

# A comparison of water quality variables and concentrations of selected toxic and nuisance elements at various distances and depths downstream from Allegheny River gravel mining operations during periods of activity and inactivity.

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## Background

River Mining is an underwater extraction activity, unrelated to the process of navigational dredging. The mining process involves the displacement of bottom sediments and underlying materials and is accomplished using a clamshell dredge in an industrial style operation. In western Pennsylvania along the Allegheny and Ohio rivers, the primary purpose for river mining has been for the uptake of gravel and sand. These materials are then most often processed and subsequently developed for use on various construction projects such as road and highway building. Penn Dot is a primary consumer of this river mined aggregate.

The process of river mining however is thought to be a potential source of numerous environmental and public health related concerns. Studies have shown that mining for gravel, particularly in the Allegheny River, has caused large areas of ecobehabitat to disappear with attendant deep holes that do not have the required oxygen for most aquatic life to survive. This habitat destruction decreases the areas of appropriate aquatic ecosystems necessary for the life cycle of freshwater mussels, removes areas where fish spawn and may increase the turbidity of the surrounding water thus decreasing fundicity of many fish species. Additional concerns include river bottom and bank erosion and the release of elemental and other contaminants into the water column during these mining activities and their effects on local residents well water and downstream municipal water systems. The primary objective of this report is to determine if river mining, currently being performed near the southwestern Pennsylvania town of Freeport, downstream from the mouth of Buffalo Creek, adds significant levels of Total Suspended Solids (TSS) and increased masses of a panel of elements to the Allegheny river.

## Objectives

Major objectives for this study include but are not limited to the following:

1. Determining turbidity levels before and during mining operations.
2. Determining any increased concentrations of arsenic (AS), mercury (Hg), cadmium (Cd), chromium (Cr), copper (Cu), cobalt (Co), Manganese (Mn), Selenium (Se), Uranium (U) and/or Zinc (Zn) in river water following the onset of river mining operation.
3. Determining if the river depth from which a sample was taken is associated with TSS elevation following the onset of mining operations.

Figure 1, River Mining Operation on the Allegheny River



## Methods

Before mining sampling was conducted from 3 to 5am on July 18, 2008, a second set of samples was taken beginning at 10AM, which was over 2 hours into the mining operational day. Sampling occurred at 7 points downstream from the clamshell dredge both before and during mining operations. At each of the 7 sampling locations water was taken using a Niskin sampler at 1 meter, and 6 meters below the waters surface and 1 meter above river bottom. The turbidity of each water sample was immediately measured using a Hanna Instruments, HI 93703, Portable Microprocessor Turbidity Meter and recorded. Additionally, water from each location and depth was archived in 50ml glass vials using a Teflon coated cap for elemental analysis. Water samples were analyzed for previously described elements using EPA approved nitric acid digestion and analysis by ICP/MS. Statistical tests were run on SPSS, version 16.0. All analysis for significance used the paired samples t-test.

Figure 2, Locations of Predetermined Sampling Locations – Relative to the River Mining Operation



## Results

Table 1 presents concentration results for each analyzed element. All concentrations are expressed in micrograms of the element per liter of water (ppb). The table presents the mean before and during mining concentrations for drops 1 through 7 at each river depth previously described. Also presented in Table 1 is the difference in means, t-test value, achieved probability and if a significant difference was reported (alpha less than or equal to .05), the 95% confidence interval for the difference in the means.

Table 2 presents turbidity data by both river level and for all levels merged. All pre-mining turbidity levels, measured in Formazin Turbidity Units, were lower than corresponding samples taken after at least 2 hours of mining operations. Table 2 presents the mean turbidity level before and during mining, the mean difference, the achieved probability and the 95% confidence interval for the difference in means.

Table 1, Element Concentrations Before and During Mining Operations and Paired Sample t-test Results

Element	Before mining (X <sub>A</sub> ) µg/L	After mining (X <sub>B</sub> ) µg/L	Diff in Means (X <sub>B</sub> - X <sub>A</sub> )	Paired Sample t Value	Probability Achieved	95% CI of Mean Difference Lower Bound	95% CI of Mean Difference Upper Bound
Arsenic	0.247	0.415	0.168	4.77	.000	.240	.094
Selenium	0.086	0.134	0.047	2.40	.027	.089	.006
Mercury	0.020	0.022	0.048	1.00	.329	-----	-----
Cadmium	0.035	0.035	N/A	N/A	N/A	-----	-----
Cobalt	0.211	0.216	0.005	0.180	0.859	-----	-----
Copper	0.797	0.846	0.049	1.693	.100	-----	-----
Zinc	4.60	5.54	0.951	2.581	.018	1.720	.1823
Chromium	0.084	0.102	0.018	.794	.437	-----	-----
Lead	0.137	0.150	0.014	.579	.569	-----	-----
Manganese	22.70	24.31	1.607	.456	.653	-----	-----
Uranium	0.065	0.066	0.001	1.365	.187	-----	-----

Table 2, Turbidity Measurements Before and During Mining Operations and Paired Sample t-test Results

Levels	N(Pairs)	Before Mining (X <sub>A</sub> ) (FTU)	After Mining (X <sub>B</sub> ) (FTU)	Difference in Means (X <sub>B</sub> - X <sub>A</sub> ) (FTU)	Probability Achieved	95% CI of Mean Difference Upper Bound	95% CI of Mean Difference Lower Bound
1 meter below surface water	7	1.52	4.94	3.41	.003	5.10	1.71
3 meters below surface water	7	2.59	5.81	3.01	.009	5.31	1.13
1 meter above river bottom	7	2.36	5.37	3.21	.004	4.60	1.41
All levels merged	21	2.16	5.37	3.21	.000	4.05	2.36

## Conclusions

- Significantly higher levels of Arsenic, Selenium and Zinc in river water were found after mining operations had been active for at least two hours compared to samples taken at 3AM before operation had begun. Further there were no rain or other weather events to change water indicators during this period.
- Turbidity levels at all sampling stations at all depths were higher after at least 2 hours of mining operations than before mining turbidity samples.
- Turbidity was found to be significantly different if the data are stratified by depth at all 3 depths. This indicates the TSS plume made by the mining operation was found to extend essentially from bank to bank and from the surface to the bottom of the river.
- Fish reproduction could be significantly impaired by the sedimentation of these suspended solids. Fish eggs and macroinvertebrates may not survive if sediment is layered over nesting or living areas. Fish will also flee areas of increased turbidity as it impairs their ability to absorb oxygen in their gills.
- Selenium is highly toxic to fish and can interfere with survival, growth and development and reproduction, although levels were not over aquatic toxicity limits—our sampling is a snapshot of possible effects. When river mining moves to new locations, particularly those more affected by coal combustion-selenium levels in water could be significantly higher.

## Public Health Implications

- While arsenic levels were not over the EPA drinking water standard of 10ppb, current research indicates that there could be effects from arsenic at levels lower than the current MCL. The current MCLG for arsenic is 0 ppb because it is a known human carcinogen. Therefore any increase in the mass of arsenic taken into the body through drinking water the higher the risk of developing certain specific forms of cancer.
- There are numerous sources of both natural and anthropogenic arsenic in the Allegheny River watershed. Coal combustion and its fly ash waste, iron and steel production and the PPG Cadogan Waste site all add arsenic to levels which are naturally high from fragmentation of sedimentary rock during the regions glacial periods. All efforts to reduce arsenic mass from man-made sources in the river should be made. Downstream municipal water plants must clean water to the new MCL of 10ppb. The impact on well water users living next to the Allegheny River should be investigated.

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