



# Constraining Sources using Pb Isotope ratios

USGS CMERSC

Michael Pribil (303) 236-9374

and

US EPA NEIC

Theresa Hosick and Steve Machermer

# Pb isotopes

## Primordial stable Pb

Isotope	<u>Stable</u>		<u>Radiogenic</u>		
	$^{204}\text{Pb}$		$^{206}\text{Pb}$	$^{207}\text{Pb}$	$^{208}\text{Pb}$
Abundances <sup>1</sup>	1.94%		19.12%	20.62%	58.31%
Radiogenic Pb	+	+	+		
Produced by radioactive decay	$^{238}\text{U}$	$^{235}\text{U}$	$^{232}\text{Th}$		
$^{206}\text{Pb}/^{207}\text{Pb}$ increases over time					
$^{208}\text{Pb}/^{207}\text{Pb}$ is dependent on the U and Th content of the source					
Common Pb	$^{204}\text{Pb}$		$^{206}\text{Pb}$	$^{207}\text{Pb}$	$^{208}\text{Pb}$
	1.43%		24.14%	22.08%	52.35%

<sup>1</sup>Anders and Grevesse, 1989

# Pb isotopes analyses by MC-ICP-MS



Rock prep



Rock prep



Acid purification, column container & resin cleaning



or



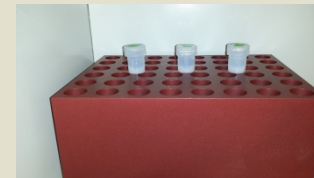
Finally  
~week



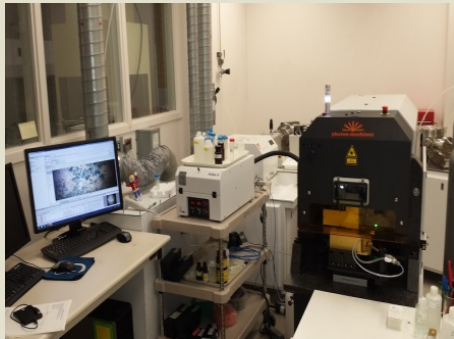
Pb column separation



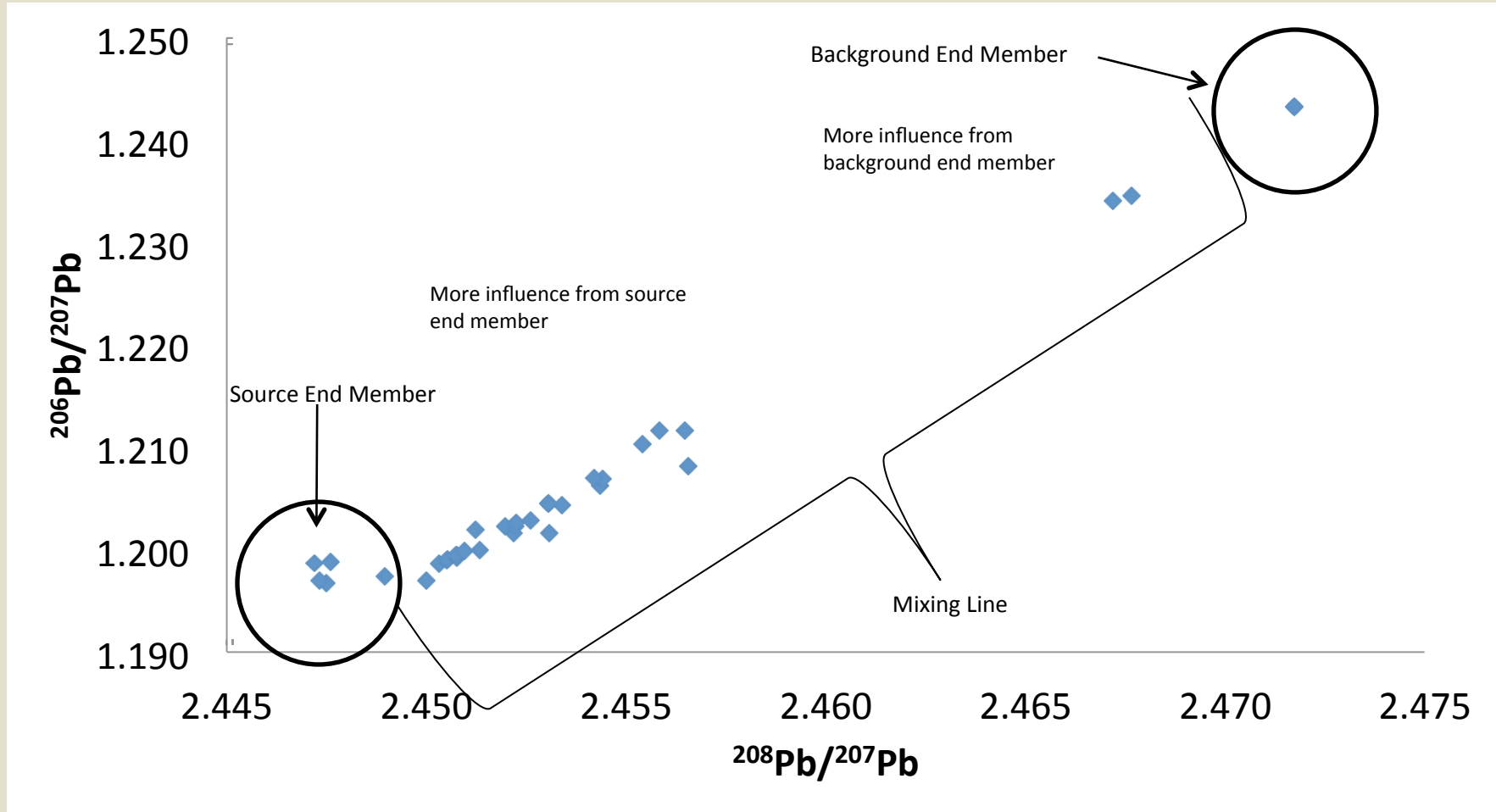
Clean lab



Acid digestion



# An example of a three Pb isotope mixing line with varying contribution from two end members



# Examples of the use of Pb isotopes for source-receptor studies

SEM characterization and ICP-MS analyses for trace metals were also conducted for some of these studies.

# Marietta Site Issues

in collaboration with Theresa Hosick and EPA NEIC

- Public concern over Mn emissions
- Elevated & widespread ambient air levels of Mn
- What is/are the sources of the high Mn?
  - Industries in the region
    - Washington County Welding Shop
    - Eramet
    - Energizer Battery
    - Marietta Industrial Enterprises
- Air filters and source material were used for the Pb isotope measurements - can also be measured by laser ablation MC-ICP-MS saving time and sample preparation costs
- Pb isotopes measurements in air filter samples are a more straight forward to interpret as legacy and multiple sources of Pb typically found in soil are not present in the air samples – sample collection can be pinpointed to a point source

# Washington County Career Center Welding Shop



# Eramet

metallurgical manufacturing company





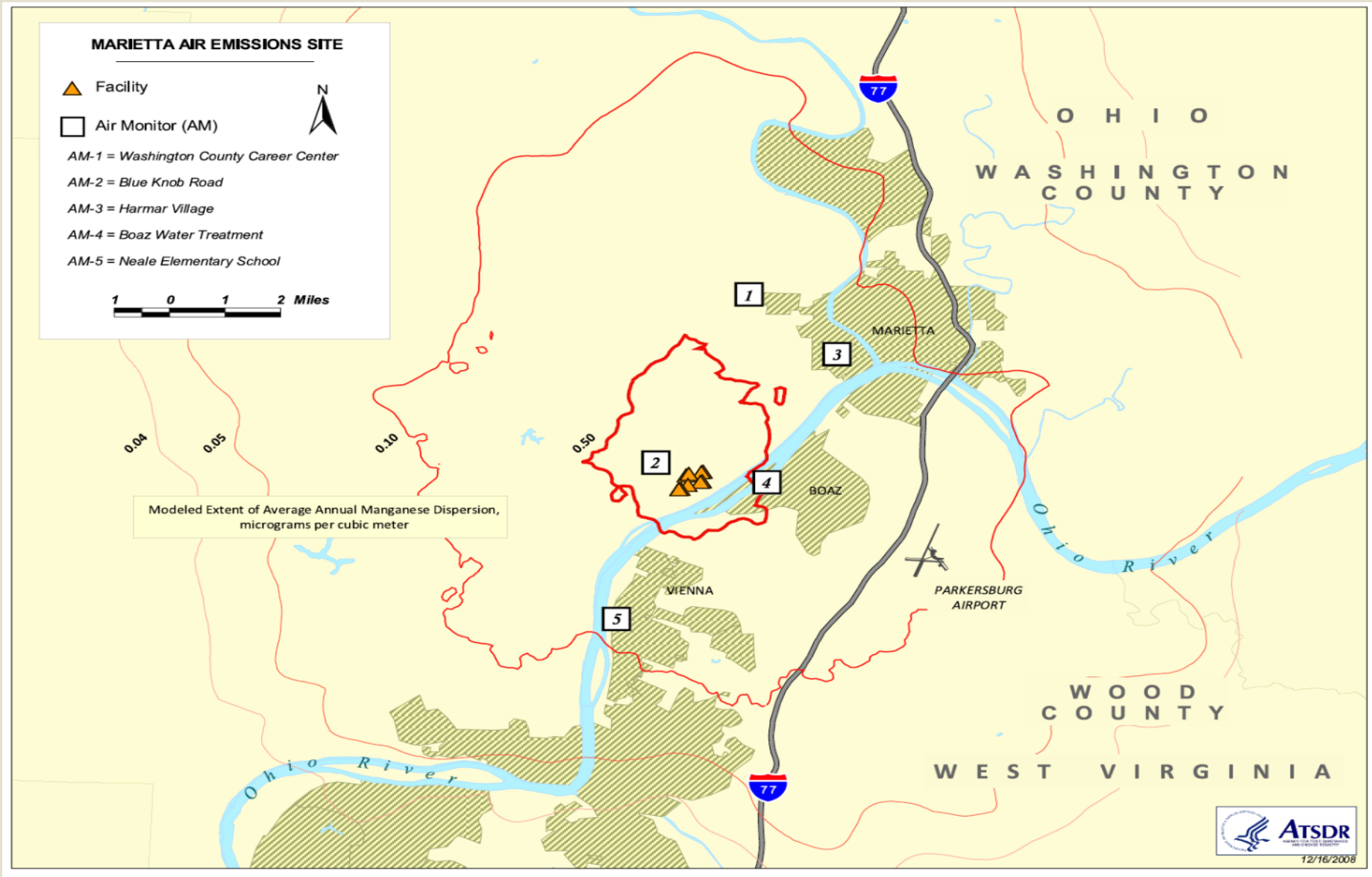
# Energizer Battery Production

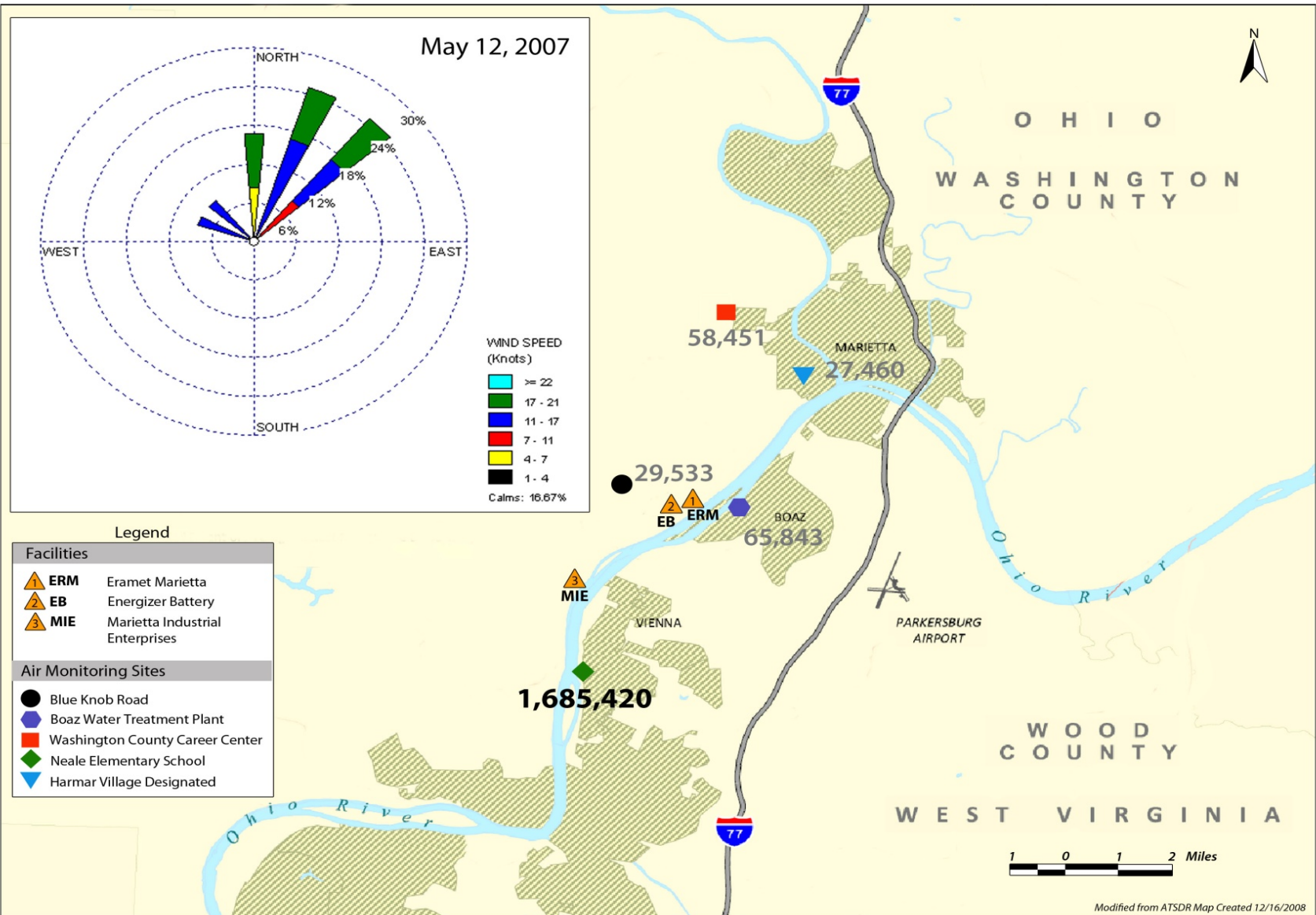


# Marietta Industrial Enterprises

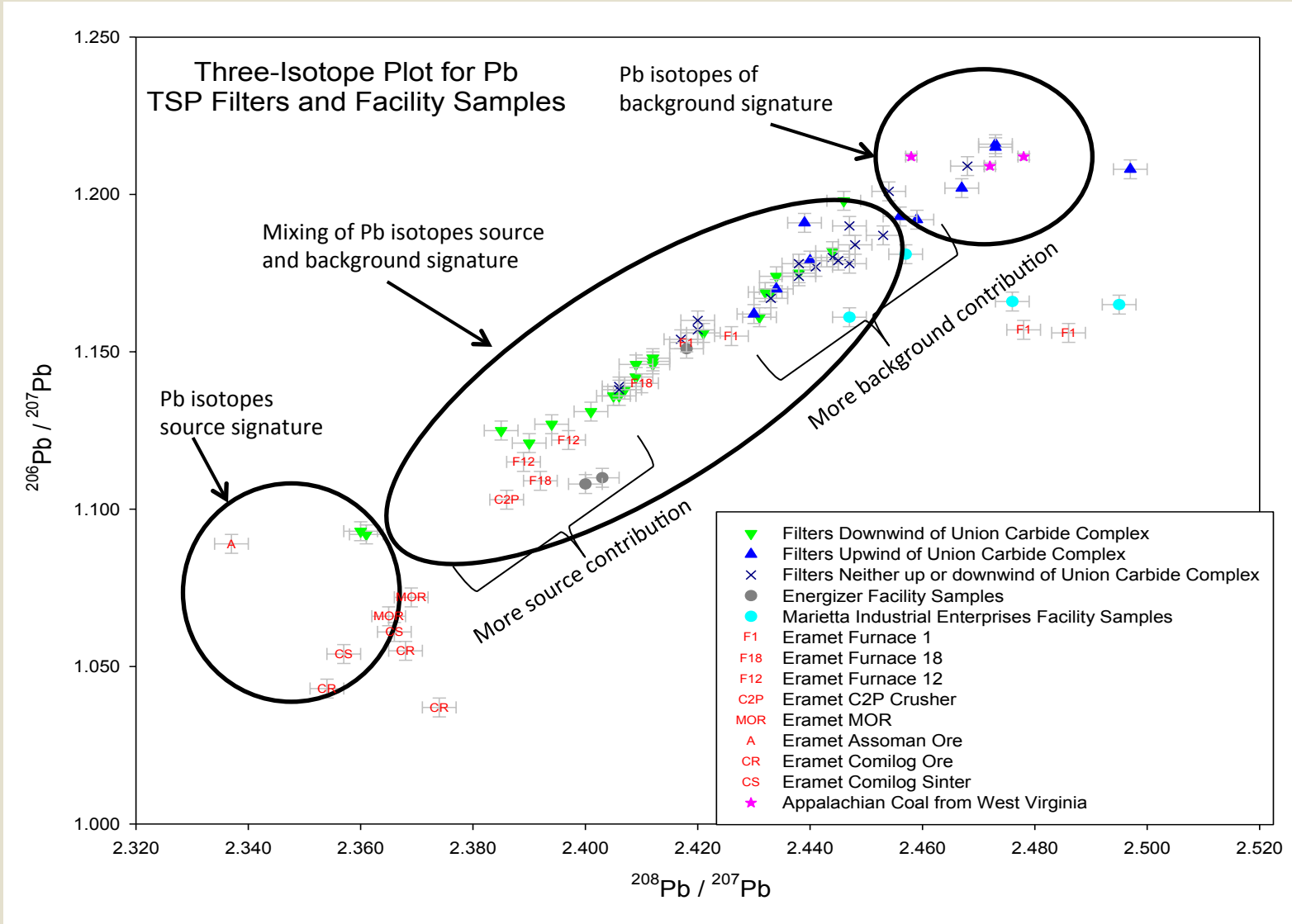
alloys sizing, mineral handling, chemical processing, recycling



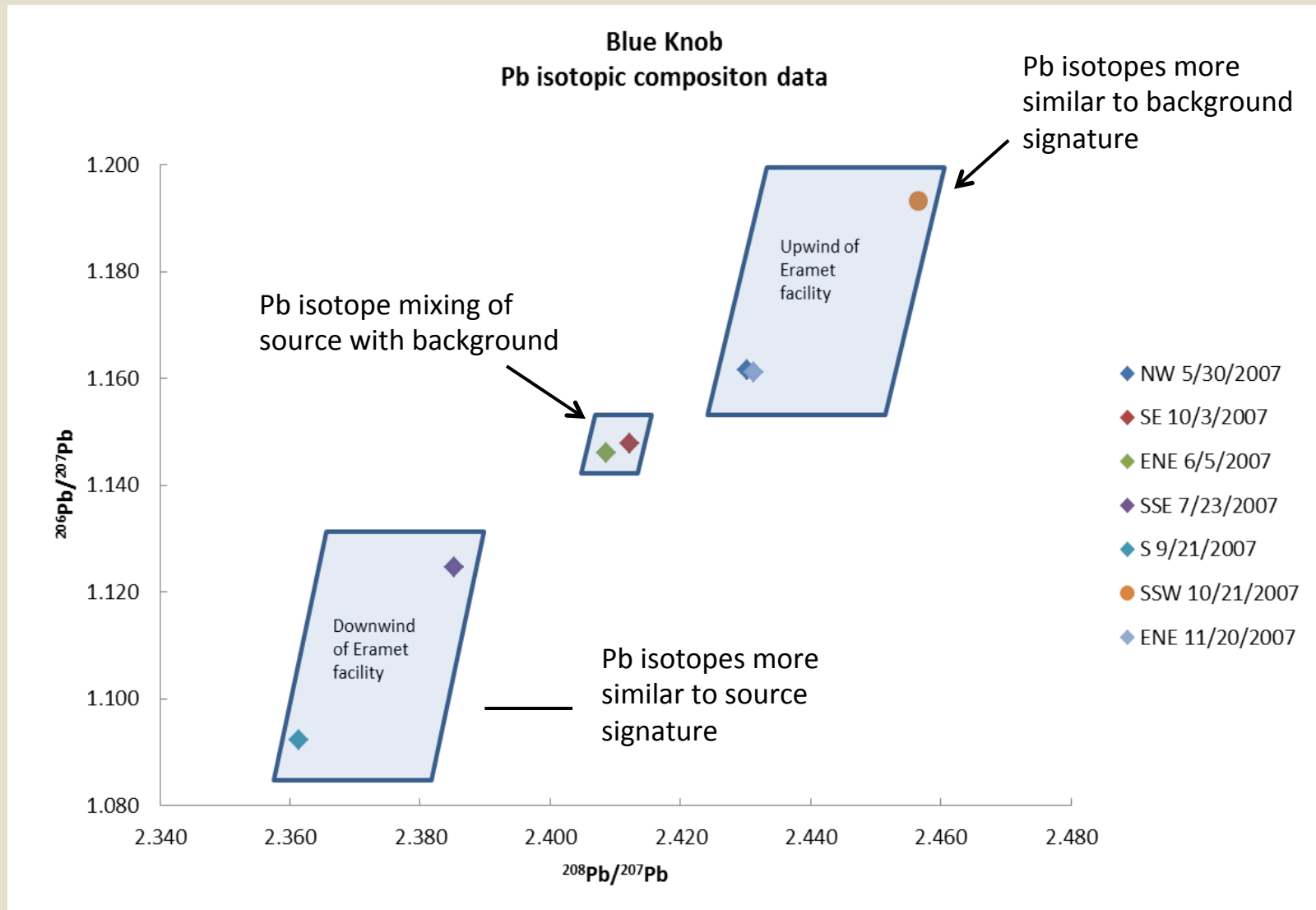




# Detailed sample three Pb isotope plot



# An example of upwind vs downwind Pb isotope variations



# Summary of Findings

- The furnace processes at Eramet were the primary source of airborne manganese particulate matter around Marietta, Ohio
- Energizer, MIE, and Eramet's MOR process were not primary sources of manganese-bearing airborne particles
- Helped justify funding for the health study in the Marietta area- ATSDR Health Consultation 2009
- OAQPS is using this information to create their proposal for a new MACT ruling for the Ferroalloy industry

# Jewett White Lead

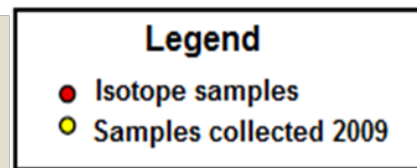
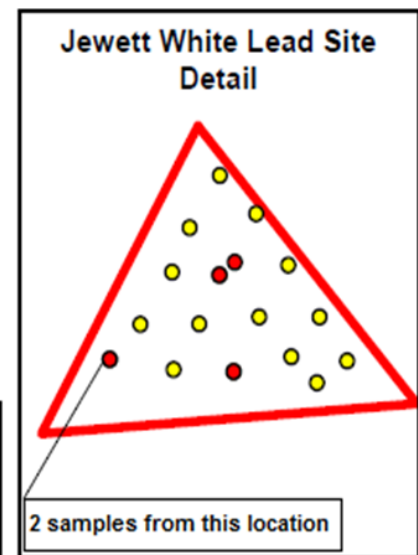
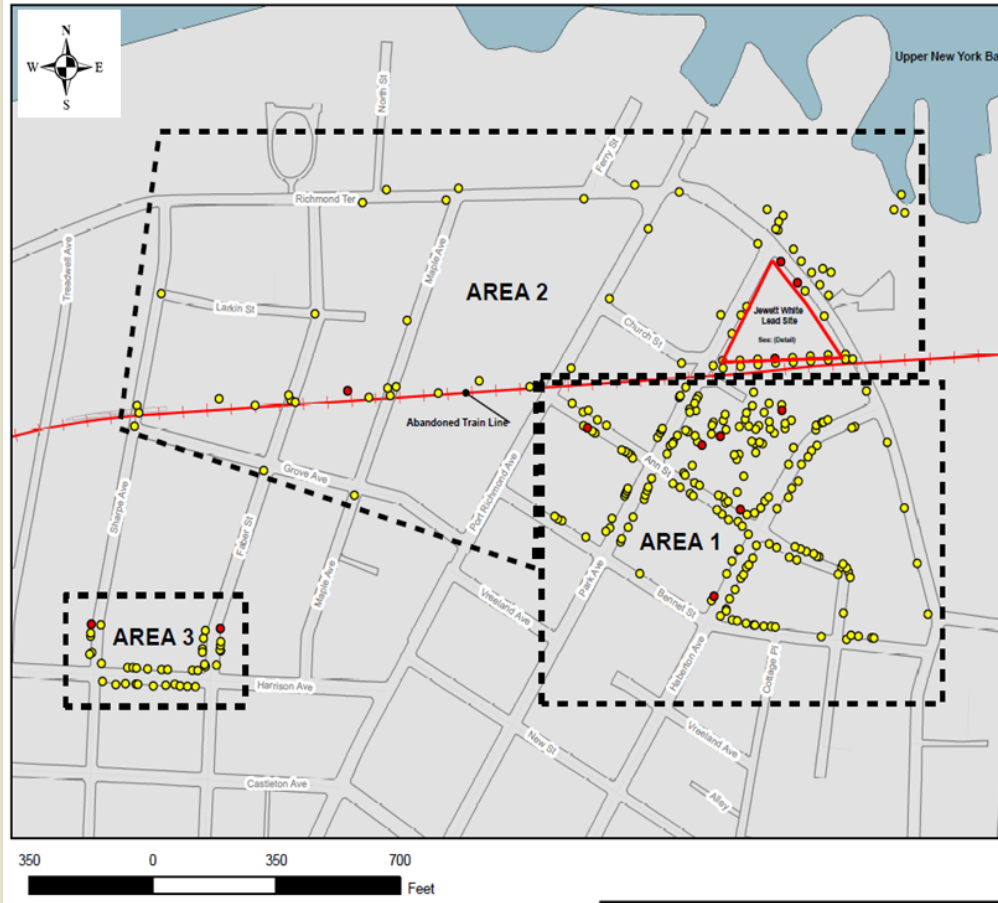
## Port Richmond area of Staten Island, NY

in collaboration with Mark Maddaloni and EPA Region II

- Public concern over elevated and wide spread Pb concentration in soil
- Historical white lead facility in the community
  - Is it the primary source of elevated Pb?
- On-site surface, on-site subsurface and soil samples from the surrounding community were used for the Pb isotope and Pb concentration measurements



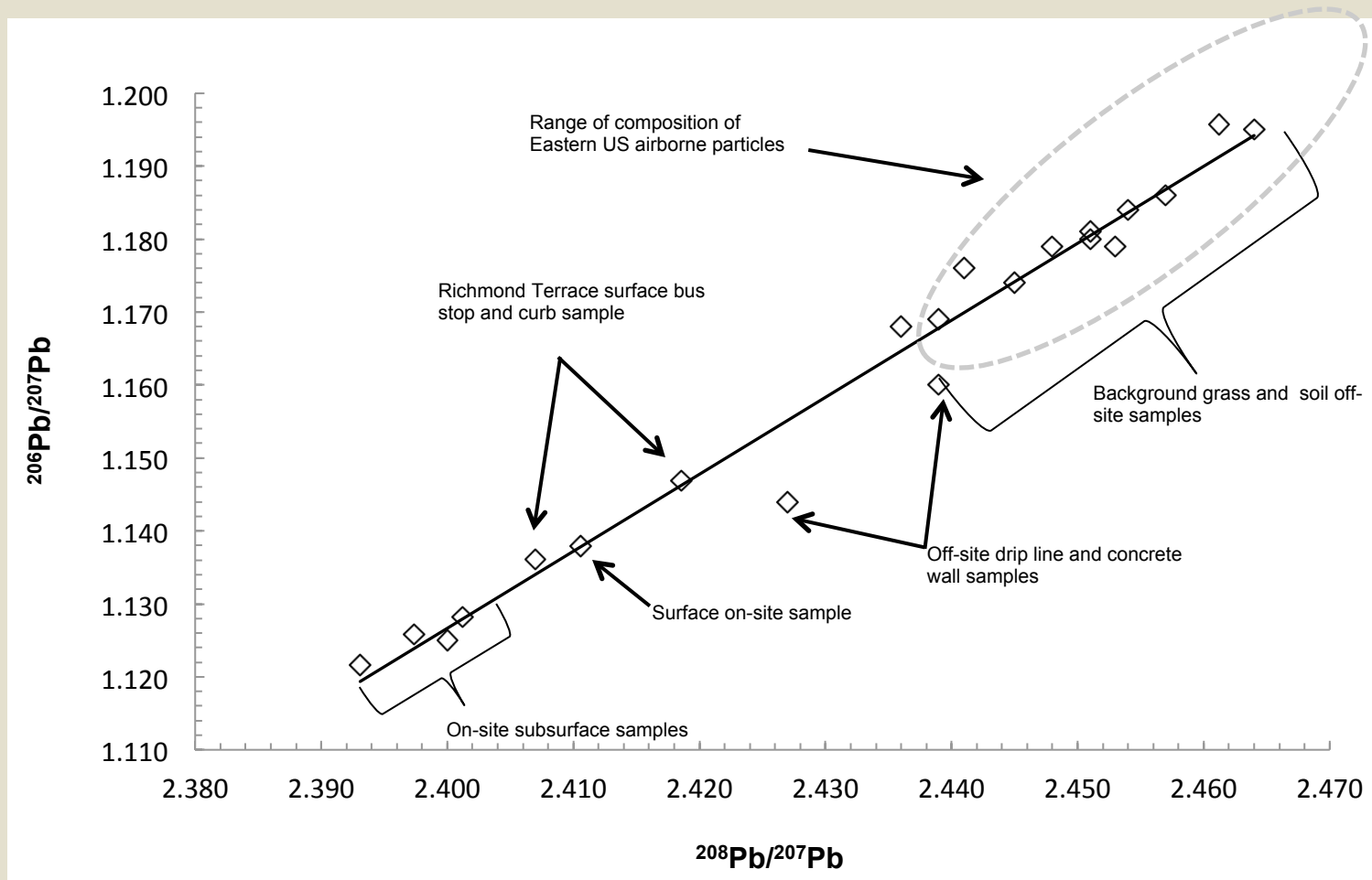
# Port Richmond, Staten Island



# Pb concentrations and isotopic composition

Sample	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	[Pb] ug/g	Sample Description
B-2-0	37.411	15.520	17.660	2.118	0.879	2.411	1.138	450	On-site 0-3" depth
A-5-0	37.192	15.498	17.443	2.132	0.889	2.400	1.125	8,000	On-site 0-3" depth
A-5-3	37.067	15.489	17.373	2.134	0.892	2.393	1.122	90,900	On-site 3' depth
G-2-2 (avg)	37.223	15.502	17.492	2.128	0.886	2.401	1.128	240,000	On-site 2' depth
C-3-3	37.173	15.506	17.457	2.129	0.889	2.397	1.126	147,000	On-site 3' depth
0-1	37.436	15.553	17.669	2.119	0.879	2.407	1.136	2,800	Off-site
0-2 (avg)	37.651	15.567	17.855	2.109	0.872	2.419	1.147	380	Off-site
BY-034A	37.735	15.550	17.792	2.121	0.874	2.427	1.144	1,300	Off-site
TT-05A	37.993	15.595	18.215	2.086	0.856	2.436	1.168	400	Off-site
BY-029A	37.984	15.574	18.073	2.102	0.862	2.439	1.160	3,500	Off-site
GP38A	38.016	15.589	18.217	2.087	0.856	2.439	1.169	1,100	Off-site
GP-007B	38.061	15.595	18.338	2.076	0.850	2.441	1.176	1,000	Off-site
GP008B	38.120	15.590	18.296	2.084	0.852	2.445	1.174	1,300	Off-site
TT-22A	38.228	15.613	18.406	2.077	0.848	2.448	1.179	2,300	Off-site
BY13A	38.276	15.615	18.431	2.077	0.847	2.451	1.180	1,100	Off-site
BY-025A	38.256	15.608	18.427	2.076	0.847	2.451	1.181	1,100	Off-site
GP-006C	38.287	15.608	18.404	2.080	0.848	2.453	1.179	840	Off-site
GP-006A	38.318	15.616	18.497	2.072	0.844	2.454	1.184	1,500	Off-site
BY-013C	38.379	15.621	18.530	2.071	0.843	2.457	1.186	720	Off-site
GP-025A	38.473	15.631	18.690	2.058	0.836	2.461	1.196	1,000	Off-site
BY-025C	38.517	15.631	18.678	2.062	0.837	2.464	1.195	2,600	Off-site

# Three Pb isotope plot



# Summary of Findings

- The Pb isotopic composition for on-site soil samples are distinct from the off-site soil samples.
- These distinct differences in Pb isotopic compositions and Pb concentrations most likely indicate source material used during white lead production.
- The off-site soil samples from the Port Richmond area and baseline areas resulted similar  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios compared to other studies of soil, dust and road grit from New York City and New Jersey and consistent with anthropogenic Pb common in the northeastern US industrialized urban areas
- Two soils collected just off-site along Richmond Terrace after major rain events did reflect minimal migration from the Jewett site

# Now the truth about Pb isotopes

- They can assist with source attribution studies
- They can be used to constrain and at times identify the source
- If the Pb isotopic composition of the source is similar to the background they won't be useful
- Best to use multiple analytical approaches such as SEM, trace metals or secondary isotope systematics in conjunction with Pb
- At times Pb isotopes can be used to assist in constraining sources other than Pb (Marietta for example)
- Other isotope systematics also exists (S, Cu, Zn, Fe, Sr, Hg and more)

Questions or interest in collaboration please contact Michael Pribil  
(303) 236-9374 or [mpribil@usgs.gov](mailto:mpribil@usgs.gov)