

## **Lake Vermilion Elemental Paleoecology**

**Written by E. D. Reavie (Center for Water and the Environment (CWE), Natural Resources Research Institute (NRRI)) for the Sportsmen Club of Lake Vermilion (SCLV)**

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### **Background**

Taconite mining associated with Minntac Inc. in Mountain Iron, MN, warranted the construction of ponds for the storage of mining waste (tailings). A plan (environmental impact statement and proposed workplan) to initiate the gradual release of water from these ponds is in development, as the ponds will soon reach their maximum capacity for the accumulation of water from precipitation. Based on the proposed alternative for discharge, water from these ponds would eventually discharge to Lake Vermilion via the Sandy and Pike rivers. This impact statement, prepared by the Minnesota Pollution Control Agency, is currently under public review. There is a public concern, notably from the Sportsmen Club of Lake Vermilion, that the release of potentially contaminated water from the tailings ponds may result in adverse environmental impacts in Lake Vermilion. Although this surface water release has not yet been initiated, there are existing release points through seeps. It is possible that these existing releases have already resulted in environmental contamination, and evidence of such contamination could reveal potential future contamination from the Minntac tailings ponds.

This report summarizes the pertinent chemical results from three sediment cores from the eastern region of Lake Vermilion, where water from the tailings ponds would eventually discharge; one core in the Pike River Flowage basin upgradient of Minnesota Rte. 1, one core downgradient of Pike Bay (near McKinley Park), and one core in Big Bay (Figure 1). These locations were selected because they are the most likely areas to be impacted by environmental insults entering via the Pike River. Detailed chemical analyses of sediments from the top and bottom of each core were performed (complete raw data from these analyses are included on the supplemental CD provided to the SCLV). Bottom sediments reflect conditions prior to European settlement of the region, and top sediments reflect the current, non-pristine condition. Comparison of bottom and top sediment intervals will provide a general indication of overall long-term environmental

impacts to the lake. All sediment intervals were analyzed for loss-on-ignition parameters, and remaining material was archived at NRRI-Ely using freeze drying, for potential future analyses.

The CD included with this report contains the following:

- This report (Adobe Portable Document format)
- A folder containing the raw data from chemical analyses (Microsoft Excel format)
- A Microsoft Powerpoint presentation of results, as presented to SCLV on 19 January 2005.
- The original (pre-signed) contract (Adobe Portable Document format)
- Field work and other photos (JPG format)

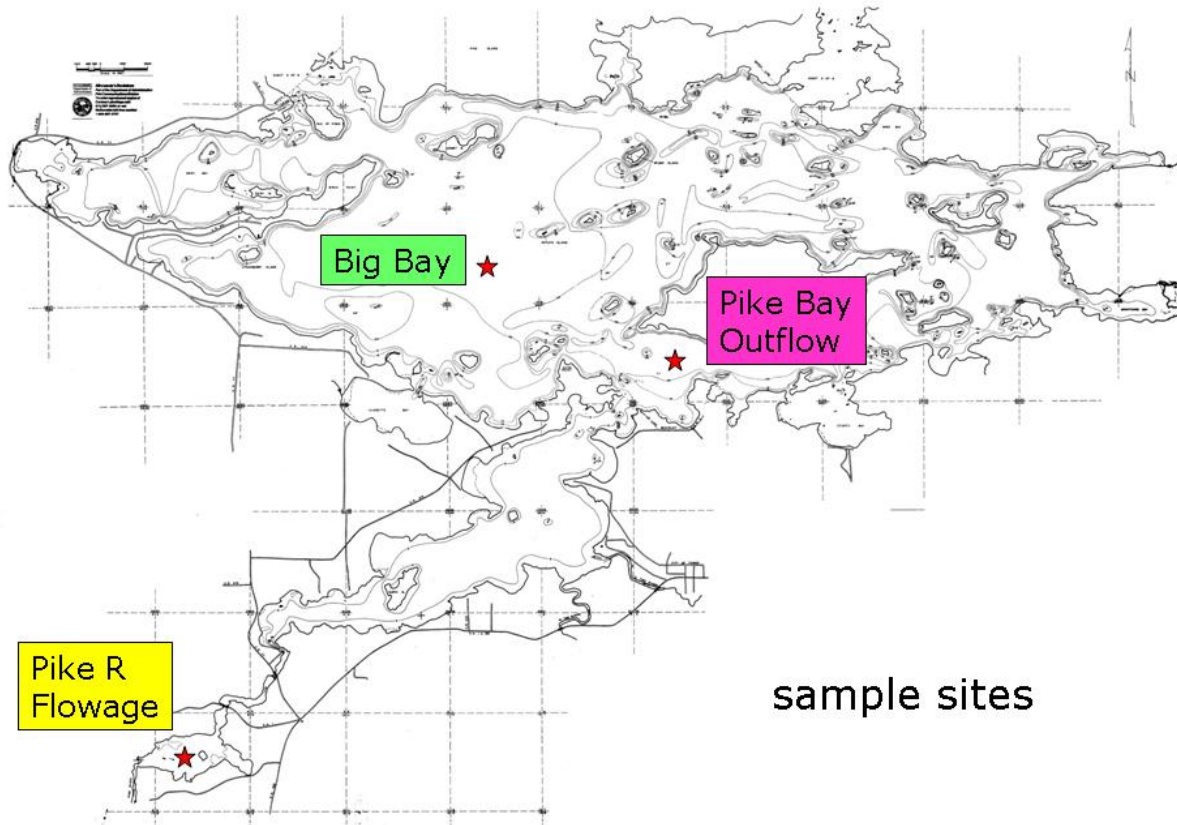


Figure 1. Locations of three sediment cores, collected 29 October 2004.

## Methods

*Coring:* Three sediment profiles were collected to represent human history in the region so that pre- and post-remedial trends may be inferred. Sediment cores were collected 29 October 2004, with the logistic aid of Mel Hintz and others associated with the SCLV. Cores were immediately extruded in 1-cm sediment intervals and stored in sterile bags, then transported to the lab for further preparations and analyses. Sediment samples were processed at the Ely Field Station (Center for Water and the Environment, Natural Resources Research Institute, University of Minnesota Duluth). Subsamples were sent to the University of Minnesota Environmental Sciences Laboratory (Minneapolis) for chemical analyses.

*General Organic and Inorganic Chemistry:* Water content, organic content, and clastic/carbonate content were determined after respectively drying (100°C), firing (550°C) and ashing (1,000°C) sediment subsamples (loss-on-ignition). Organic content, in particular, can be used to track the accumulation of materials from large construction projects and indicate changes in increased productivity caused by anthropogenic inputs.

*Specific Inorganic Chemistry:* Standard methods were used to analyze metals (including Cu, Zn, Cd, Pb, Al, V, Cr, Fe, Mn, Co, Ni, Mo, Ba, Hg) and other inorganic compounds (e.g., S, P). An acid extraction technique was used to analyze for non-volatile elements, and total composition analysis and digestion were used to analyze for major oxidants and trace elements. Top/bottom changes in sulfate load to Lake Vermilion were estimated from total S analysis, as sulfates are reactive and mobile, and so do not remain as sulfate in the sediment matrix.

Geochemical results for Cu, Zn, Pb and Cd were compared to similar results from the surface sediments of 55 lakes in Minnesota with no known mining impacts. This comparison was employed to identify whether sedimentary contaminant levels in Lake Vermilion are typical for the region. In other words, we can identify if there has been a significant increase in contaminants since pre-human times, and if this increase has been greater than that observed in other lakes in the region (i.e., more than that resulting from atmospheric deposition). Such comparisons can reveal evidence of augmented contamination from mining sources and the relative sensitivity of Lake Vermilion to inorganic contamination.

*Preservation:* All remaining sediments were freeze-dried for long-term storage. Freeze-drying allows physical, chemical and biological sediment analyses to be performed long after collection (whereas wet-stored sediments may be subject to chemical degradation and fungal infection).

## Results

*Organic content:* The organic profiles from the three cores (Figure 2) track human influences over the last ~100 or more years. The decline in organic material between 30 and 20 cm in the Pike Bay outflow, and between 19 and 10 cm in Big Bay, reflects an increased relative flux of inorganic material from human activities, probably including projects such as agricultural and property clearance, and road building, which were prominent beginning in the early 20<sup>th</sup> century. The subsequent increases in organic material likely reflect increases in productivity resulting from increased anthropogenic nutrient flux, which in turn resulted in increased productivity in the water column. The Pike River flowage shows only an increase from the bottom to the top of

the core, indicating that the core probably does not capture pre-settlement conditions, but likely contains a complete record of the 20<sup>th</sup> century. While these results are not necessarily useful in indicating potential mining impacts, they provide a cost-effective quality assessment of the core profiles, and indicate anthropogenic impacts that have occurred in the local watershed.

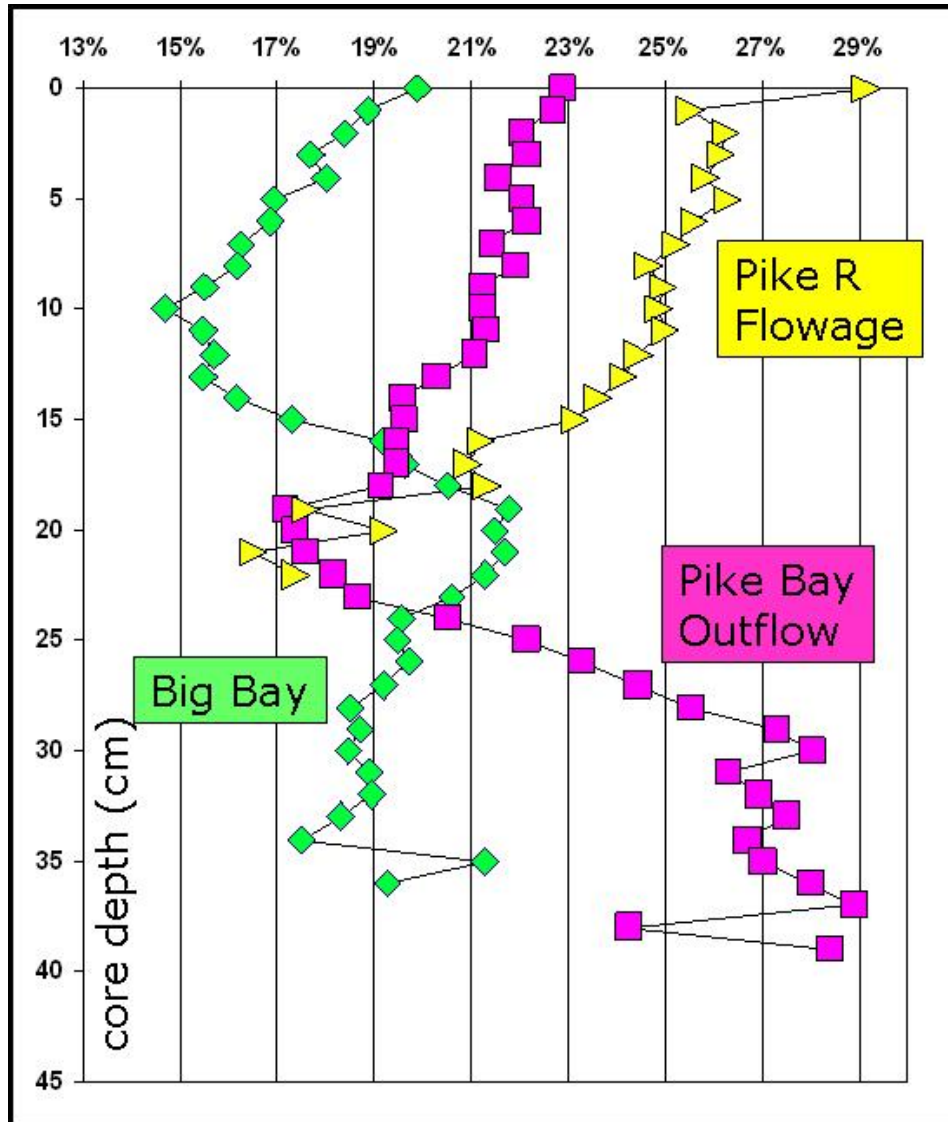


Figure 2. Organic content of sediments from Pike River Flowage (triangles), Pike Bay outflow (squares) and Big Bay (diamonds).

*Chemical Results:* Chemical trends for pertinent elements are presented below in histograms. Figure 3 shows an example of the data presentation using arbitrary data. If these data were real, the trends would show a pre-impact-to-current increase in element “X” in Pike River Flowage and Pike Bay Outflow, and a decrease in Big Bay. The results would also show that the modern concentrations of element “X” do not exceed concentrations measured in other lakes (with no known mining impacts) from the region.

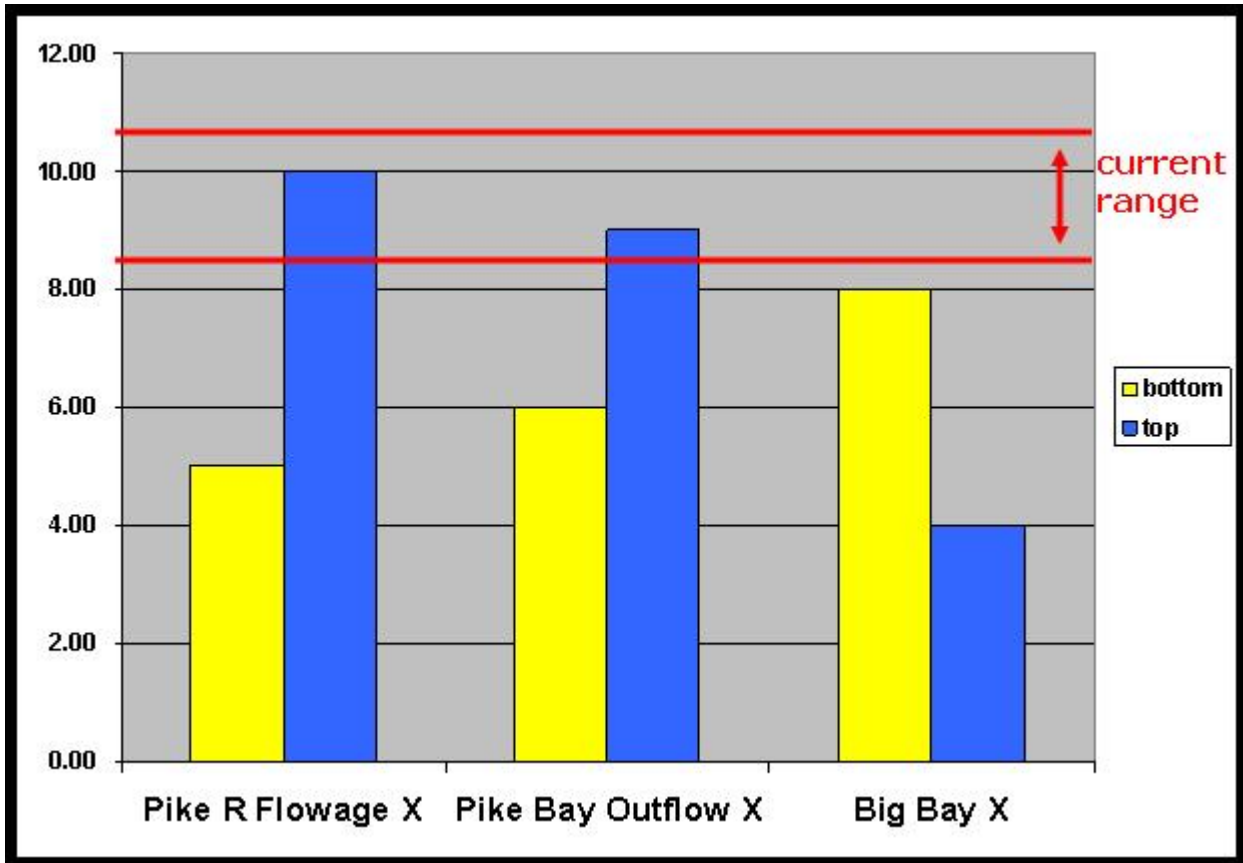


Figure 3. Example chemical results using arbitrary data and a hypothetical element “X.” The x-axis shows the three core locations, and the y-axis shows element concentrations in parts per million (ppm; analogous to mg/kg), unless otherwise specified. Elemental concentrations in core bottom and top intervals are shown, as well as the range (standard deviation) of results from the surface sediments of other lakes in the region (if available for the selected element).

*Sulfur*: Sulfur content was analyzed to track possible mining-related changes in the sulfate flux to Lake Vermilion. The Minntac tailings ponds are known to contain high concentrations of sulfates, which can have detrimental effects on water quality and biota. Sulfates can be particularly harmful because they aid in the methylation of mercury, increasing the toxicity of mercury species to biota such as fish.

The results from Lake Vermilion sediments (Figure 4) indicate that sulfur concentrations have declined. Reasons for the decline in sulfur are difficult to confirm without additional analyses; however, it is apparent that sulfur (and likely sulfate) flux to Lake Vermilion is not higher than pre-anthropogenic inputs.

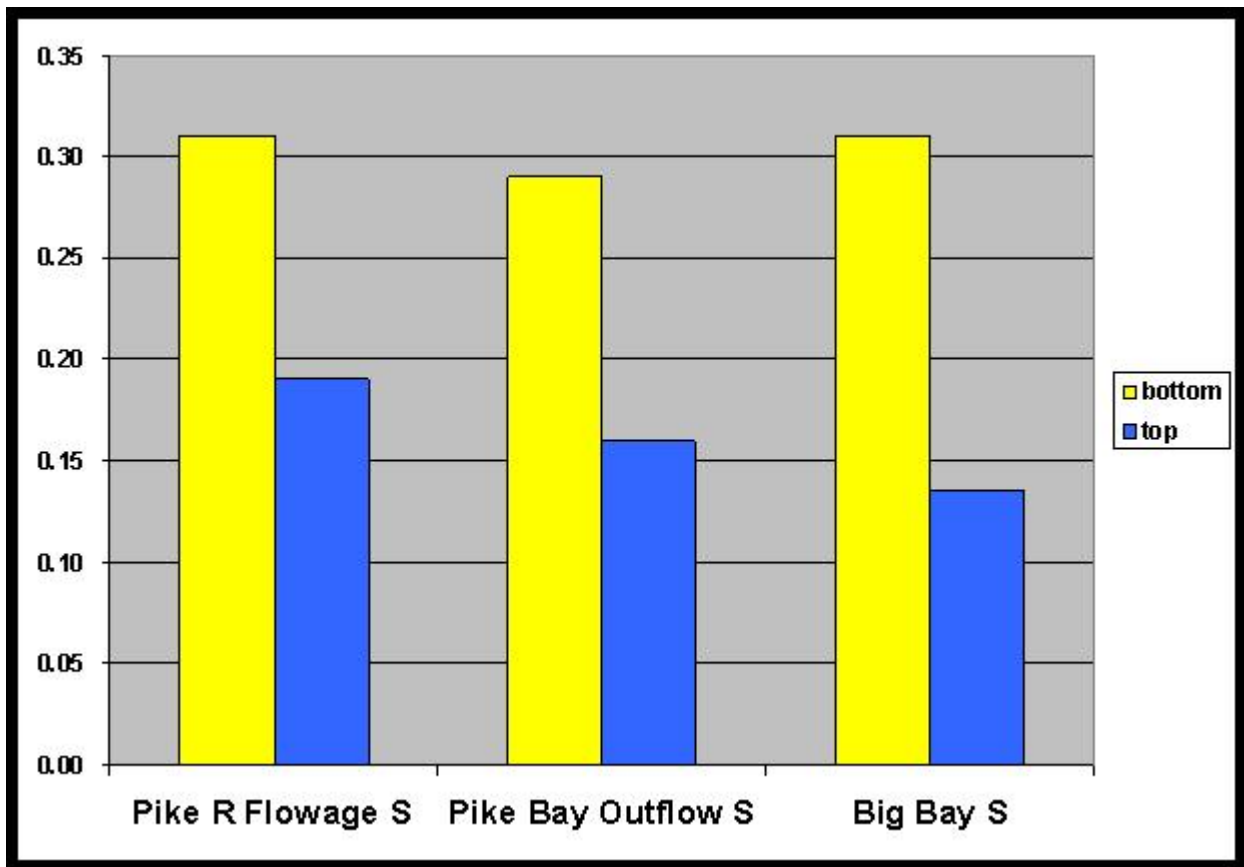


Figure 4. Sulfur content (%) of Lake Vermilion sediments.

*Mercury* (Figure 5): Mercury is a known atmospheric contaminant in northern Minnesota. Concentrations show little discernable change in Pike River Flowage and Pike Bay outflow, and a decline in Big Bay. However, overall these concentrations are relatively low and any bottom-top changes in Pike River Flowage and Pike Bay Outflow are within the instrumental detection error. No long-term increase in Hg is inferred at the three sites.

Table 3-12, page 3-14 of the Mercury and Methylmercury Impact Assessment Technical Memorandum (September 2004) reports that 0.188 ppm total mercury was recorded in sediments from the Pike River Flowage in 2001. Samples collected for the Technical Memorandum combined the top 10 cm of sediment, whereas we used the top 1 cm; a comparison of these results indicates a slightly lower Hg concentration in modern sediments collected in late 2004, when compared to an average for the last few decades.

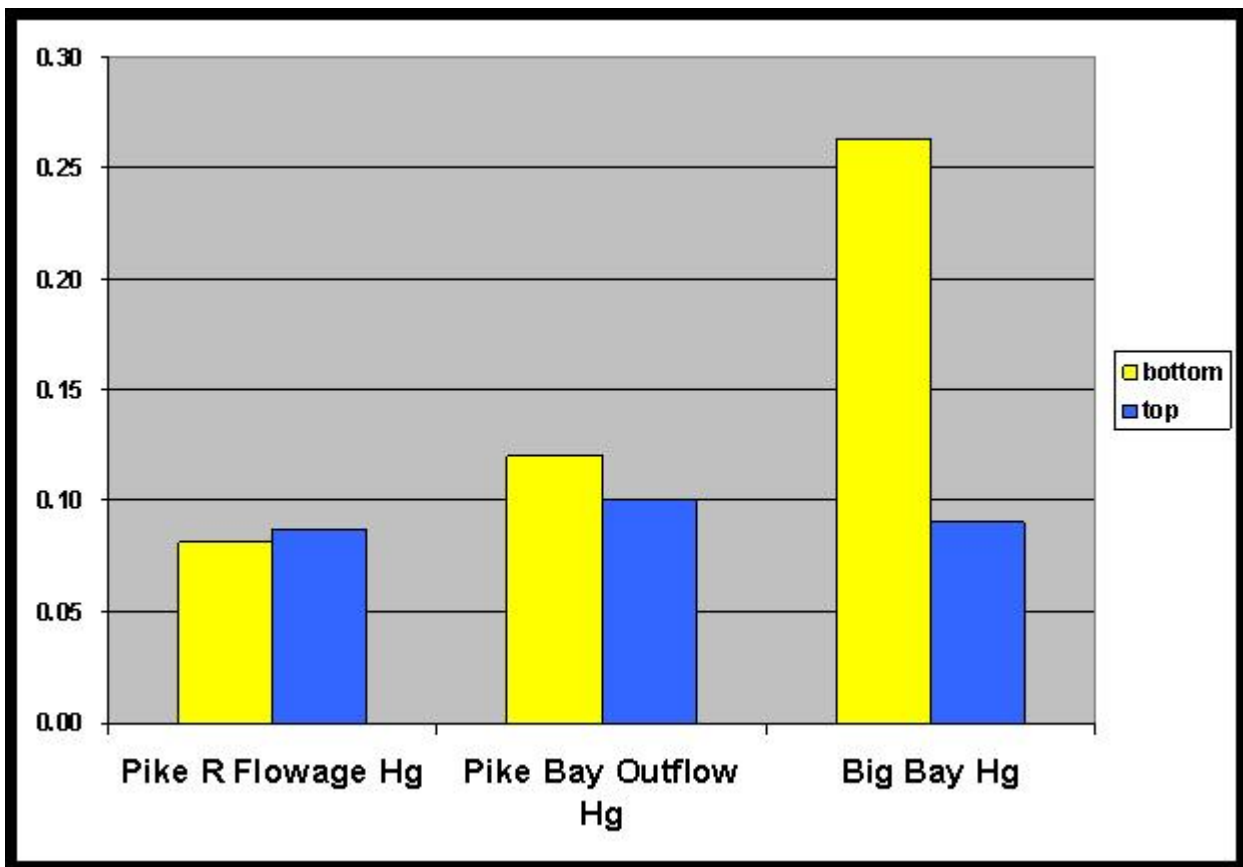


Figure 5. Mercury content (ppm) of Lake Vermilion sediments.

*Copper* (Figure 6): Cu is a known atmospheric contaminant in some areas of northern Minnesota. A slight decrease in Cu is observed in Pike Bay outflow and Big Bay. It is also notable that pre-anthropogenic sediments contained a naturally high concentration of Cu – two sites had higher than the range of modern concentrations for the region.

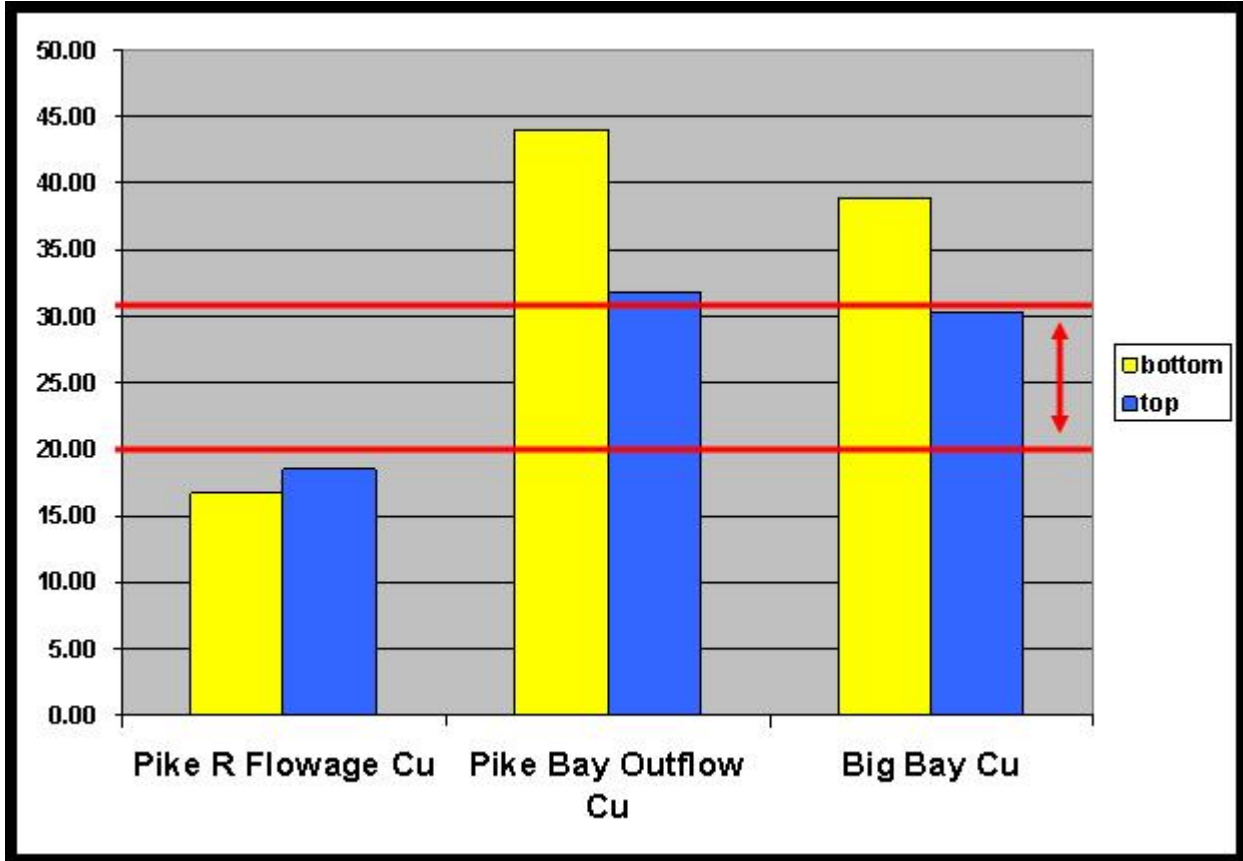


Figure 6. Copper content (ppm) of Lake Vermilion sediments.



*Zinc* (Figure 7): Zn is a known atmospheric contaminant in some areas of northern Minnesota. An increase in Zn is noted in Pike River flowage, and no long-term change is inferred at the other two sites, farther downstream. Like Cu, It is notable that pre-anthropogenic sediments contained a naturally high concentration of Cu, as modern concentrations from other lakes in the region fall below pre-anthropogenic concentrations in Lake Vermilion. The increase in Zn at Pike River flowage (the farthest upstream) may be a result of mobilization from the watershed (aided by low-pH rainwater) and subsequent deposition in the flowage basin. It is possible that no long-term increase is noted farther downstream as Zn concentrations equilibrate to natural conditions after passing through the flowage. Based on comparison to data collected within the Minntac tailings basins (see Minntac Draft EIS, September 2004), the increase in Zn in sediments of the Pike River Flowage is unlikely to be attributed to mining activities.

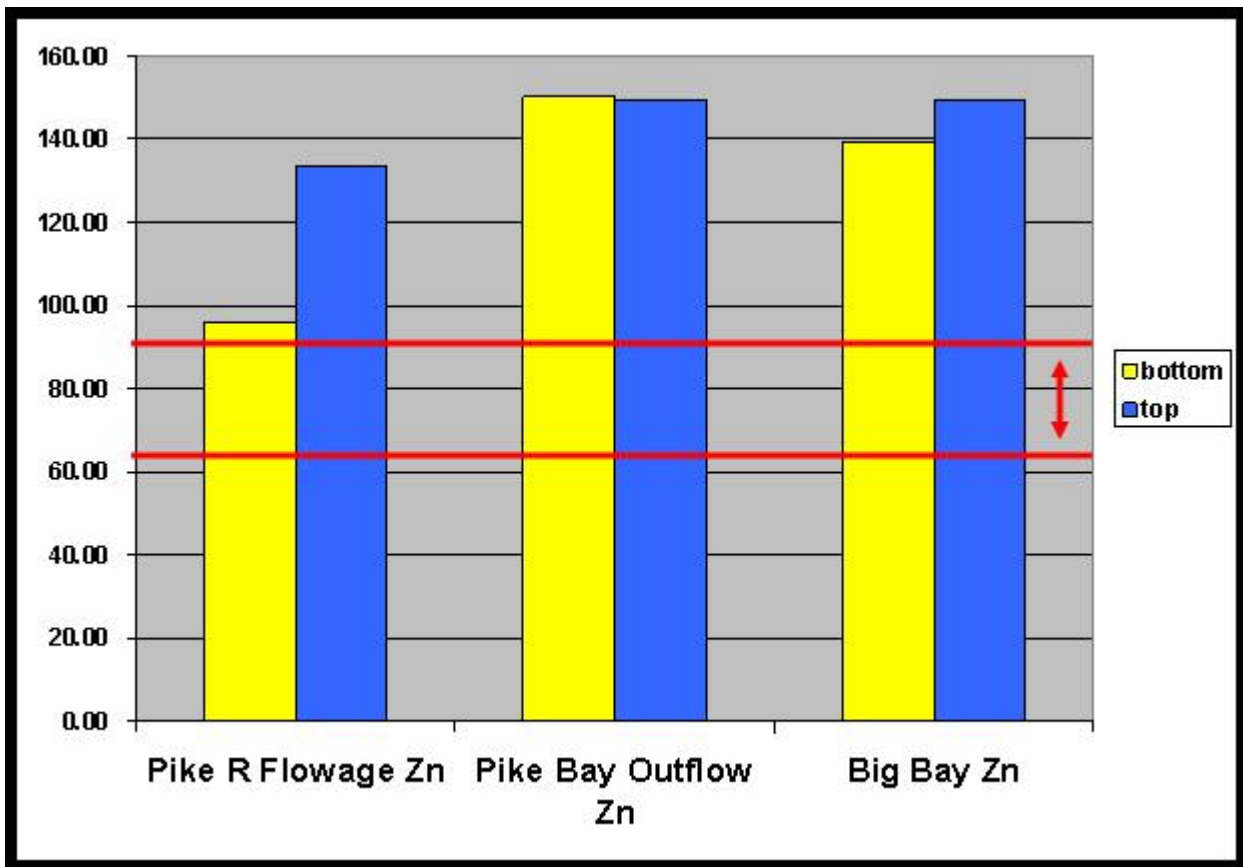


Figure 7. Zinc content (ppm) of Lake Vermilion sediments.

*Lead* (Figure 8): Pb is a known atmospheric contaminant in some areas of northern Minnesota. All three sites revealed an increase in Pb, probably from atmospheric deposition. Pb concentrations in the sediments fall within the range of contemporary sediment concentrations for the region. Based on data collected within the Minntac tailings basins (see Minntac Draft EIS, September 2004), these increases in Pb concentrations in Lake Vermilion are not attributed to mining activities.

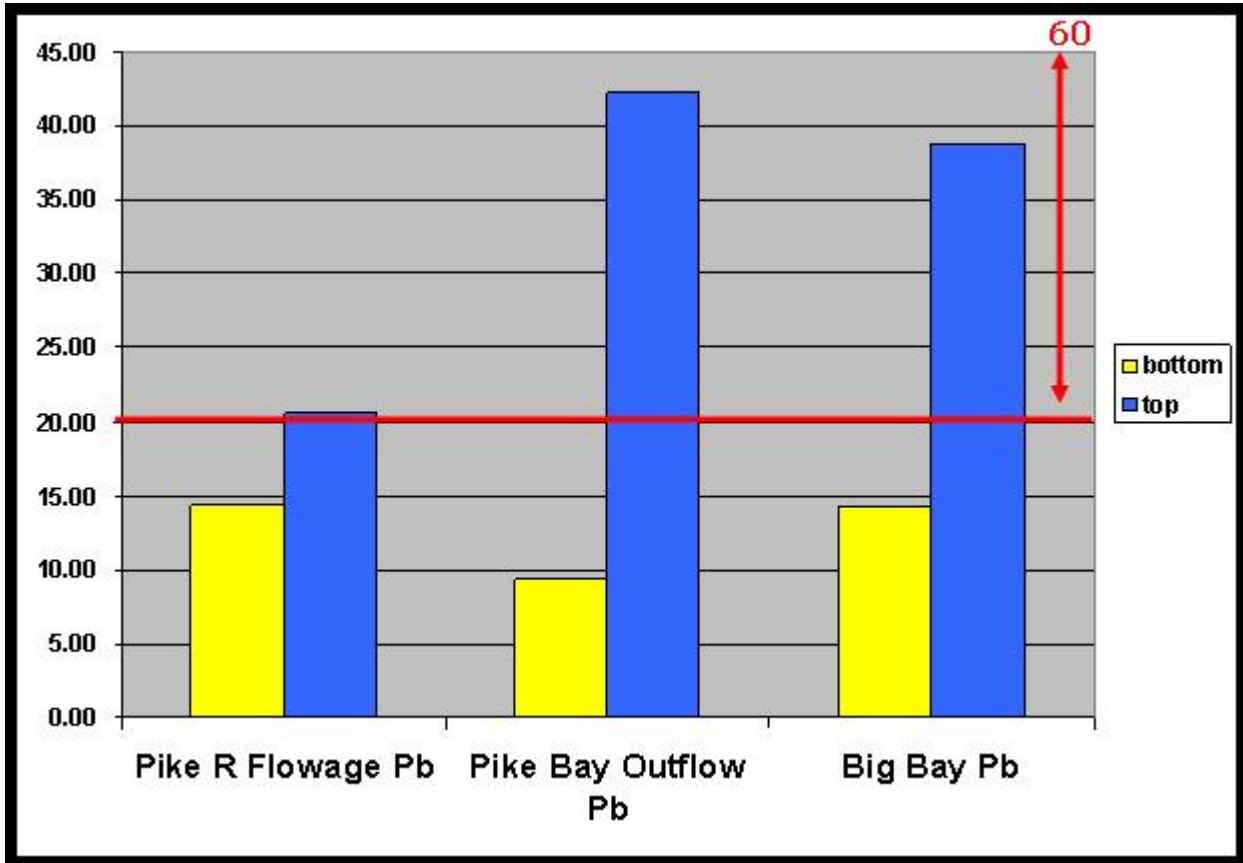


Figure 8. Lead content (ppm) of Lake Vermilion sediments.

*Cadmium* (Figure 9): Cd is a known atmospheric contaminant in some areas of northern Minnesota. Like Pb, all three sites revealed an increase in Cd, probably from atmospheric deposition. Cd concentrations in the sediments fall within the range of contemporary sediment concentrations for the region. Based on data collected within the Minntac tailings basins (see Minntac Draft EIS, September 2004), the observed increases in Cd concentrations in Lake Vermilion are not attributed to mining activities.

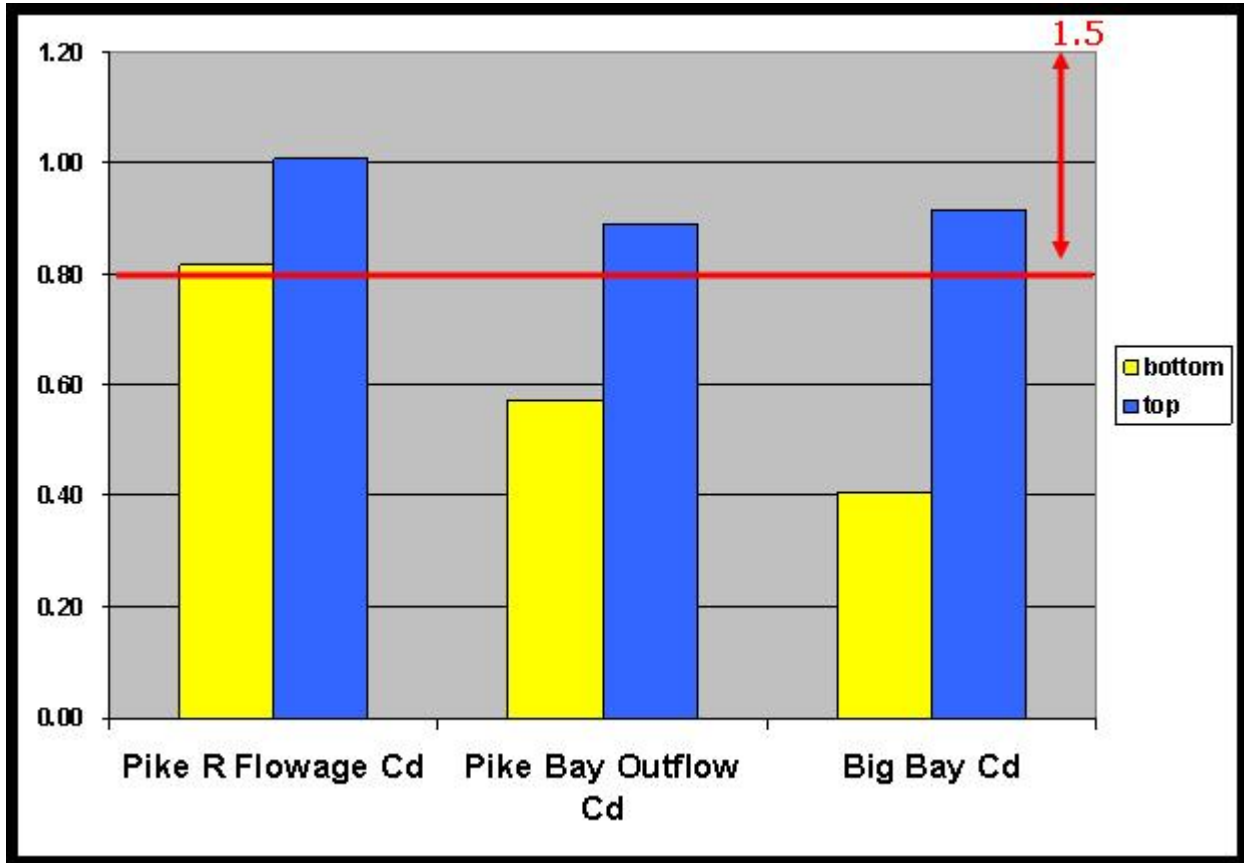


Figure 9. Cadmium content (ppm) of Lake Vermilion sediments.

*Magnesium* (Figure 10): Mg is a natural component of the local bedrock and mobilized metals in the water. The increase in sedimentary Mg at all three sites is probably partially attributed to additional mobilization from the watershed due to acid rain (i.e., lower pH rainwater in recent decades). Magnesium is a component of hardness, which is used as a diagnostic measure in the Minntac EIS. Although hardness is elevated at the Sandy River seepage point (point 030; see EIS for details of point locations), downstream monitoring stations in the Sandy River (e.g., point 701, approximately 20,000 ft downstream from point 030) indicate that tailings seepage is not contributing to an elevation of hardness in the River. While contributions of Mg from the tailings to Lake Vermilion cannot be ruled out, contributions are likely to have been minimal compared to local sources.

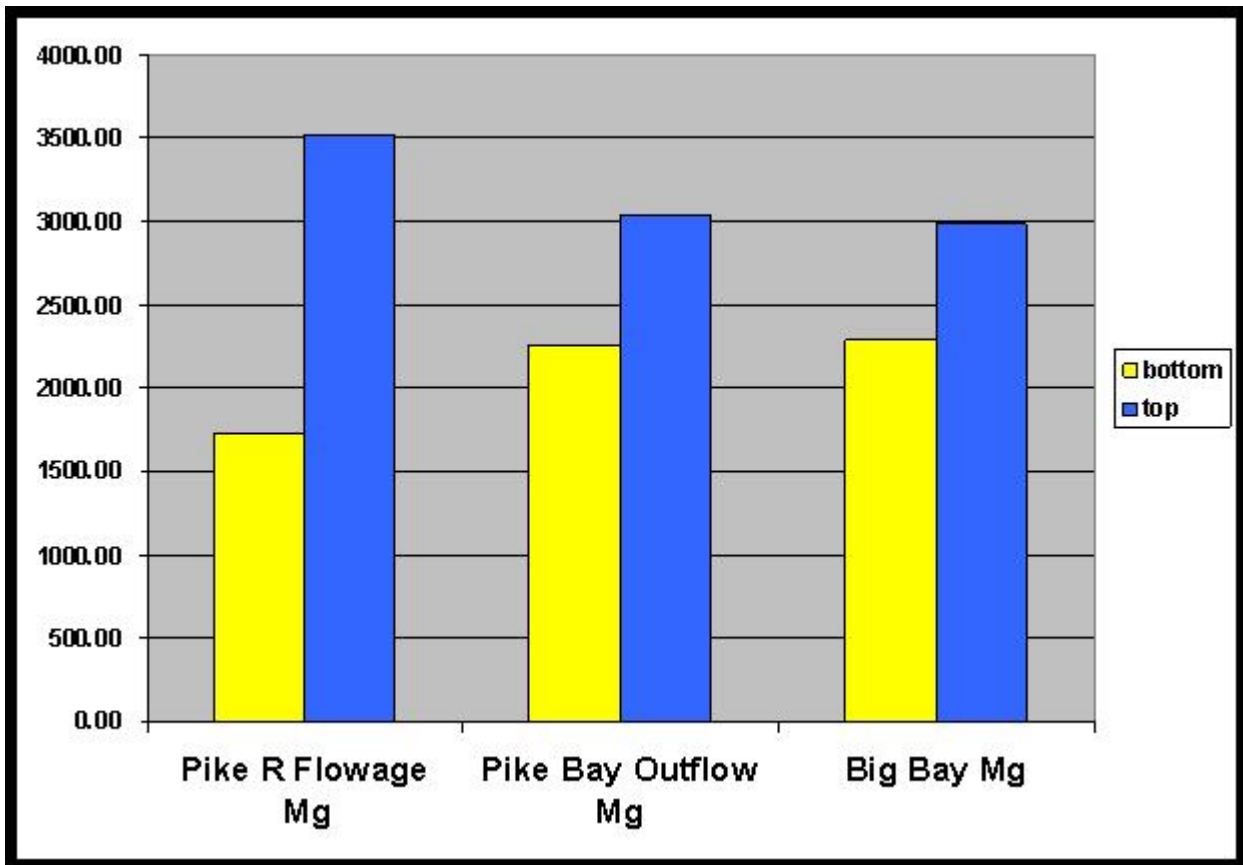


Figure 10. Magnesium content (ppm) of Lake Vermilion sediments.

*Aluminum* (Figure 11): Al is a natural component of bedrock, and mobilized concentrations can increase as a result of acid rain (i.e., lower pH in recent decades). An increase in Al is noted in Pike River flowage, and no long-term change is inferred at the other two sites, farther downstream. The increase in Al at Pike River flowage (the farthest upstream) may be a result of mobilization from the watershed (aided by low-pH precipitation) and subsequent deposition in the flowage basin. It is possible that no long-term increase is noted farther downstream as Al concentrations equilibrate to background levels after passing through the flowage (similar to Zn concentrations).

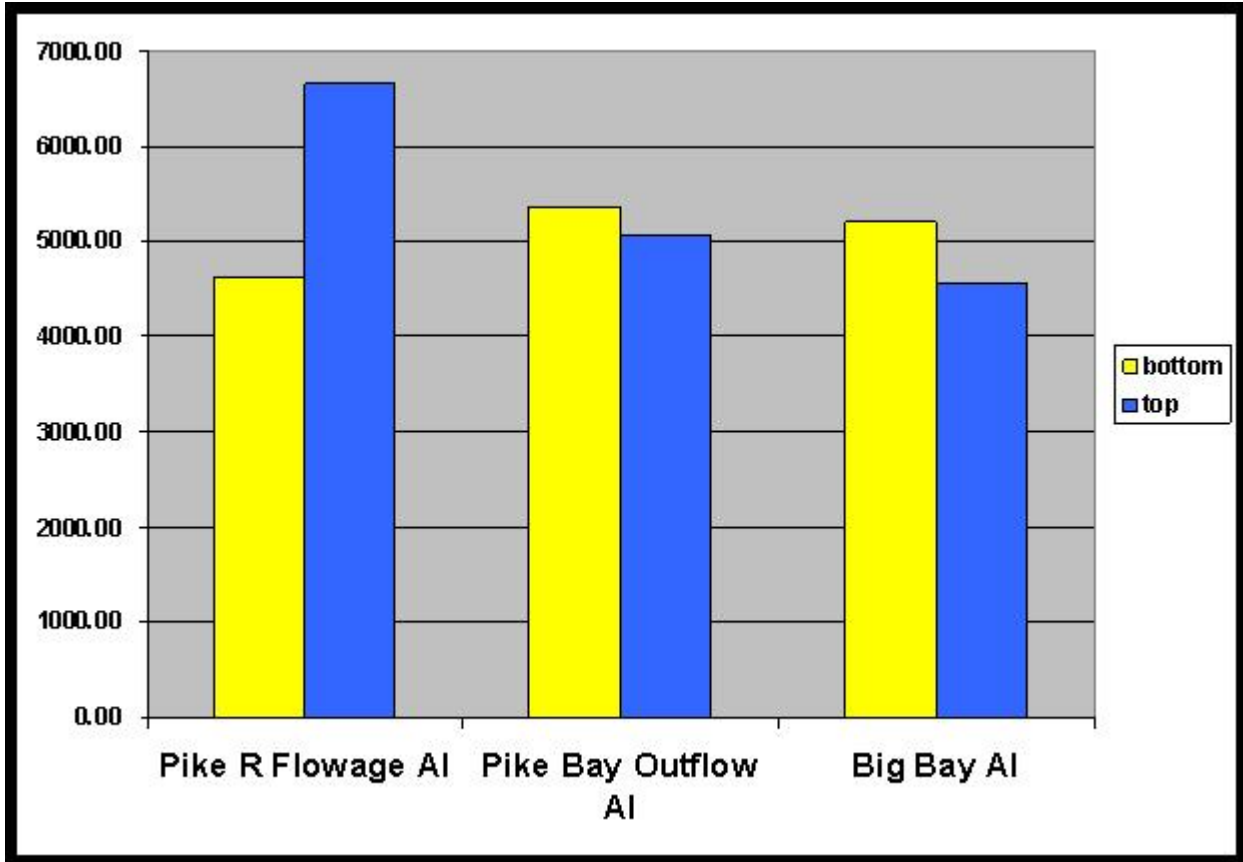


Figure 11. Aluminum content (ppm) of Lake Vermilion sediments.

*Iron* (Figure 12): Iron is a natural component of bedrock, and mobilized concentrations can increase as a result of acid rain (i.e., lower pH in recent decades). An increase in Fe is noted in Pike River flowage and to a lesser degree in Pike Bay outflow, and no long-term increase is inferred in Big Bay. As noted for Zn and Al, the notable increase in Fe at Pike River flowage (the farthest upstream) may be a result of mobilization from the watershed (aided by low-pH rainwater) and subsequent deposition in the flowage basin. The long-term increase subsides farther downstream possibly because Fe concentrations equilibrate to natural conditions after passing through the flowage and Pike Bay.

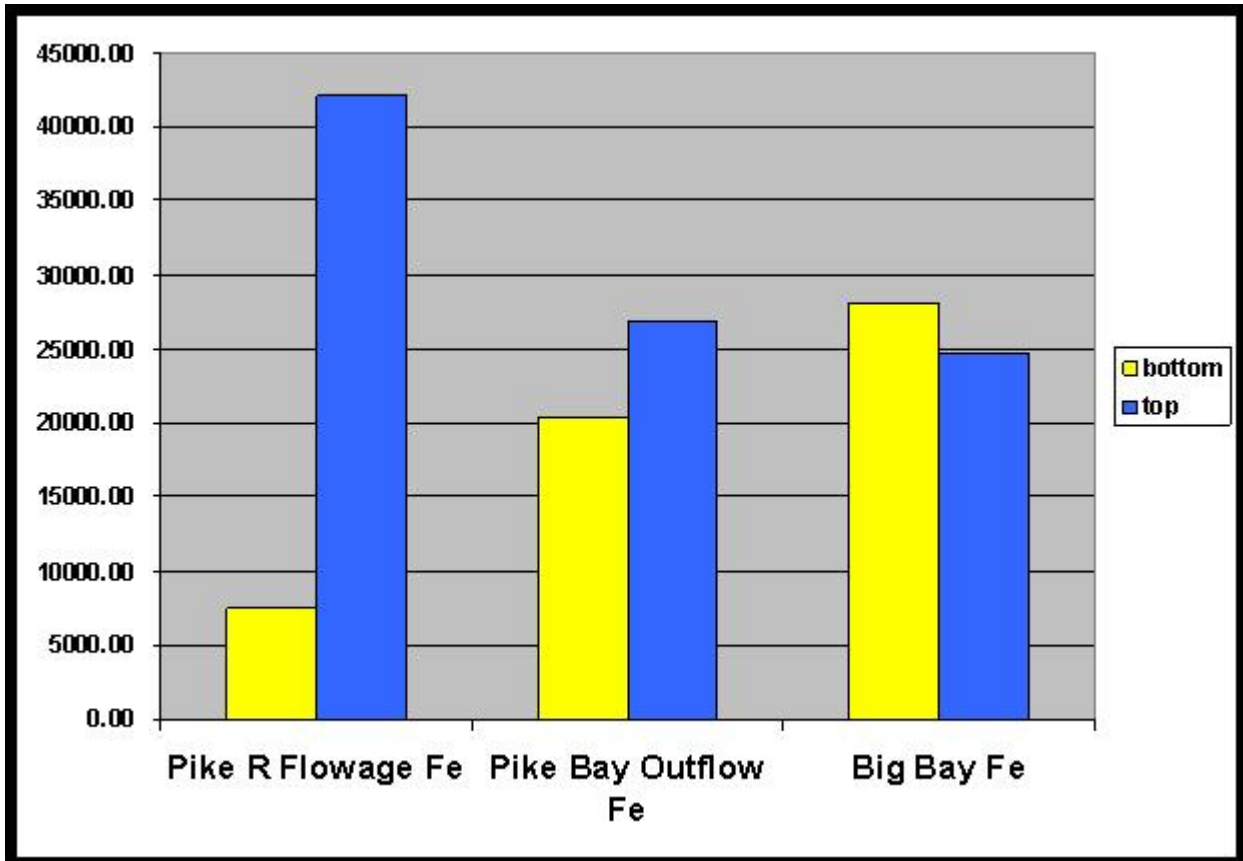


Figure 12. Iron content (ppm) of Lake Vermilion sediments.

*Manganese* (Figure 13): Notable increases in Mn occurred at all three sites. Like Fe, Mn is a natural component of bedrock, and mobilized concentrations can increase as a result of acidified precipitation (i.e., lower pH in recent decades). While Mn is an essential trace element for aquatic and terrestrial biota, it is toxic to aquatic organisms in excessive amounts. Similar to Mg, Mn is elevated at the Sandy River seepage point (point 030, see the Minntac EIS), while downstream monitoring stations in the Sandy River (e.g., point 701, approximately 20,000 ft downstream from point 030) show Mn concentrations less than 10% of that measured at the seepage point. At the intersection of the Sandy River and the Pike River (point S-1) Mn concentrations are even lower, and well within drinking water standards for Mn. These data indicate that tailings seepage is not contributing to an elevation of Mn that persists downriver. While small contributions of Mn from the tailings to Lake Vermilion cannot be fully ruled out, contributions are likely to have been minimal compared to local sources.

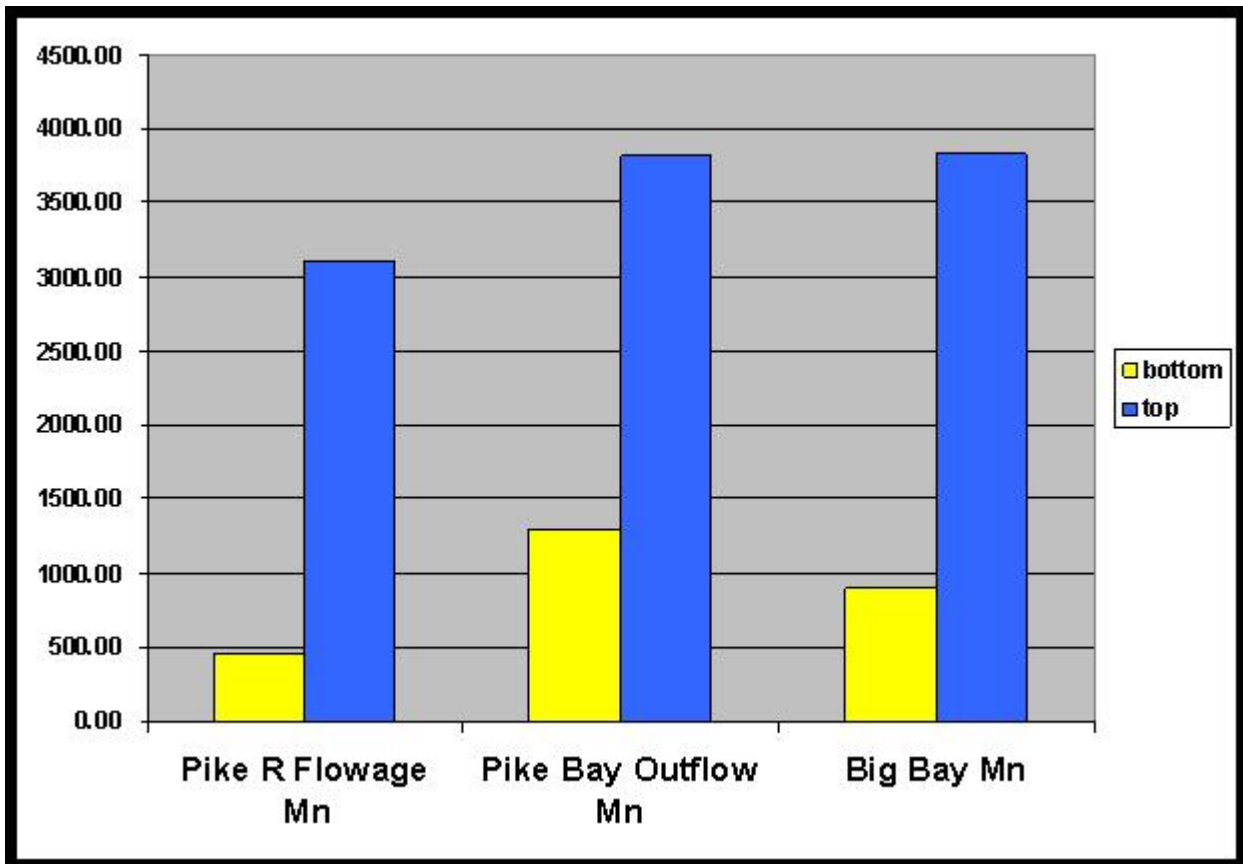


Figure 13. Manganese content (ppm) of Lake Vermilion sediments.

*Sodium* (Figure 14): Na concentrations in pre-anthropogenic sediments were below instrumental detection limits, whereas modern concentrations at all three sites were between 40 and 50 ppm. It is likely the modern inputs of sodium are almost solely from road salt (NaCl) applications. Although ecological effects on Lake Vermilion have not been quantified, Na is a pollutant that may be having impacts on near-shore aquatic ecology, especially during snow-melt in the spring. Studies on the flux of excess road salt pollution to Minnesota freshwater systems would be worthwhile to identify the impact of this pollutant.

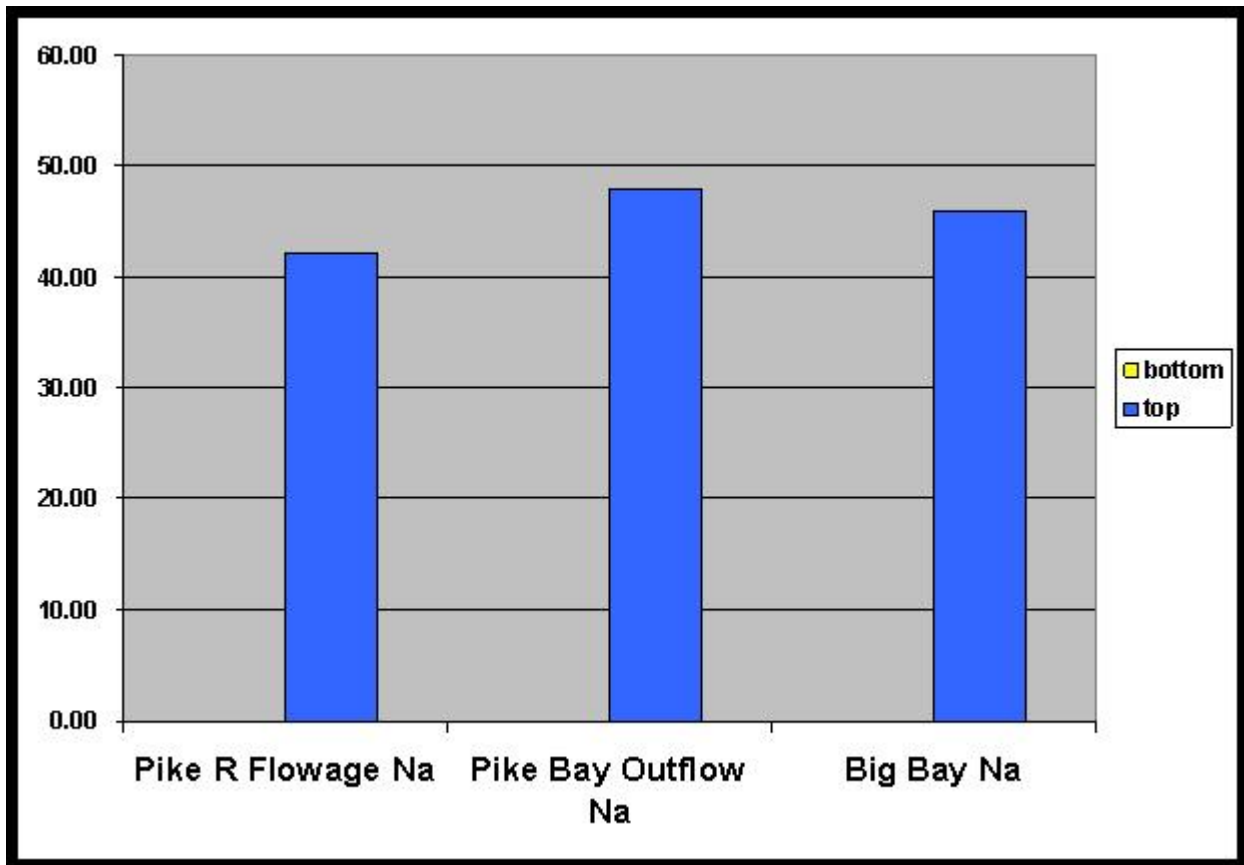


Figure 14. Sodium content (ppm) of Lake Vermilion sediments.



*Phosphorus* (Figure 15): An approximate 2-3-fold increase in phosphorus content has occurred at the three core sites. This is a fairly typical trend in lakes such as Vermilion which have significant shoreline development. Although there are several potential anthropogenic sources, P pollution generally results from fertilizer applications and failing septic systems in the lake watershed. Lake Vermilion is generally not considered a nutrient-rich lake, but nutrient concentrations have undoubtedly increased since settlement of the area. As discussed during the 19 January 2005 presentation to the SCLV (PowerPoint presentation included on CD), cursory analyses of algal remains in the sediments indicate a change in the species composition of primary producers, likely resulting from a change in nutrient load. This long-term change is most likely related to local influences, and not mining.

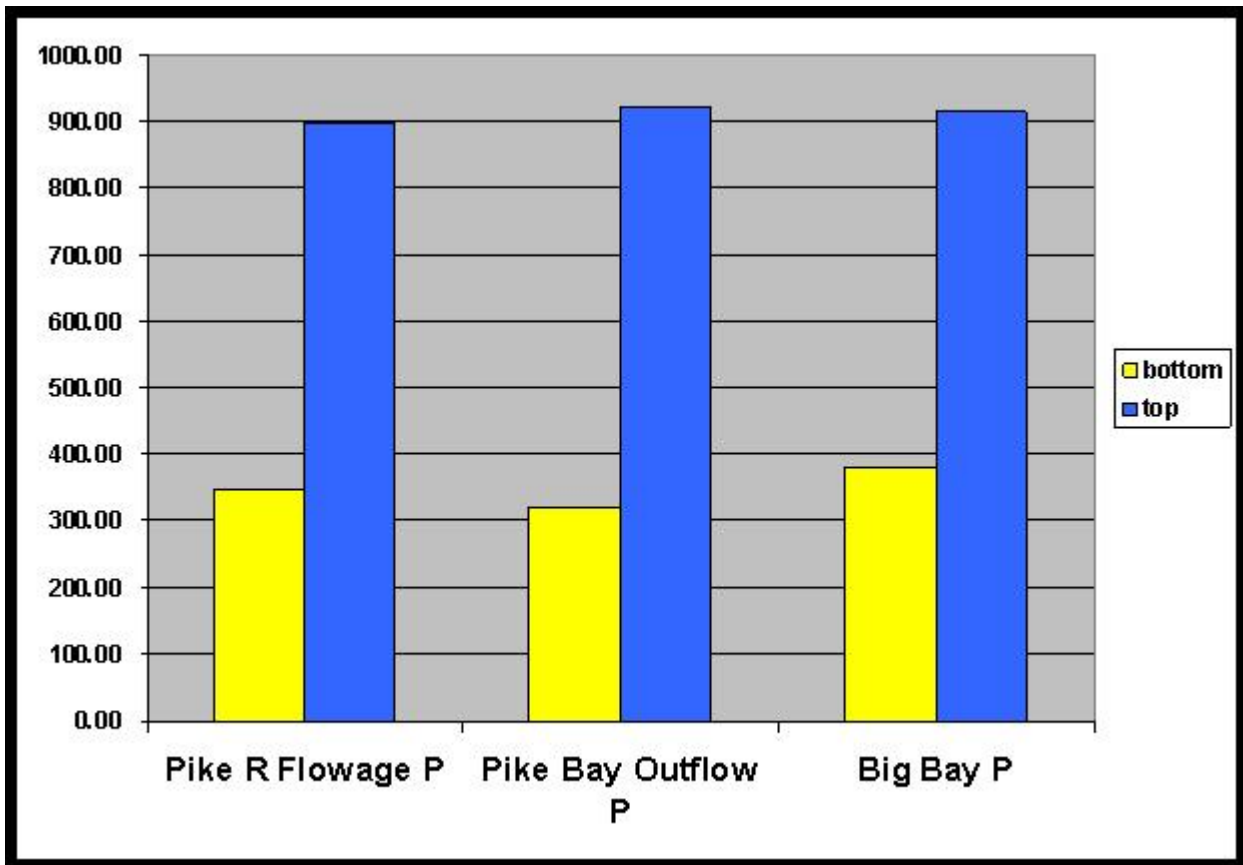


Figure 15. Phosphorus content (ppm) of Lake Vermilion sediments.

## Conclusions

This investigation of sedimentary chemical markers indicates that local factors such as watershed development, road salt applications and ongoing anthropogenic activities have probably been dominant factors in changing Lake Vermilion's ecology (i.e., water and sediment quality, organism communities) in the last ~150 years. A decrease in precipitation pH resulting from anthropogenic emissions has likely also caused the increase in many sedimentary metals concentrations, including Fe, Mn and Al. Atmospheric metals contamination has also likely resulted in some of the changes observed in the sediments (e.g., Pb, Cd). Nutrient (e.g., P) and salt (identified by Na concentrations) contamination is most probably a result of human activities in the local catchment. Based on a comparison of these chemical results to data in the Minntac EIS, there is no detectable evidence that tailings pond discharge has had an effect on Lake Vermilion. However, future monitoring will be critical to ensure protection of the lake following initiation of tailings pond releases.