	
2	Mica	1842 +/-	278	175.1	+/-	26.4	0.63	Ar-Purged	14	
5	Mica	1448 +/-	285	137.6	+/-	27.1	0.35	Ar-Purged	18	
7	Mica	1413 +/-	180	134.3	+/-	17.1	0.63	Ar-Purged	16	

Core #	Sta. No.*	DOC Flux (ug/cr	m²-yr)	DOC Flux (umole	s/m²-h)	r ²	Treatment	n	Comments
9	Main Channel	1694 +/-	412	161.0 +/-	39.1	0.32	Aerated	16	
10	Main Channel	2917 +/-	355	277.3 +/-	33.8	0.69	Aerated	15	
11	Main Channel	3677 +/-	340	349.6 +/-	32.3	0.74	Aerated	17	
12	Main Channel	2634 +/-	181	250.4 +/-	17.2	0.84	Ar-Purged	17	
13	Main Channel	3076 +/-	287	292.4 +/-	27.2	0.74	Ar-Purged	17	
16	Main Channel	2038 +/-	344	193.8 +/-	32.7	0.49	Ar-Purged	17	