

Note: this document may contain some elements that are not fully accessible to users with disabilities. If you need assistance accessing any information in this document, please contact ORD_Webmaster@epa.gov.

Wastewater from Gas Development: Chemical Signatures in the Monongahela Basin

Paul Ziemkiewicz, PhD
Director, West Virginia Water Research Institute
30 Mar 11

Key Water Issues

- Water Management
 - withdrawals
 - Reuse
- Returned Frac Water/Produced Water
- Disposal Options
- **Effects on Streams**

Major sources of TDS

Coal: AMD treatment plants: Regulated under CWA-NPDES
Active coal mines
Abandoned mines

Gas: Coal Bed Methane (CBM)
Shale gas-Marcellus
abandoned wells

Need to quantify each source's contribution to TDS

Dissolved solids from coal mines

- Active mines in the Pittsburgh Basin are up to 10 square miles
- The seam is about six feet thick and about 80% of coal is removed
- the down dip sections are pumped to control water levels in the mines
-
- The water is treated to remove acidity and metals
- Resulting discharge can have high concentrations of sodium and sulfate

Pittsburgh Basin Major AMD treatment plants

- Clyde PaDEP
- Rices Ldg Dilworth
- Greene
- Blackshear Warwick 2
- Colvin Robena
- Steele Shaft Shannopin
- Bowlby Mills Christopher
- Beaver Pond Blacksville 2
- Building Run Federal 2
- 1 South Federal 2
- St. Leo Loveridge 22
- Sugar Run Loveridge 22
- Llewlyn Jamison 9
- Thorn O'Donnell
- Low Robinson Run
- Monongalia
- Dogwood Lk Fairmont Pool/Jordan
- Sears Arkwright
- Flaggy Meadows Arkwright
- Fairmont

Image U.S. Geological Survey
Image USDA Farm Service Agency
© 2010 Google
Image © 2010 DigitalGlobe

© 2010 Google

Imagery Dates: Jan 31, 2008 - Jun 8, 2009

39°44'03.46" N 79°58'30.17" W elev. 1115 ft

Eye alt. 55.45 mi

The TDS Management Model

MODEL CONDITIONS

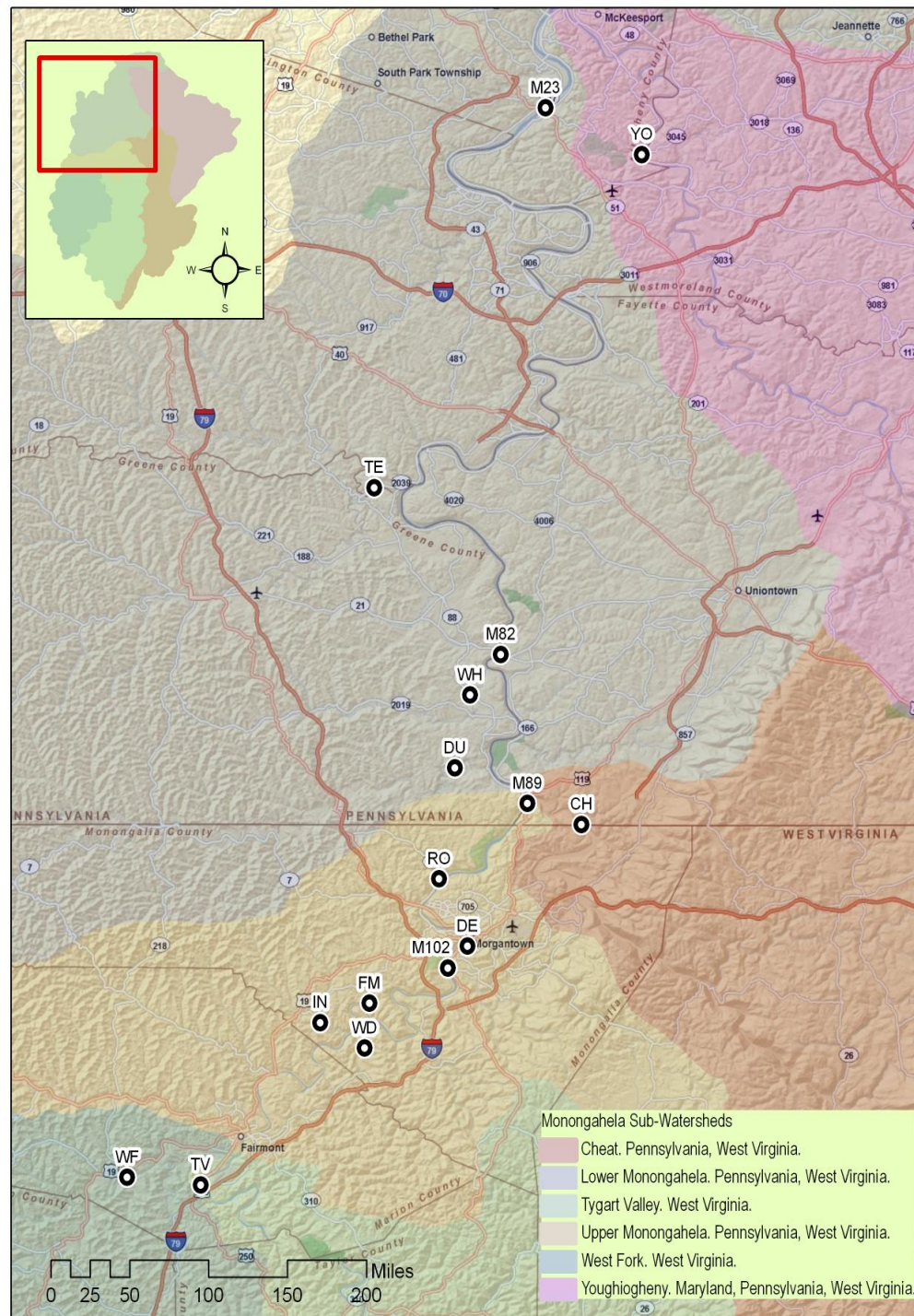
Target instream [TDS]	500	mg/L
Stream Q (cfs)	1500	cfs
Factor of safety	2.0	

BASELINE CONDITIONS									MODEL OUTPUT		
Treatment		Operator	discharge to	Actual Pumping Rate		Actual [TDS] mg/L	Est. TDS (TPY)	% total	allocation (TPY)	Pumping Rate Q	
Plant	Mine			(gpm)	(cfs)					[TDS] mg/L	(TPY)
1	No. 1 Refuse	ABC	WH	1,500	3.3	5000	16,537	2.8%	10,568	2.1	1,065
2	No. 2 Refuse	ABC	WH	250	0.6	4250	2,343	0.4%	1,497	0.4	178
3	No. 1 Refuse	DEF	TM	1,800	4.0	3500	13,891	2.4%	8,877	2.6	1,278
4	No. 2 Refuse	DEF	TM	1,100	2.4	3500	8,489	1.5%	5,425	1.6	781

Estimated TDS loads (tpy) from Upper Mon AMD treatment plants

	average observed	maximum observed	full pump capacity
Dunkard Ck	153,340	190,784	257,950
Robinson Run (Mon Co.)	11,000	22,000	17,600
Flaggy Meadows Run	12,205	34,166	47,300
Indian Ck	12,975	30,008	115,500
Paw Paw Ck	2,200	4,400	11,550
Buffalo Ck	10,043	36,938	36,300
Robinson Run (Marion Co.)	3,900	9,779	27,500
Total	205,662	328,075	513,700

**West Virginia
Water Research
Institute's
monitoring
network:
16 stations
Na, Mg, Ca, Cl,
Br, SO₄ ..., Q,
concentration
and loads**



Samples every two weeks since July 2009

Brines from Shale Gas Development

Returned Frac Water Chemistry

Returned frac water

Water Research Institute

Returned frac water chemistry from five Marcellus wells

RFW is predominantly Na, Ca, Cl

West Virginia University

10

	RFW 4	RFW 5	RFW 3	RFW 2	RFW 1
TDS	189,000	104,000	38,700	12,610	8,800
Cl	107,000	65,000	17,100	7,172	6,575
Na	48,100	33,700	8,560	2,863	3,550
Ca	22,200	12,800	1,640	1,749	319
Mg	2,000	1,470	193	122	31
Sr	2,970	1,440	301	nd	nd
K	668	444	243	57	
SO4	49	414	28	71	99
Ba	1,300	176	175	nd	27
Fe	48	30	37	27	37
pH	5.7	6.3	7.4	6.1	7.6
TSS	519	570	99	220	44
O&G	3	nd	5	49	5

Returned frac water

Water Research Institute

The flow back from an horizontal Marcellus well greatest initially (~ 5,000 barrels per day)

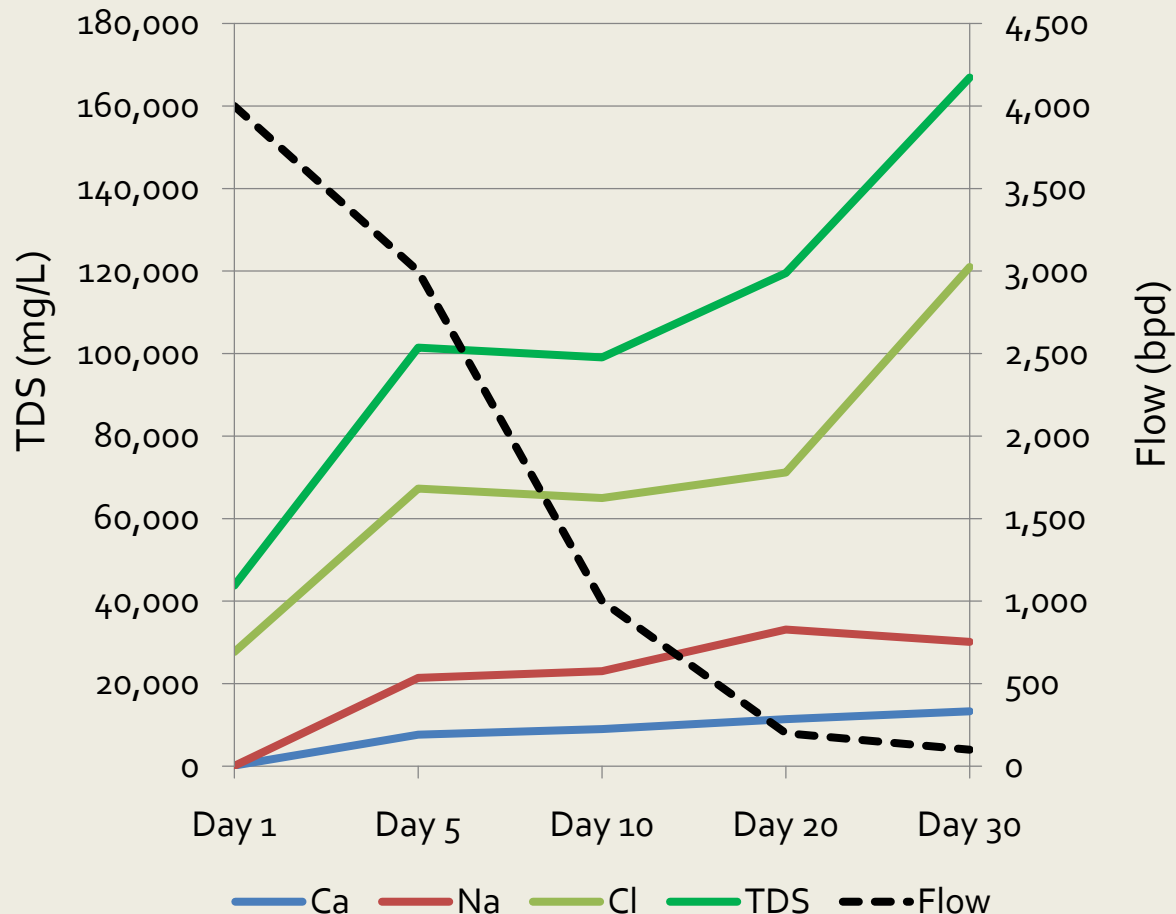
It slows to about 10 bpd after the first couple of weeks.

The initial flow back reflects injected water more while later flow back is more influenced by salts in the formation.

Salt concentrations increase as flow decreases

West Virginia University

11



Relative TDS loads

Water Research Institute

This analysis compares the TDS loadings from large, treated coal mine discharges and Marcellus wells.

One large mine discharge generates as much TDS as 44 Marcellus wells.

Mines vs. Marcellus

West Virginia University

12

	Relative Loadings		
	1 frac job 6 million gal*	1 UG mine	
discharge	2.3	3,000	gpm
TDS	150,000	5,000	mg/L
TDS	753	33,000	tpy
ratio Frac/mine	44	1	
# units	613	14	
TDS	462,000	462,000	tpy

* assumes 20% RFW

Treatment options

- Underground injection
- Pre-treat then send to sewage treatment plant
- Evaporation/crystallization
- Recycle
- Illegal dumping

Treatment options

Water Research Institute

Pre-treatment normally required to remove barium and strontium

Sulfate is normally added to precipitate insoluble

BaSO_4 and SrSO_4

That leaves substantial sulfate plus sodium and chloride in the STP's effluent.

Sewage Treatment Plant

West Virginia University

14



Partial treatment and discharge

Water Research Institute

These facilities add flocculating agents to RFW or produced water to precipitate hazardous ions, landfill the salts and discharge water to a stream.

Treated brine is sold for winter deicing.

This process does not significantly lower the total salt content

RFW treatment facilities in Pennsylvania

West Virginia University

15



Washington PA
OBSERVER REPORTER:

Waste hauler accused of illegal dumping 3/18/2011

By Tara Kinsell, Staff
writer

- State prosecutors charged a Greene County man Thursday with illegally dumping millions of gallons of Marcellus Shale wastewater in holes, mine shafts and waterways in a six-county region from 2003 to 2009.
- The drivers told the grand jury that the accused showed them how to leave water valves open at gas wells in order to allow production water to flow onto the ground and into nearby waterways. The drivers said this was typically done after dark or during heavy rains in order to conceal the illegal discharge.
- ... directed them to dump residual wastewater left in the trucks at the end of the day down a drain at his business. The drain leads to Tom's Run, a tributary of Dunkard Creek.
- It is also alleged that the accused directed waste products to be dumped into the Morris Run air shaft at the abandoned Blacksville No. 1 Mine along Morris Run Creek

Stream Effects

Water Research Institute

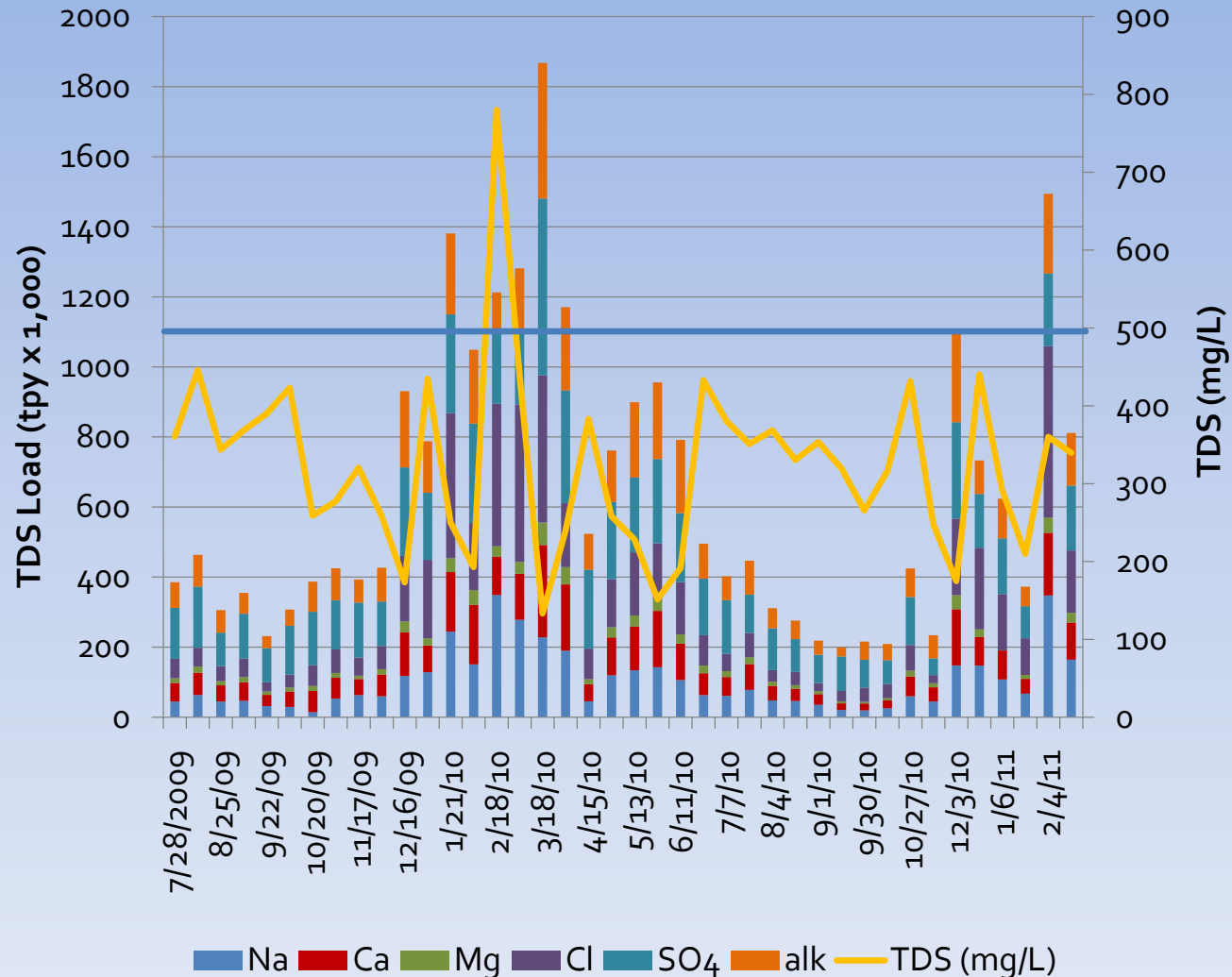
During the wet season in both 2010 and 2011 sodium and chloride loadings increased dramatically in the Youghiogheny River.

Since this took place during a period of high flows, it only accounted for a short period when [TDS] exceeded 500 mg/L

Brine Disposal in the Youghiogheny River

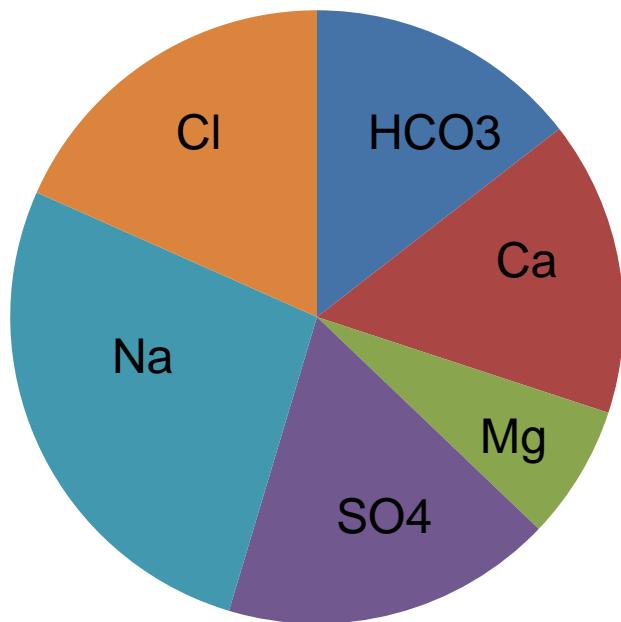
West Virginia University

17

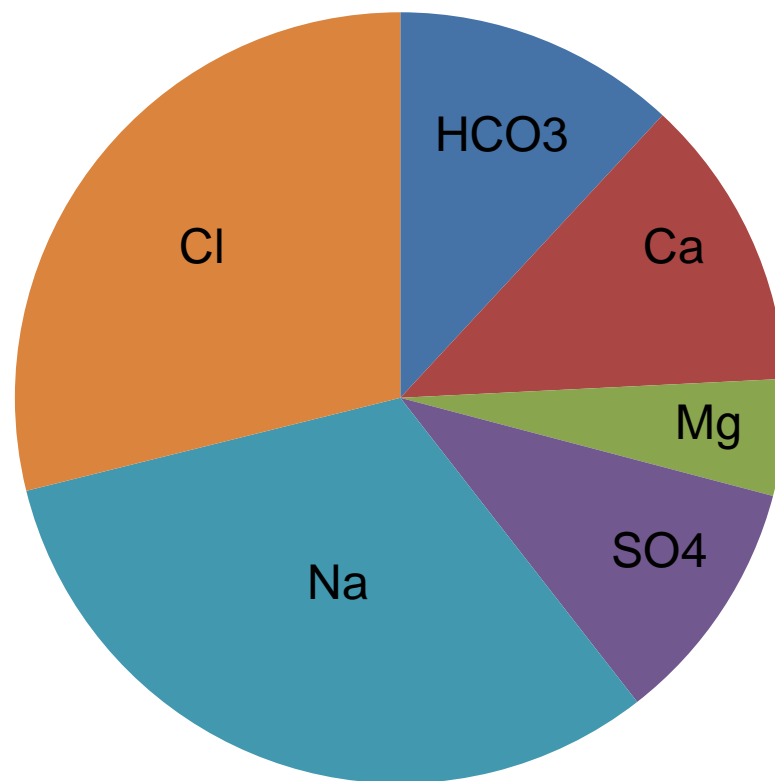


Youghiogheny River: Seasonal shift in NaCl signature (mmol/L)

DRY SEASON
AVG TDS=335,000 TPY

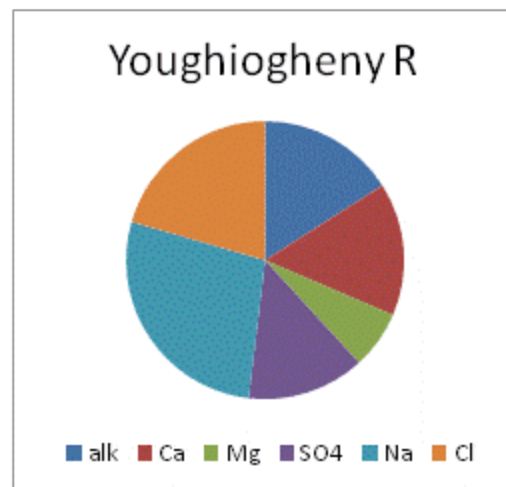
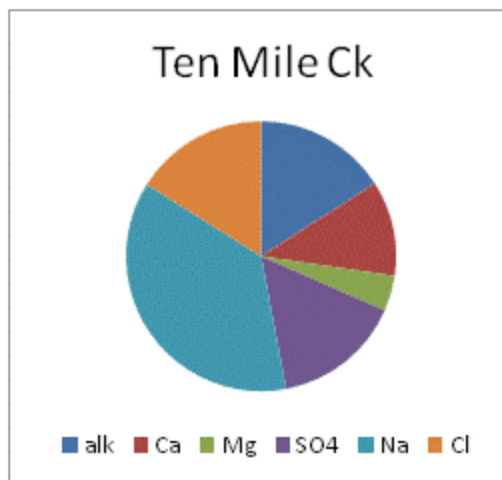
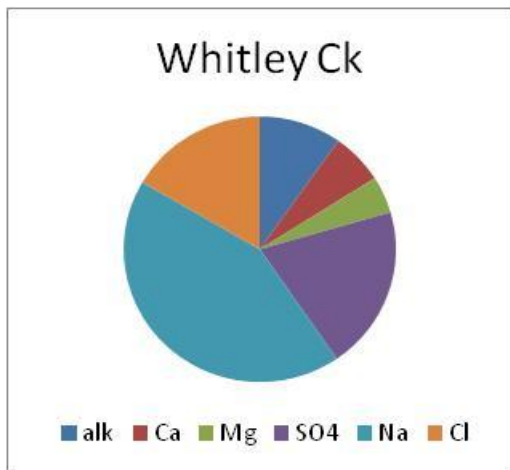


WET SEASON
AVG TDS=971,000 TPY

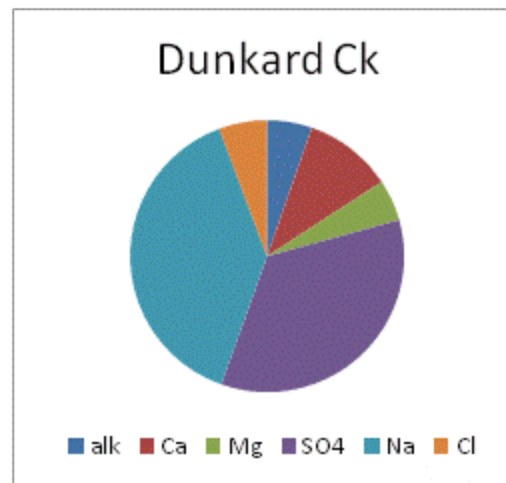
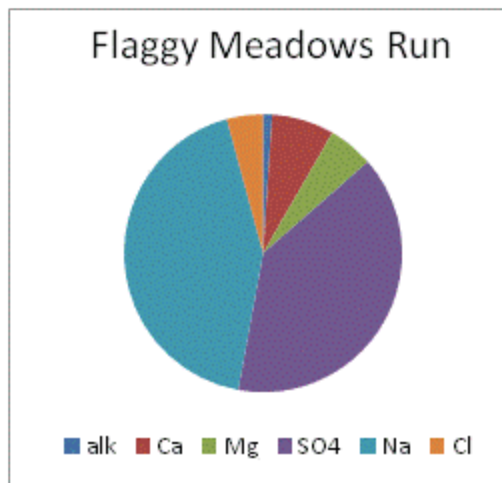
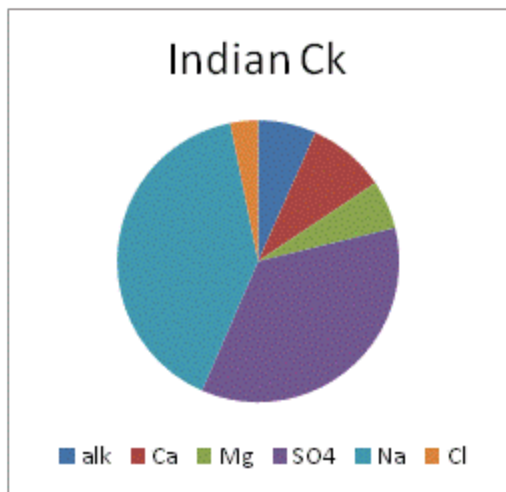


CBM/Marcellus Brine and Mine Water Have Different chemical signatures (mmol/L)

Brine

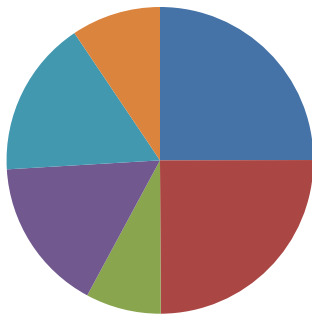


Mine water

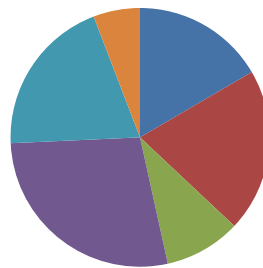


Monongahela mainstem chemistry (mmol/L): Na and Cl increase downstream

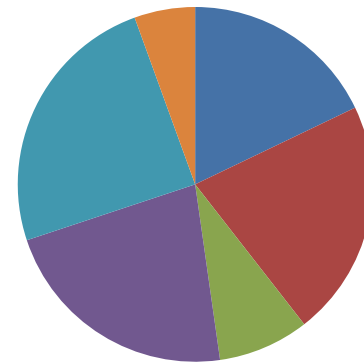
Tygart Valley



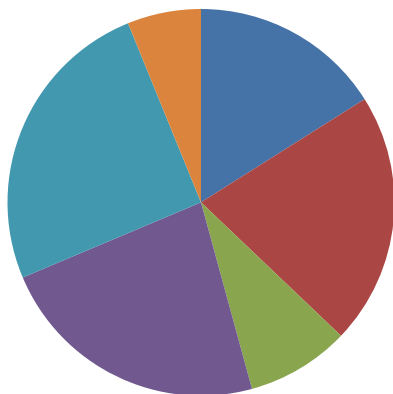
West Fork



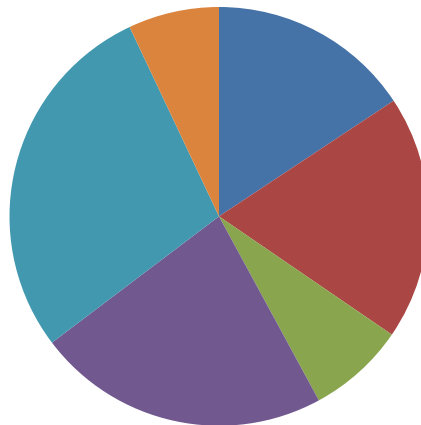
Mon 102



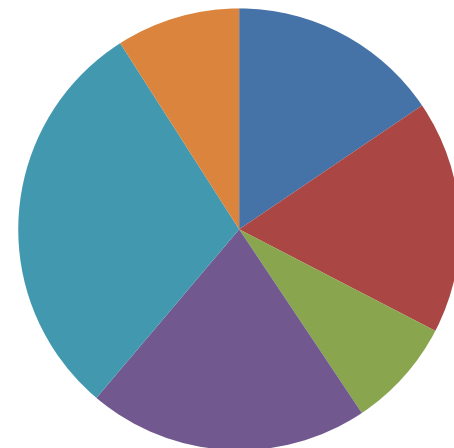
Mon 89



Mon 82

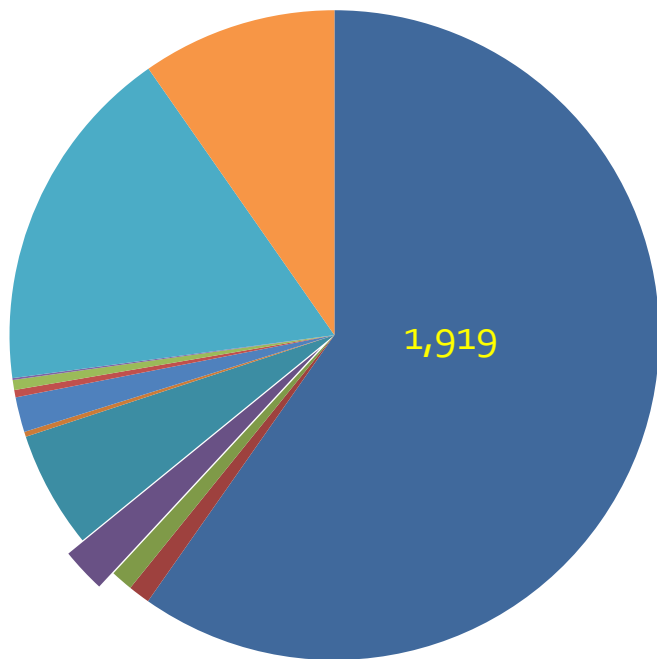


Mon 23



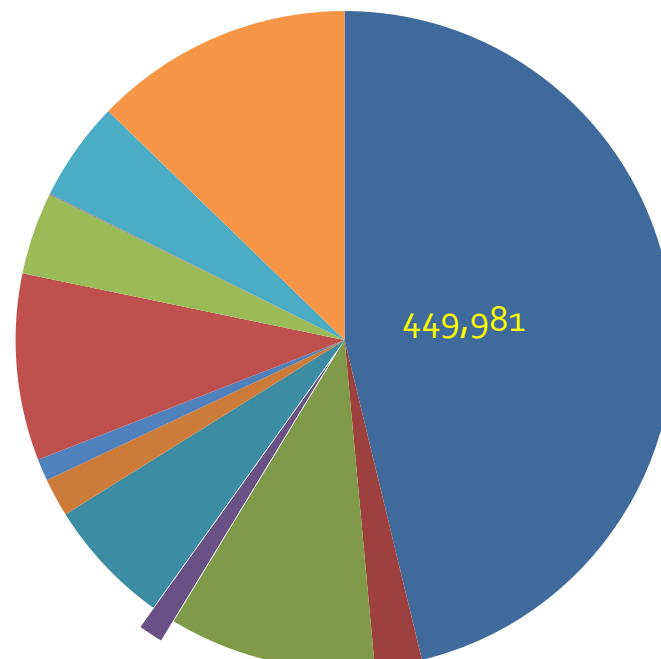
Loads produced in the major tributaries (tpy)

FLOW (CFS)



- Yough
- Ten Mile
- Whitley
- Dunkard
- Cheat
- Robinson
- Deckers
- Flaggy M
- Indian
- White D
- Tygart V
- West Fk

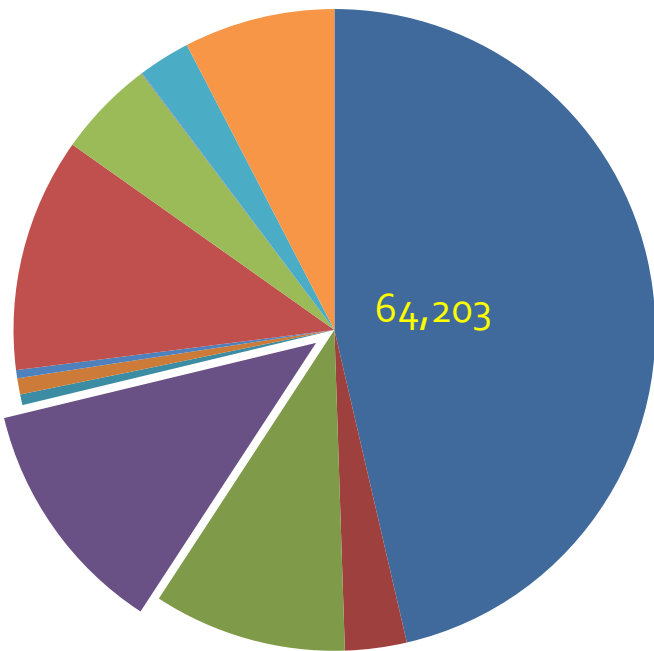
TDS



- Yough
- Ten Mile
- Whitley
- Dunkard
- Cheat
- Robinson
- Deckers
- Flaggy M
- Indian
- White D
- Tygart V
- West Fk

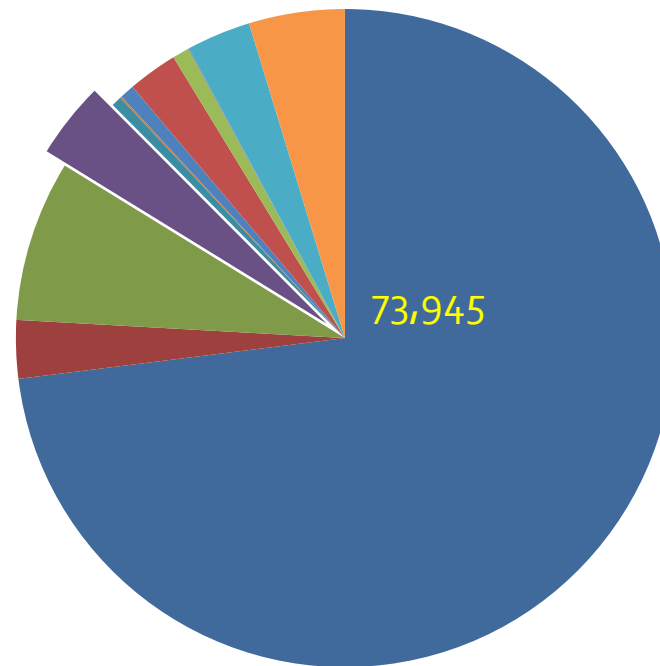
Loads produced in the major tributaries (tpy)

SODIUM



- Yough
- Ten Mile
- Whitley
- Dunkard
- Cheat
- Robinson
- Deckers
- Flaggy M
- Indian
- White D
- Tygart V
- West Fk

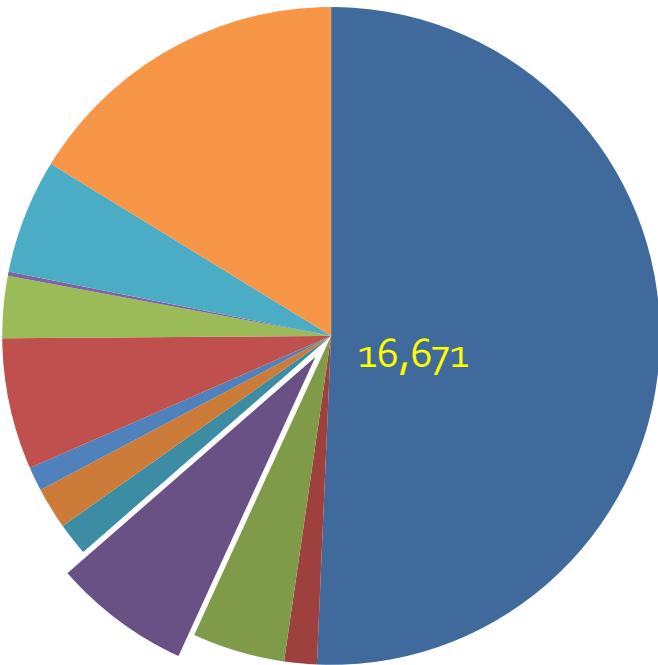
CHLORIDE



- Yough
- Ten Mile
- Whitley
- Dunkard
- Cheat
- Robinson
- Deckers
- Flaggy M
- Indian
- White D
- Tygart V
- West Fk

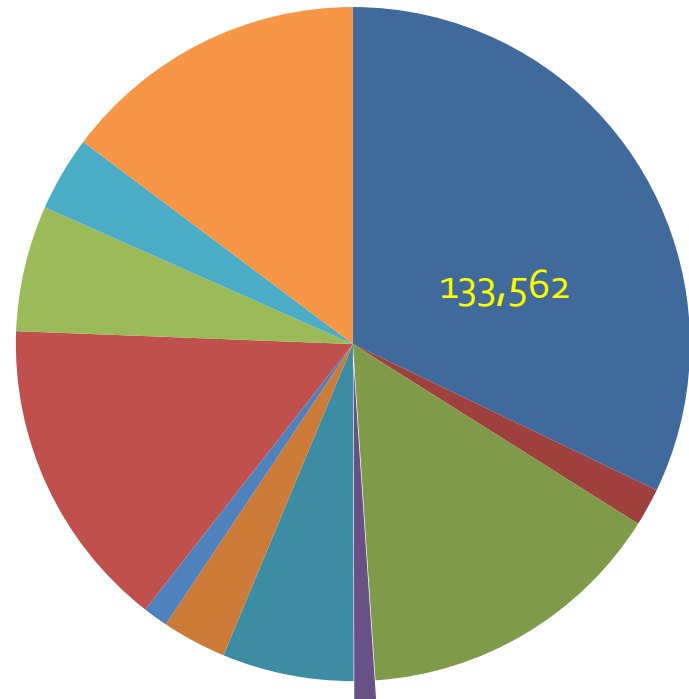
Loads produced in the major tributaries (tpy)

MAGNESIUM



- Yough
- Ten Mile
- Whitley
- Dunkard
- Cheat
- Robinson
- Deckers
- Flaggy M
- Indian
- White D
- Tygart V
- West Fk

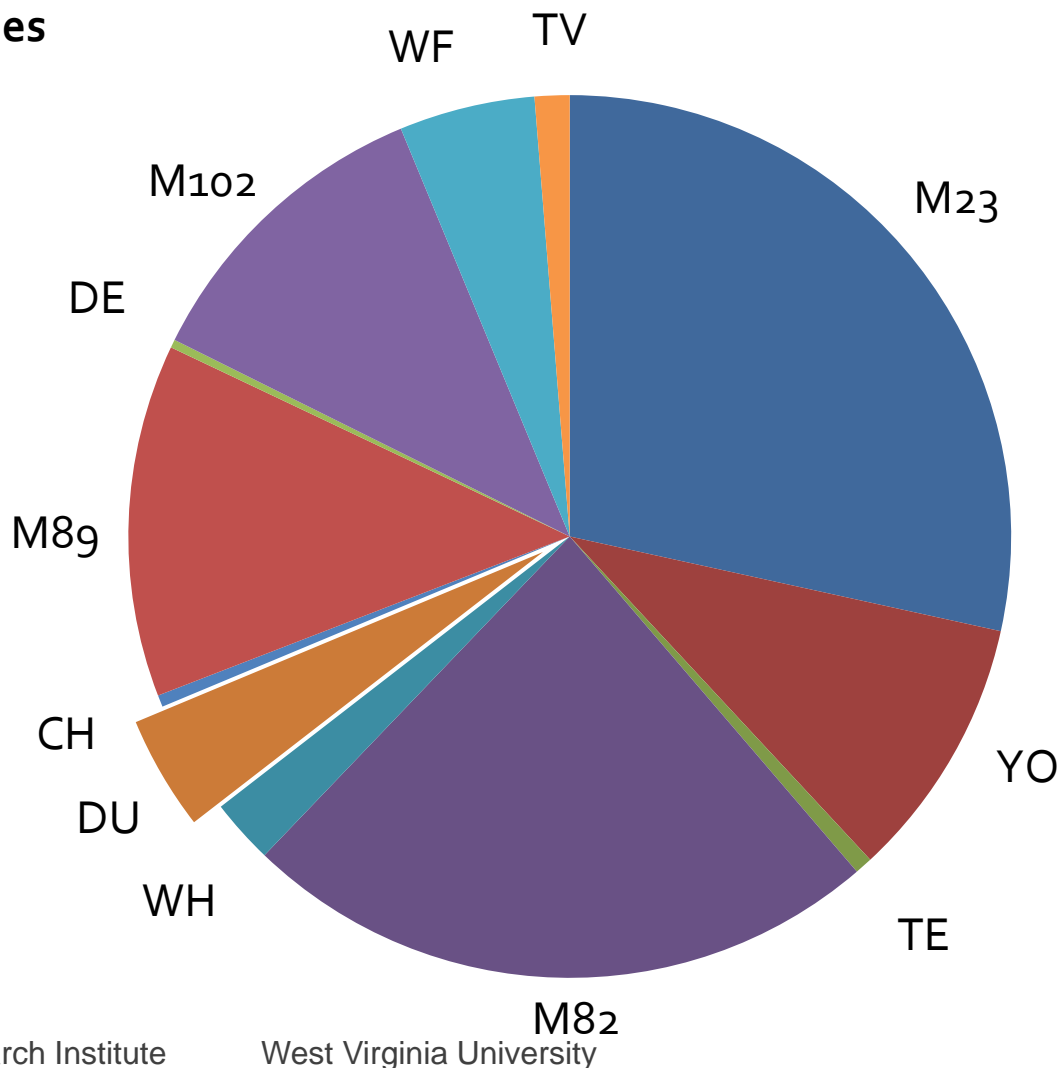
SULFATE



- Yough
- Ten Mile
- Whitley
- Dunkard
- Cheat
- Robinson
- Deckers
- Flaggy M
- Indian
- White D
- Tygart V
- West Fk

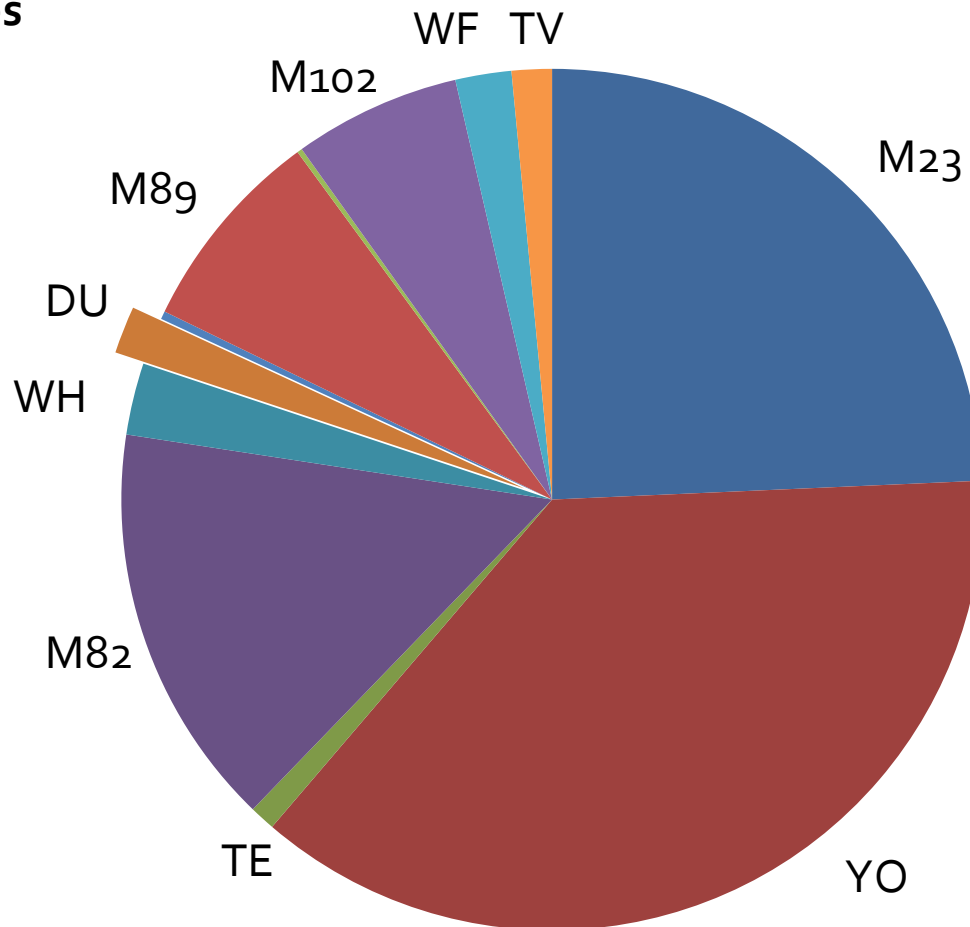
Proportion of SO₄ Load in the Monongahela @ McKeesport PA (^M15)

2010 averages



Proportion of Cl Load in the Monongahela @ McKeesport PA (^M15)

2010 averages

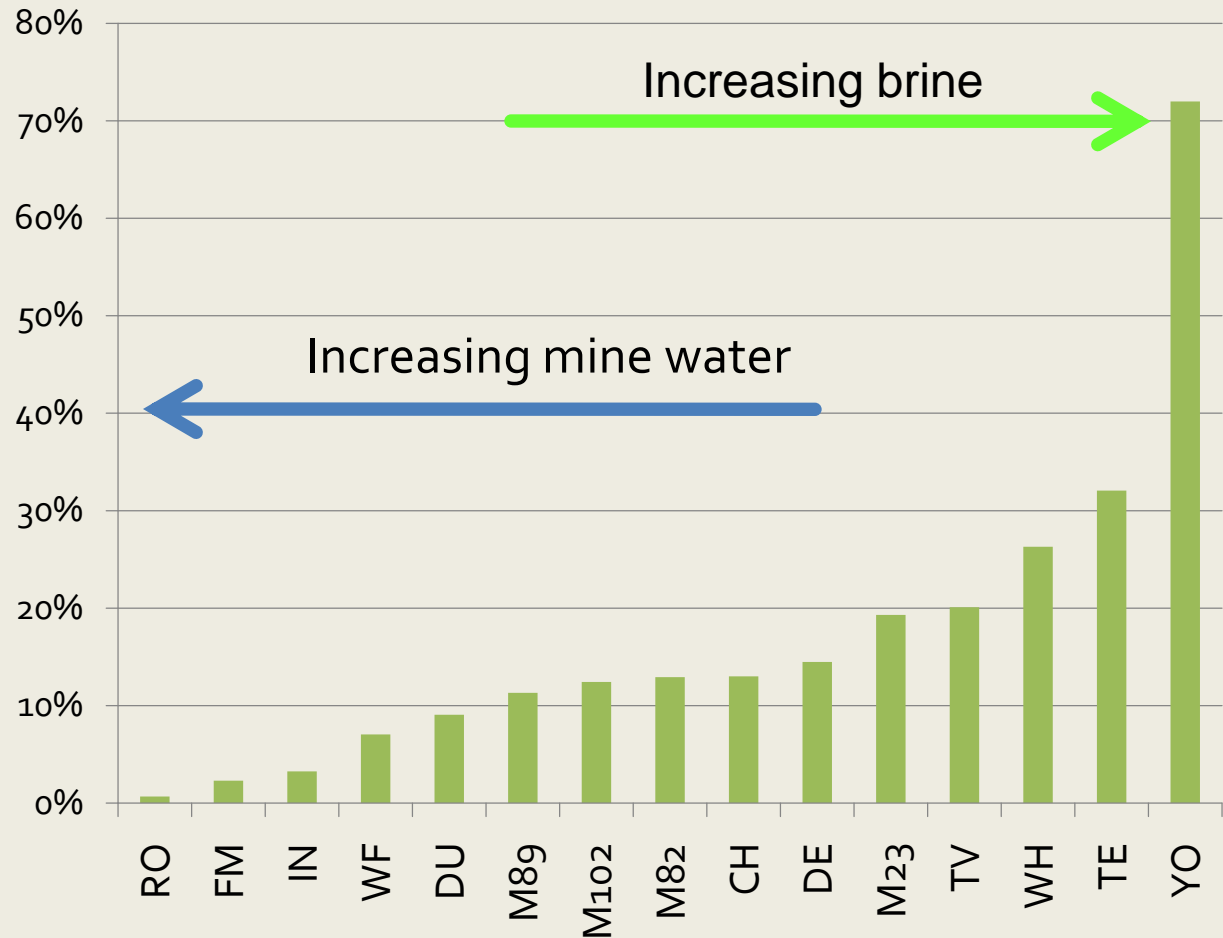


Stream effects

The ratio to chloride to sulfate ions appears to distinguish coal mine discharge from brine.

Is that treated mine water or frac water in my stream?

Average Cl/SO₄ July 09 to June 10



Discharge Management

Water Research Institute

Controlling AMD plant discharges from the upper Monongahela basin during the dry season substantially reduced the TDS at mile 82.

TDS remained below 500 mg/L at both mile 82 and mile 23 but concentrations and loads were about double during the dry season at mile 23

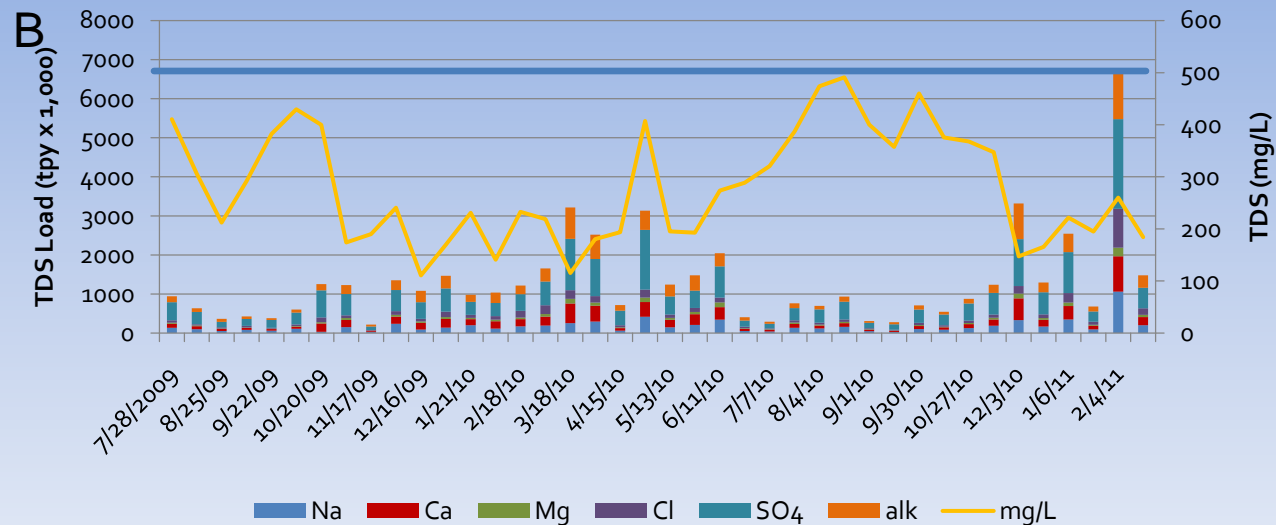
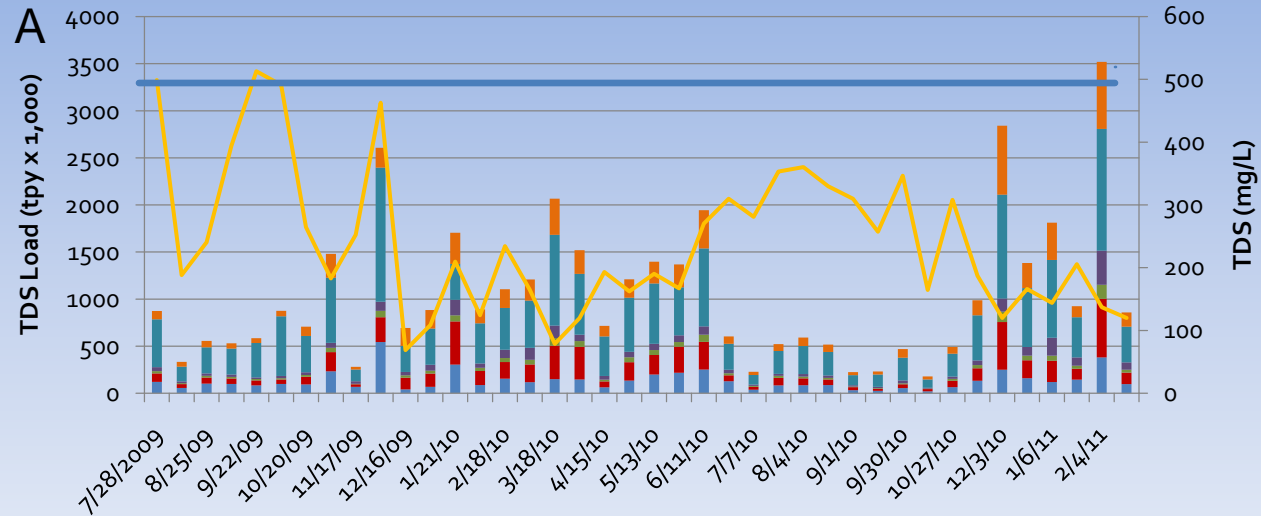
Monongahela River July 09 to Feb 11 @

A: mile 82 (Masontown) PA

B: mile 23 (Elizabeth) PA

West Virginia University

27



Other than the Tygart Valley River, most charge balances over 2010 were reasonably good

2010 avg (keq)

Site	2010 avg (keq)		charge balance
	anion	cation	
Dunkard Ck	2,132	2,061	3%
West Fork R	2,931	2,833	3%
Tenmile Ck	543	571	5%
Decker's Ck	176	187	6%
Whiteley Ck	1,543	1,416	9%
Youghiogeny R	10,573	11,658	10%
Mon mile 15	29,402	32,932	11%
Mon mile 23	18,829	21,274	12%
Mon mile 102	7,072	8,098	14%
Mon mile 82	14,428	16,919	16%
Mon mile 89	7,854	9,283	17%
Cheat R	282	337	18%
Tygart Valley R	1,016	1,515	39%

Regulatory implications

- Our sampling has not identified a [TDS] in excess of 500 mg/L since December 09
- [TDS] did not exceed 400 mg/L at Mile 82 in 2010
- [TDS] did not exceed 500 mg/L at Mile 23 in 2010
- The coal industry adjusts its discharge to stream flow by controlling its mine pumping rates
- There is evidence that brine disposal is also seasonal
- Managed discharge is effective
- Brine management and abandoned mines must be accounted for, otherwise assimilative capacity could be exhausted
- **Mass balances are useful method for evaluating the effectiveness of TDS control options**

Conclusions: after 20 months of monitoring

- Brine chemistry is dominated by NaCl
- Treated coal mine drainage is mainly Na/Ca SO_4
- The results indicate brine disposal in three PA streams
- TDS load in the Monongahela River (McKeesport PA) averaged 2,000,000 tpy
- Coal mine drainage accounts for between 250,000 and 500,000 tons of TDS/year
- **We have no comparable data for brine disposal or discharges from abandoned mines**

Questions?

Wastewater from Gas Development: Chemical Signatures in the Monongahela Basin

Paul Ziemkiewicz, PhD
WV Water Research Institute

Wastewater from Gas Development: Chemical Signatures in the Monongahela Basin

Paul Ziemkiewicz, PhD
West Virginia University

The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

The West Virginia Water Research Institute began monitoring the Monongahela River and its major tributaries in July 2009 after reports of increasingly high dissolved solids concentrations in the River near Pittsburgh in the late summer of 2008. A sampling network of sixteen stations was established extending from mile 23 at Elizabeth PA to the Rivers two major sources, the Tygart and West Fork Rivers. Based on earlier surveys by the Pittsburgh District, US Army Corps of Engineers and PaDEP, the chemical constituents of interest were determined to be: sodium, sulfate, chloride, calcium, magnesium and alkalinity. Total dissolved solids (TDS), iron, aluminum and manganese were also determined in the laboratory. Field parameters including pH and electrical conductivity were also measured. It was decided that loadings were needed in order to identify significance of the various ion sources so sampling stations were located near gauges where possible and flows were estimated in non-gauged streams. Sampling took place every two weeks, data were compiled and results placed on a publicly available website: monWQ.net.

While sampling made no assumptions as to the sources of the high TDS readings we suspected that two sources would predominate: treated coal mine discharges and brines from the gas industry. The former were easy to characterize as the coal mine discharges are regulated under the NPDES program of the Clean Water Act. Brines are not. Streams dominated by coal mine discharge were characterized by sodium sulfate as the dominant ions. Brines are characterized by sodium chloride and three streams in Pennsylvania: the Youghioghney, Ten Mile Creek and Whiteley Creek show a distinct sodium chloride signature suggesting heavy brine loadings. So, after 20 months it is possible to identify the major sources of TDS and their chemical signatures. The results also indicate seasonality with respect to higher TDS concentrations during low flow periods. This has led to a successful program with the coal industry whereby pumping rates are restricted during sensitive, low flow periods in late summer and fall with corresponding, higher discharges during high flow periods. As a result, the data show substantially reduced TDS concentrations on the Monongahela River since adoption of the managed discharge program in December 2009 and our data show no instances of TDS concentrations exceeding 500 mg/L on the Monongahela since December 2009.

The presentation focuses on major ion loadings and concentrations in the Monongahela River and its tributaries, the relative contributions of the major ions to TDS and their proportional contribution per tributary.