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Community participatory driven research; Comparisons of water quality variables and concentrations of toxic elements downstream from Allegheny River gravel mining operations during periods of activity and inactivity.

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Presenter Disclosures

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(1) The following personal financial relationships with commercial interests relevant to this presentation existed during the past 12 months:

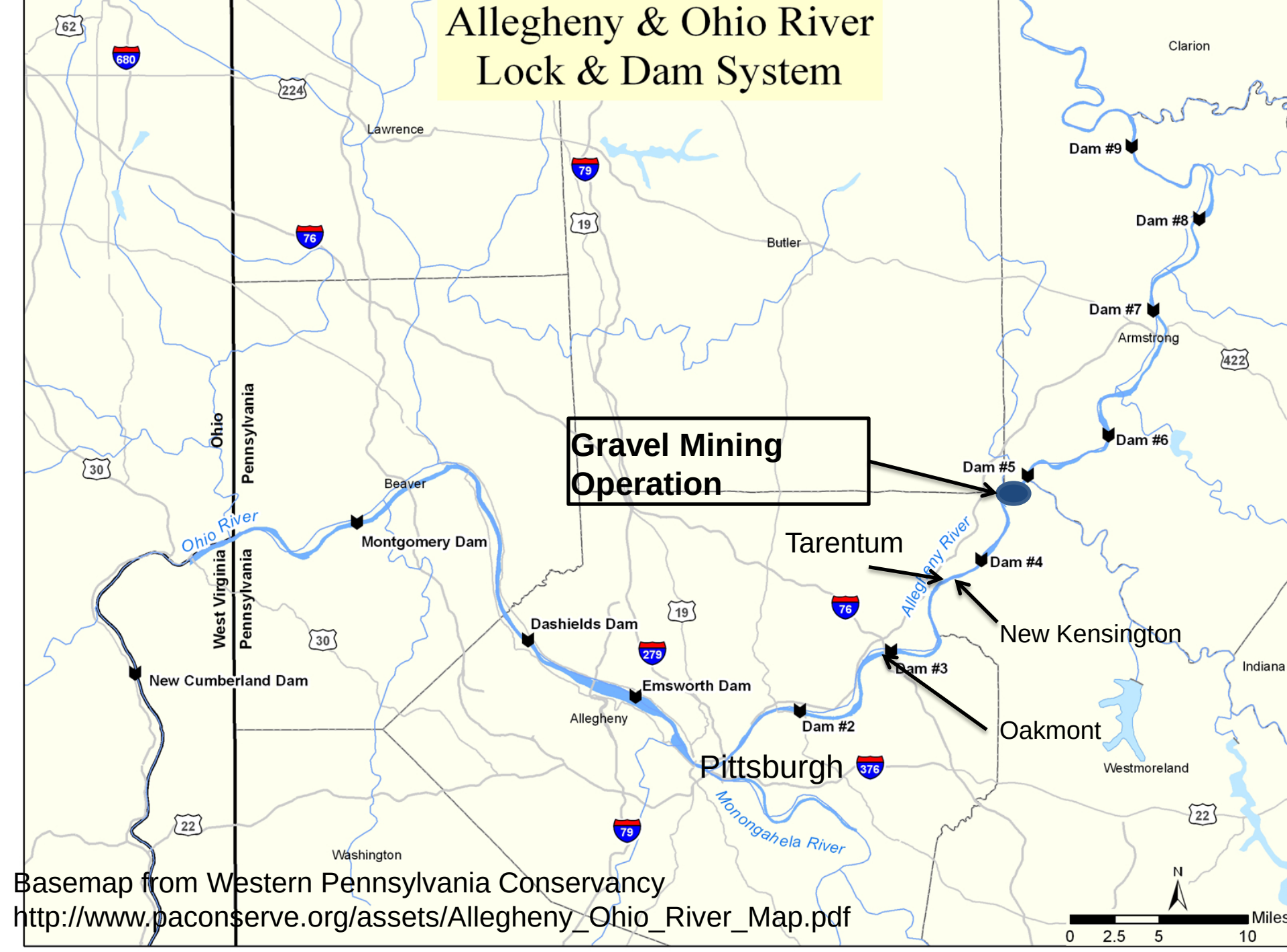
"No relationships to disclose"

What Lead to the River Mining Study? Community-Based Participatory Research Approaches to Prioritization of Environmental Problems in the Allegheny River Basin

1. Scoping expedition in June 2007 to identify environmental problems- used also to announce the Allegheny River Stewardship Project (ARSP) to communities through print and broadcast media.
2. Series of three (3) community meetings where participants filled out pollution narratives and engaged in a Delphi-like prioritization process for top three (3) environmental problems facing Allegheny River communities.
3. Women's focus group results.
4. High school presentations and pollution narratives.

Evidence that River Mining has Important Effects on River Hydrology, Ecology, and Water Quality Variables

- River Mining disrupts the dynamic ecotone between surface and groundwater called the hyporheic zone in a river system (Hancock,PJ, 2002).
- Disruption of the hyporheic zone impairs interstitial bacterial and invertebrate biota and disrupts the hydrological connections between the hyporheic zone and stream, groundwater, riparian, and floodplain ecosystems (Hancock,PJ, 2002).
- Caused reduction of hydraulic head in unconfined aquifers bordering mined portions of Spain's Fluvia River (Mas-Pla J. et al.,1999).
- Gravel mining significantly altered the geomorphology, fine-particle dynamics, turbidity levels, and overall composition of biotic communities in the Ozarks, Arkansas (Brown, AV et al., 1984).
- Rivers with widespread sediment removal are sediment-starved (hungry water) and prone to erode the channel bed and banks, producing channel incision (downcutting), coarsening of bed material, and loss of spawning gravels for fish (Kandolff, GM, 1997).



Basemap from Western Pennsylvania Conservancy
http://www.paconserve.org/assets/Allegheny_Ohio_River_Map.pdf

Initial Hypotheses

1. River Mining will significantly increase surface water turbidity (total suspended solids in water) over levels observed during periods of inactivity.
2. Further, since disturbance of bottom sediments and release of particles from the mining bucket scooping and drainage, respectively occurs continuously from the bottom to the top of the river, including overage into the river- turbidity levels should be elevated throughout the water column.
3. River Mining will significantly raise levels of toxic elements, metals and metalloids in water over levels found before mining activity begins.
4. River Mining will raise levels of Total Dissolved Solids (TDS) in river water over levels found before mining activity begins.

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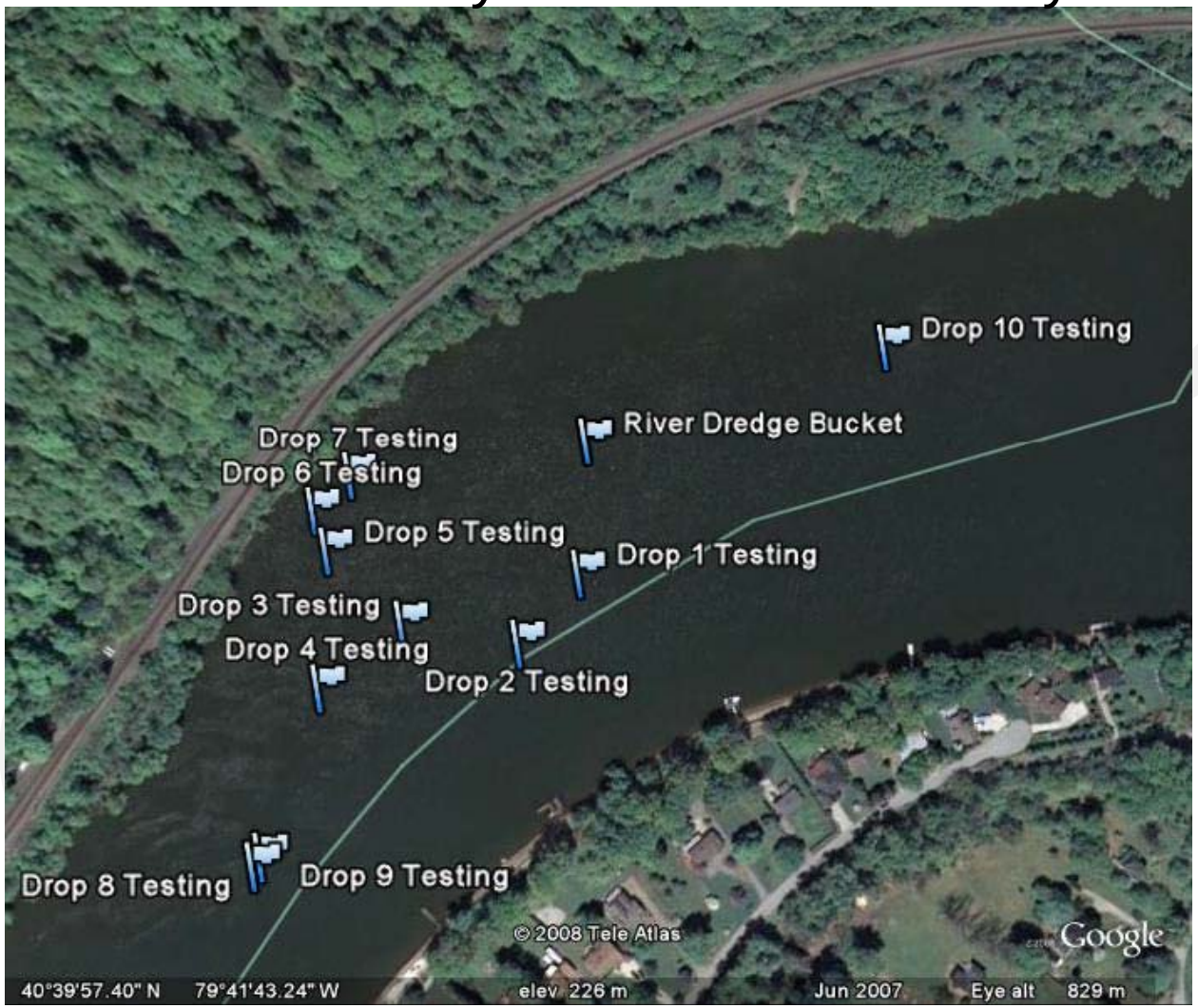
Methodologies

1. Attempts at sampling above and below mining operations were abandoned after 2 attempts on two separate days. Mining operations ceased in response to observation of sampling activities.
2. Before mining sampling was conducted from 3 to 5am on July18, 2008, a second set of samples was taken beginning at 10AM, which was over 2 hours into the mining operational day. Mining operations ceased in response to movement to upstream sampling locations.
3. 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, 3 meters below the waters surface and 1 meter above river bottom. Figure 1 presents a map of sampling locations.
4. The turbidity of each water sample was immediately measured using a Hanna Instruments, HI 93703, Portable Microprocessor Turbidity Meter and recorded.

Figure 1; Location of River Mining and Monitoring Stations for Water Turbidity and Elemental Analysis

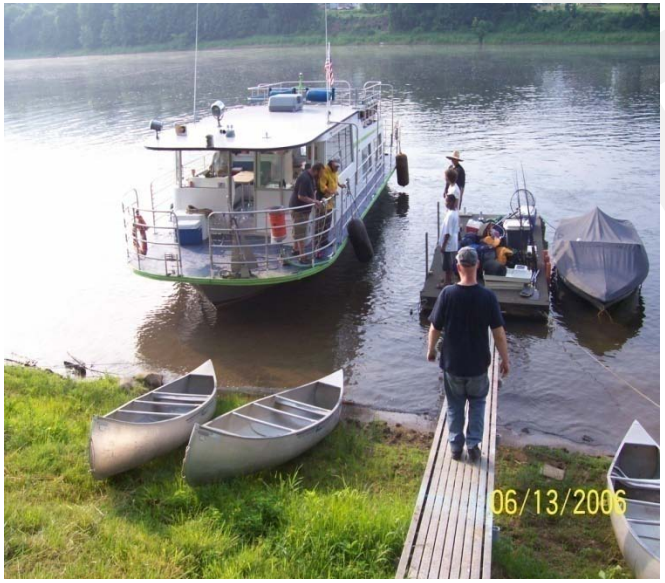


Stations 8, 9, and 10 sampled during mining only because of approach of river mining crew.

Methodologies Continued

5. Water from each location and depth was archived in 50 ml glass vials using a Teflon coated cap for elemental analysis. Water samples were analyzed for As, Se, Hg, Cd, Co, Cu, Zn, Cr, Pb, Mn and U using EPA approved nitric acid digestion and analysis by ICP/MS methodologies. Detection limits were; As, .001; Se, .002; Hg, .001; Cd, .0005; Co, .0005; Cu, .0005; Zn, .001; Cr, .0005; Pb, .0005; Mn, .0005 and U, .0005 (µg/L).
6. Total Dissolved Solids were measured before and after mining operations using a Hanna Instrument 9128 Multiparameter Water Probe. The probe, at 6 meters depth, was moved through the water by boat action in a serpentine fashion. TDS and geo-positions were recorded approximately every 3 seconds.
7. Turbidity and elemental concentrations in samples taken during both regimens were compared using the paired sample t-Test (alpha ≤ .05), using SPSS Version 16.0.
8. TDS data from both regimens were plotted on ArcGIS and smoothed using the ordinary kriging interpolation.
9. Kriged TDS results from both regimens were extracted to rasters, matched geographically, and subtracted to quantitatively show the geographic distribution of TDS increases.

Results



1. Turbidity levels (TSS) by depth and merged, before and after mining onset.
2. Analysis of water for toxic elements, metals and metalloids, all levels merged, before and after mining onset.
3. Analysis of water for toxic elements, metals and metalloids by depth (top water, 3 meters below surface and bottom water), before and after mining onset.
4. Kriging interpolation of Total Dissolved Solid (TDS) measurements: before and after mining interpolated maps.
5. Increases in TDS levels 6 meters below surface, after mining results subtracted from before mining results.

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Turbidity Levels by Depth and Merged Before and After Mining Onset

Levels	N (Pairs)	Before Mining Mean Turbidity (FTU)[1]	After Mining Onset Mean Turbidity (FTU)	Difference in Means (FTU)	Probability (p) α=.05 [2]	95% CI of dif in Means Upper Limit (FTU)	95% CI of dif in Means Lower Limit (FTU)
1 meter below water surface	7	1.52	4.94	3.41	**.003**	**5.10**	**1.71**
3 meters below water surface	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	**≤.0001**	**4.05**	**2.36**

All after mining turbidity levels at all points and depths were higher than before mining turbidity levels;[1] Formazine Turbidity Unit; [2] Paired t-test

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Elemental Analysis: All Levels Merged

Element	Before mining µg/ L	After mining µg/L	Diff in Means µg/L	Paired Sample t Value	Probability α =. 05	95% CI of Mean Difference Lower Bound	95% CI of Mean Difference Upper Bound
Arsenic	0.103	0.370	0.267	4.45	**<.0001**	**0.142**	**0.392**
Selenium	0.076	0.132	0.056	2.40	**.023**	**0.009**	**0.103**
Mercury	BDL	One detect	NA	NA	NA	NA	NA
Cadmium	BDL	BDL	NA	NA	NA	NA	NA
Cobalt	0.211	0.216	0.005	0.180	0.859	NS	NS
Copper	0.797	0.846	0.049	1.693	.100	NS	NS
Zinc	4.60	5.55	0.951	2.581	**.018**	**0.182**	**1.720**
Chromium	0.084	0.102	0.018	.794	.437	NS	NS
Lead	0.137	0.150	0.014	.579	.569	NS	NS
Manganese	22.70	24.31	1.607	.456	.653	NS	NS
Uranium	0.065	0.066	0.001	1.37	.187	NS	NS

Results are for 21 paired results; BDL-Below Detection Limit; NA –Not Applicable; NS –Not Significant at alpha = .05

Elemental Analysis: 1 Meter Below Surface

Element	Before mining µg/ L	After mining µg/L	Diff in Means µg/L	Paired Sample t Value	Probability α =. 05	95% CI of Mean Difference Lower Bound	95% CI of Mean Difference Upper Bound
Arsenic	0.228	0.440	0.212	3.89	**.008**	**0.071**	**0.348**
Selenium	0.115	0.160	0.045	.940	.383	NS	NS
Cobalt	0.216	0.205	-0.010	0.143	.891	NS	NS
Copper	0.817	0.863	0.046	0.800	.454	NS	NS
Zinc	4.49	5.35	0.863	1.452	.197	NS	NS
Chromium	0.106	0.149	0.043	0.651	.559	NS	NS
Lead	0.141	0.138	-0.003	0.078	.940	NS	NS
Manganese	19.87	19.72	-0.152	0.026	.980	NS	NS
Uranium	0.065	0.066	0.001	0.947	.380	NS	NS

Results are for 7 paired results; NS –Not Significant at alpha = .05

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Elemental Analysis: 3 Meters Below Surface

Element	Before mining µg/ L	After mining µg/L	Diff in Means µg/L	Paired Sample t Value	Probability α =. 05	95% CI of Mean Difference Lower Bound	95% CI of Mean Difference Upper Bound
Arsenic	0.323	0.463	0.140	1.83	.118	NS	NS
Selenium	0.079	0.129	0.049	1.30	.291	NS	NS
Cobalt	0.218	0.265	0.047	1.14	.300	NS	NS
Copper	0.812	0.846	0.034	6.94	.514	NS	NS
Zinc	5.08	6.25	1.17	1.43	.204	NS	NS
Chromium	0.085	0.098	0.013	.682	.520	NS	NS
Lead	0.145	0.177	0.032	1.00	.356	NS	NS
Manganese	25.46	31.22	5.75	.949	.379	NS	NS
Uranium	0.065	0.067	0.002	.778	.466	NS	NS

Results are for 7 paired results; NS –Not Significant at alpha = .05

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Elemental Analysis: 1 Meter Above River Bottom

Element	Before mining µg/ L	After mining µg/L	Diff in Means µg/L	Paired Sample t Value	Probability α =. 05	95% CI of Mean Difference Lower Bound	95% CI of Mean Difference Upper Bound
Arsenic	0.190	0.339	0.149	2.81	**.031**	**.278**	**.019**
Selenium	0.063	0.111	0.048	3.38	**.016**	**.083**	**.013**
Cobalt	0.199	0.178	-0.021	.472	.653	NS	NS
Copper	0.762	0.830	0.068	1.31	.238	NS	NS
Zinc	4.220	5.040	0.821	1.45	.197	NS	NS
Chromium	0.059	0.058	-0.001	.037	.972	NS	NS
Lead	0.123	0.136	0.013	.258	.804	NS	NS
Manganese	22.80	21.91	-0.781	.113	.914	NS	NS
Uranium	0.064	0.065	0.001	.619	.559	NS	NS

Results are for 7 paired results; NS –Not Significant at alpha = .05

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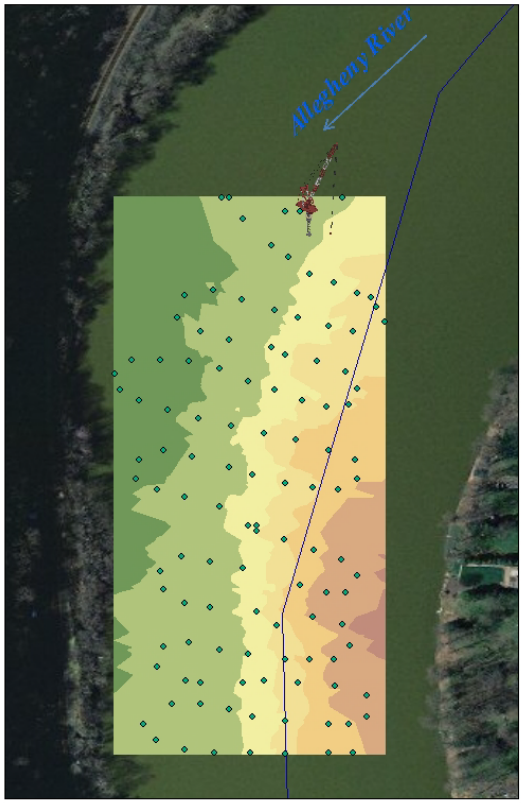
Kriging Interpolation: TDS

TDS Before Mining

Total Dissolved Solids (TDS) in ppm Before Riving Mining Event
Allegheny River, Allegheny and Westmoreland Counties
Using Ordinary Kriging Interpolation



Legend

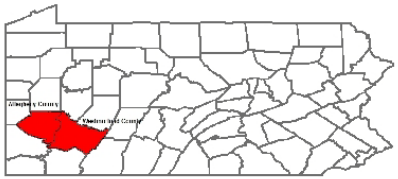
Clamshell

Streamline

Before River Mining

TDS Before (ppm)

115.03 - 117.47
117.47 - 121.61
121.61 - 125.74
125.74 - 129.88
129.88 - 134.01
134.01 - 138.15
138.15 - 142.28
142.28 - 146.42
146.42 - 150.55



N W E S

0.03 Miles

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-World Imagery from ESRI ArcGIS Online Standard Services, 2008

TDS After Mining

Total Dissolved Solids (TDS) in ppm After Riving Mining Event
Allegheny River, Allegheny and Westmoreland Counties
Using Ordinary Kriging Interpolation

Legend

Clamshell

After River Mining

Streamline

TDS After (ppm)

113.34 - 117.47
117.47 - 121.61
121.61 - 125.74
125.74 - 129.88
129.88 - 134.01
134.01 - 138.15
138.15 - 142.28
142.28 - 146.42
146.42 - 150.55

N W E S

0.03 Miles

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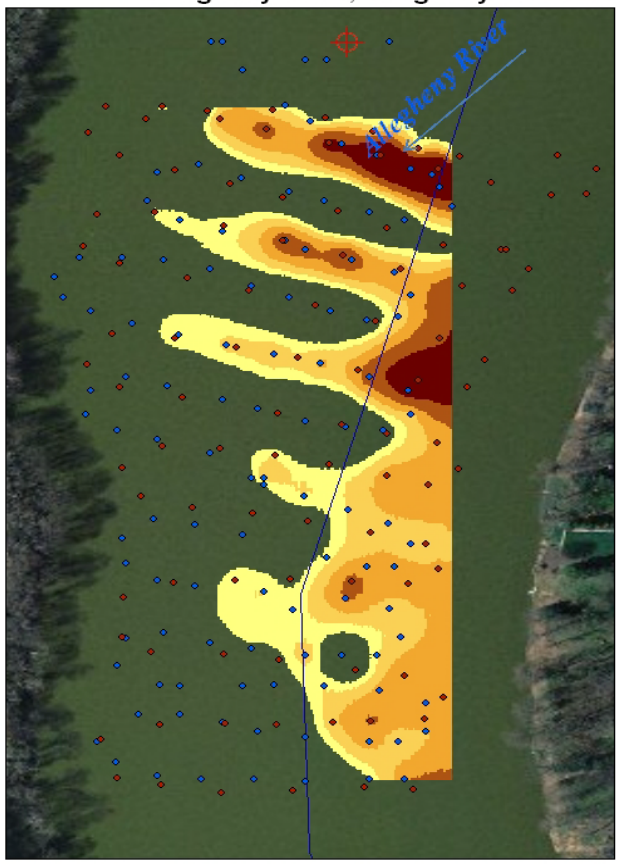
-World Imagery from ESRI ArcGIS Online Standard Services, 2008

TDS Increases

Increase in Total Dissolved Solids (TDS) in PPM
After Gravel Mining event near Freeport, PA
Allegheny River, Allegheny and Westmoreland Counties



This map displays total positive change in total dissolved solid levels after gravel mining event in the Allegheny River. Ordinary Kriging was utilized to produce surface maps for both before gravel mining events and after at respective points. These surfaces were extracted to rasters and matched by the same geographical rectangular extent. The After surface was then subtracted from the before surface to produce change in TDS levels. Only positive values or higher levels after are displayed. displayed

Legend

- Clamshell
- Streamline

TDS After Minus Before Values

PPM

- 0 - 1.683
- 1.684 - 3.986
- 3.987 - 6.593
- 6.594 - 10.113
- 10.114 - 19.181

World Boundaries and Places

World Imagery

200 Feet

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-World Imagery from ESRI ArcGIS Online Standard Services, 2008

Conclusions and Public Health and Ecological Implications

A. Hypotheses 1 and 2 - Turbidity increased significantly during active mining operations over before mining levels for all levels merged, and at each depth. All active mining turbidity samples were above before mining levels at all monitoring stations and depths.

- Small increases in the turbidity of treated drinking water have been linked to increased occurrence of acute gastrointestinal illnesses among children and the elderly in Milwaukee and Philadelphia, Pa, even though the water is in compliance with Environmental Protection Agency standards (Gaffield et al., APHA Journal, 2003).
- Excessive fine sediment impacts benthic organisms that characterize a healthy stream. Sediment can abrade aquatic organisms gills and smothers them upon deposition. The embedding nature of fine sediment also causes the loss of microhabitat in the spaces between larger substrate particles (Reylea, 2000).

Volz et al.,2009; APHA Conference: **http://www.chec.pitt.edu**

Conclusions and Public Health and Ecological Implications Continued

B. Hypothesis 2 - River Mining will significantly raise levels of toxic elements, metals and metalloids in water over levels found before mining activity begins.

- Levels of As, Se, and Zn in water increased significantly during active mining over before mining levels (As 3.6X, Se 1.7X, and Zn 1.2X) when all levels were merged, indicating increased levels throughout the water column. Non-significant increases in mean levels of Co, Cu, Cr, Pb, Mn and U in the water column were observed.
- The level of As in top water (1 meter below surface level) increased significantly during the active mining regimen. The mean of As in top water was elevated 1.9 X before mining levels. Non-significant increases in mean levels of Se, Cu, Zn, Cr and U were observed.
- Mid-level water (3 meters below surface) showed no significant increases in elemental levels during the active mining period. Non-significant increases in As, Se, Co, Cu, Zn, Cr, Pb, Mn and U were observed.
- Bottom water (1 meter above river bottom) increased significantly for As and Se during active mining over before mining levels(both 1.8X). Non-significant increases in Cu, Zn, Pb, and U were observed.

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Conclusions and Public Health and Ecological Implications Continued

- As levels, although significantly ,elevated are still well below US EPA SDWA standards-however the addition of mass of arsenic to this critical drinking water source should be discouraged since arsenic is a known non-anthropogenic contaminant in the watershed. Other sources of arsenic in water are from coal fired power plant; emission deposition; wastewater; and fly ash leachate.
- Elevated concentrations of Se have degraded many freshwater ecosystems throughout the United States, and additional systems are expected to be affected as anthropogenic activities increasingly mobilize Se into aquatic systems. Se is a very toxic essential trace element in aquatic systems.
- Toxic Se threshold concentrations in water, dietary items, and tissues are only 2-5 times normal background concentrations for aquatic organisms. Levels that are certainly within the 95% CI of the difference in means shown in this study.
- Although Zn was significantly elevated, the PNEC for Zn ranges between 22.1 and 46.1 µg Zn/L (Van Sprang et al., 2009). The Deterministic Risk Ratio for aquatic species is thus less than 1.

Conclusions and Public Health and Ecological Implications Continued

C. Hypothesis 3 - River Mining will raise levels of Total Dissolved Solids (TDS) in river water over levels found before mining activity begins.

- TDS levels increased markedly in the interior bend of the river during mining as opposed to before mining began. Elevated levels of TDS in this region ranged from over 1 to almost 20 ppm higher than during the pre-mining period.
  - While dissolved solids was significantly elevated, this elevation does not approach Secondary Water standards for TDS (500 mg/L)-it is unlikely there would be any taste change in water resulting from such a low increase.
  - Dissolved solids adversely impact aquatic life by altering the osmotic pressure of the external environment, which interferes with organisms' osmoregulatory functions (Title 25 – ENVIRONMENTAL PROTECTION ENVIRONMENTAL QUALITY BOARD [25 PA. CODE CH. 96] Water Quality Standards Implementation, November 20, 2001).

Freshwater Mussels, Aquatic Water Quality and River Mining

- Why be concerned about freshwater mussels?
- As natural filter feeders, freshwater mussels strain out suspended particles and pollutants from the water column and help improve water quality. Some mussels can filter up to 10 gallons of water per day, which helps to improve water quality for other animals, including humans (***www.nrcs.usda.gov, 2007)***.
  - River mining destroys freshwater mussel habitat.
  - Increases in Se particularly affect freshwater mussels - toxicity patterns in the freshwater bivalve sentinel species *Corbicula fluminea* have recently been demonstrated. Waterborne selenomethionine (SeMet) exposure was used to mimic dietary organo-Se uptake. Results of this study demonstrate that SeMet is accumulated to a relatively high extent with a concentration factor of 770 (wet weight basis).
  - Deposition of particulates in water spoils freshwater mussel habitat, and interferes with reproduction and offspring survival.

Volz et al.,2009; APHA Conference: **http://www.chec.pitt.edu**

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• Dartmouth Trace Metals Laboratory

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