Heavy Metal and Metalloid Contamination From the Battle of Verdun

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Preview

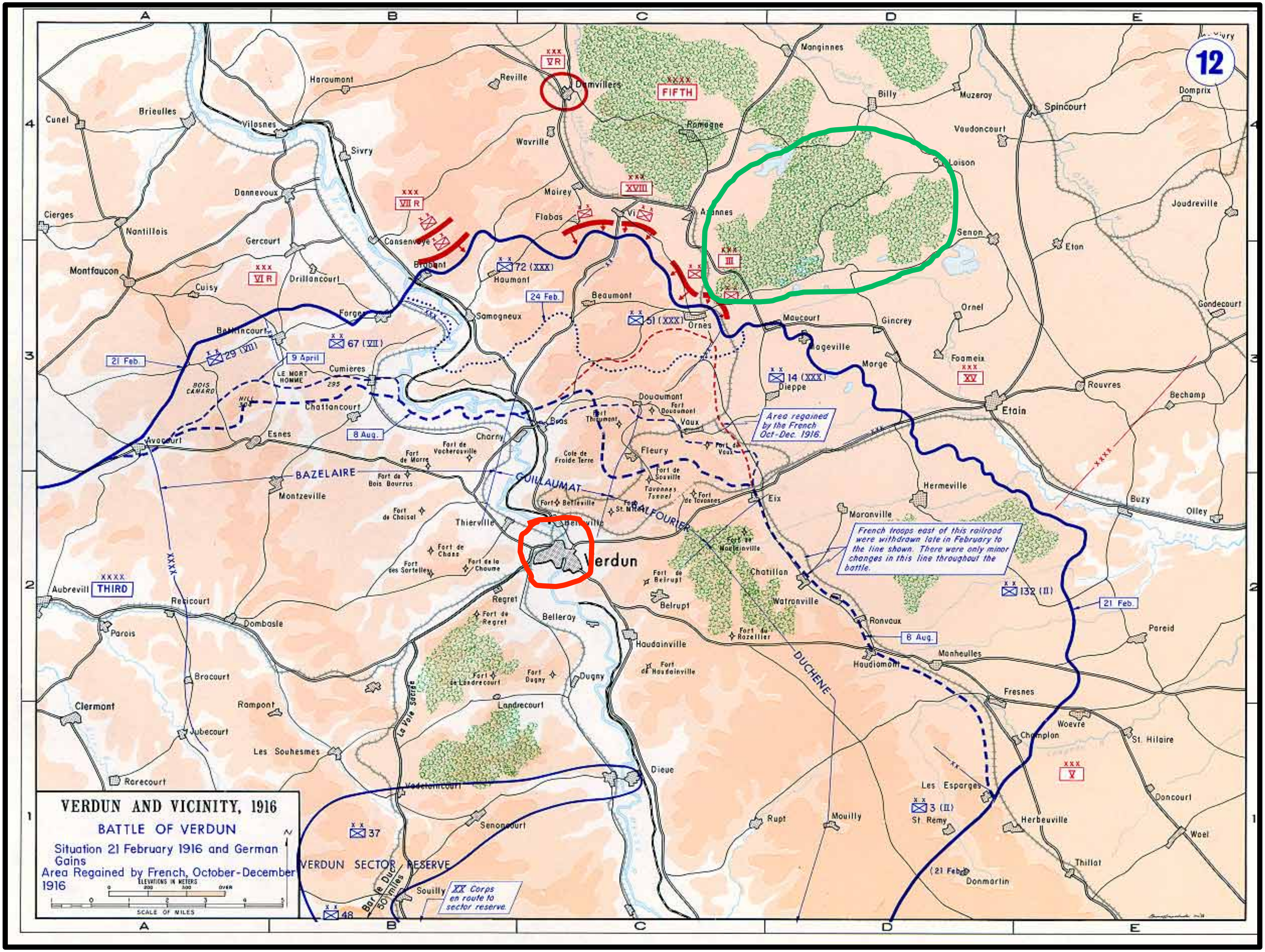
- Background and contaminated area
- Water pollution
- Contaminant mobility
- Arsenic contamination

Background

- Battle of Verdun: Feb. 21 – Dec. 18, 1916
- High heavy metal contamination
  - Lead and Copper
    - Shell casings
  - Zinc
    - Fuses
  - Arsenic
    - Organoarsenic compounds (chemical weapons)
  - Many other contaminants
- Contaminated area of 96 km^2

Contaminated Area

- Most contaminated site of the battle
  - Place-à-Gaz in the Spincourt Forest
  - 20 km Northeast of Verdun, France
- Cause of contamination
  - Previous fighting
  - Burning of leftover weapons
    - 1928
- Massive amounts of arsenic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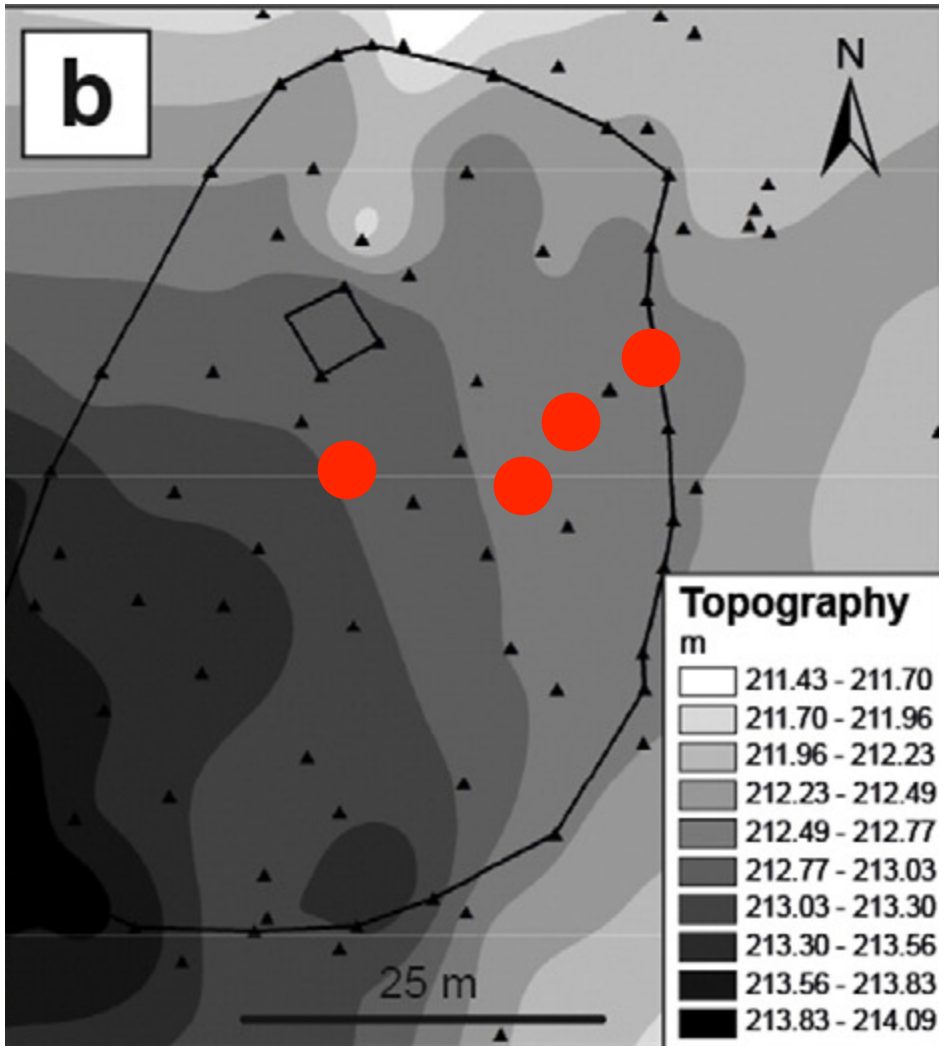
VERDUN AND VICINITY, 1916
BATTLE OF VERDUN
Situation 21 February 1916 and German Gains
Area Regained by French, October-December 1916
ELEVATIONS IN METERS
SCALE OF MILES
FIFTH
VR
VII R
VI R
XVIII
III
XV
V
THIRD
72 (XXX)
51 (XXX)
67 (VII)
29 (VII)
14 (XXX)
132 (II)
3 (II)
37
48
24 Feb.
21 Feb.
9 April
8 Aug.
Area regained by the French Oct-Dec. 1916.
French troops east of this railroad were withdrawn late in February to the line shown. There were only minor changes in this line throughout the battle.
XX Corps en route to sector reserve.
VERDUN SECTOR RESERVE
BAZELAIRE
GUILLAUMAT
BALFOURIER
DUCHENE
Verdun
Damvillers
Reville
Haraumont
Brieulles
Cunel
Vilosnes
Sivry
Wavrille
Dannevoux
Moirey
Flabas
Consenvoye
Brabant
Haumont
Samogneux
Beaumont
Ornes
Maucourt
Mogeville
Gincrey
Ornel
Foameix
Morgne
Dieppe
Manginnes
Billy
Muzeray
Spincourt
Vaudoncourt
Loison
Romagne
Azannes
Senon
Eton
Joudreville
Dompriz
Gondecourt
Rouvres
Bechamp
Etain
Hermeville
Buzy
Olley
Moranville
Eix
Chatillon
Watronville
Ronvaux
Haudiomont
Manheulles
Fresnes
Pareid
Woevre
St. Hilaire
Champlon
Les Esparges
Herbeuville
Doncourt
Woel
Thillot
Donmartin
St. Remy
Mouilly
Rupt
Dieue
Dugny
Landrecourt
Haudainville
Belrupt
Belleray
Regret
Belleville
Thierville
Charny
Bras
Douaumont
Vaux
Fleury
Cumières
Chattancourt
Esnes
Avocourt
Bethincourt
Forges
Drillancourt
Gercourt
Cuisy
Montfaucon
Nantillois
Cierges
Montzeville
Aubreville
Recicourt
Dombasle
Parois
Brocourt
Clermont
Rampont
Jubecourt
Les Souhesmes
Rarecourt
Senoncourt
Souilly
Vadelaincourt
La Voie Sacrée
Bar le Duc 50 miles
LE MORT HOMME
BOIS CAMARD
Fort de Douaumont
Fort de Vaux
Fort de Souville
Fort de Tavannes
Tavannes Tunnel
Fort Belleville
Fort St. Michel
Fort de Marre
Fort de Vacherauville
Fort de Bois Bourrus
Fort de Choisel
Fort de Chana
Fort des Sartelles
Fort de la Chaume
Fort de Belrupt
Fort de Regret
Fort de Landrecourt
Fort Dugny
Fort de Haudainville
Fort du Rozellier
Fort de Moulainville
Cote de Froide Terre
Fort Thiaumont

Contaminated Area (cont.)

- Average rainfall: 758 mm
- Average Temp: 10.7°C
- Little plant life



Water Pollution

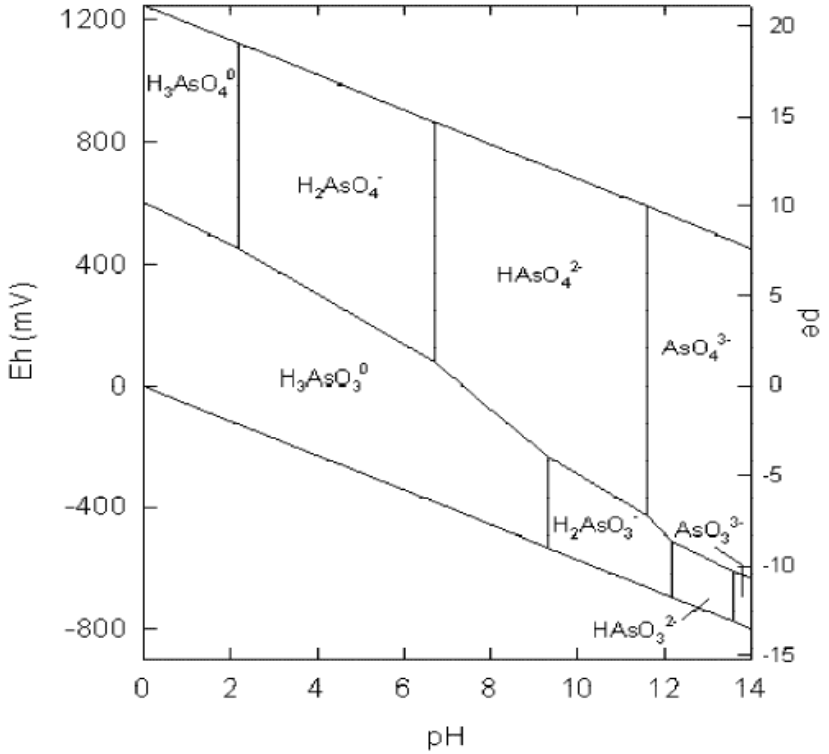
- Leaching test
  - Copper, lead, zinc
  - Concentrations determined by AAS
- Percolation test
  - Arsenic
  - Oxidation of As(III) to As(V)
  - Concentrations determined by ion exchange and AAS

Sample	As	Cu	Pb	Zn
1	77.2	3.0	2.9	103.9
2	40.5	2.8	4.6	70.8
3	21.8	2.8	4.2	59.9
4	26.3	3.0	2.2	74.5
WHO*	0.01	2.0	0.01	3.0

*World Health Organization water quality standards for clean drinking water

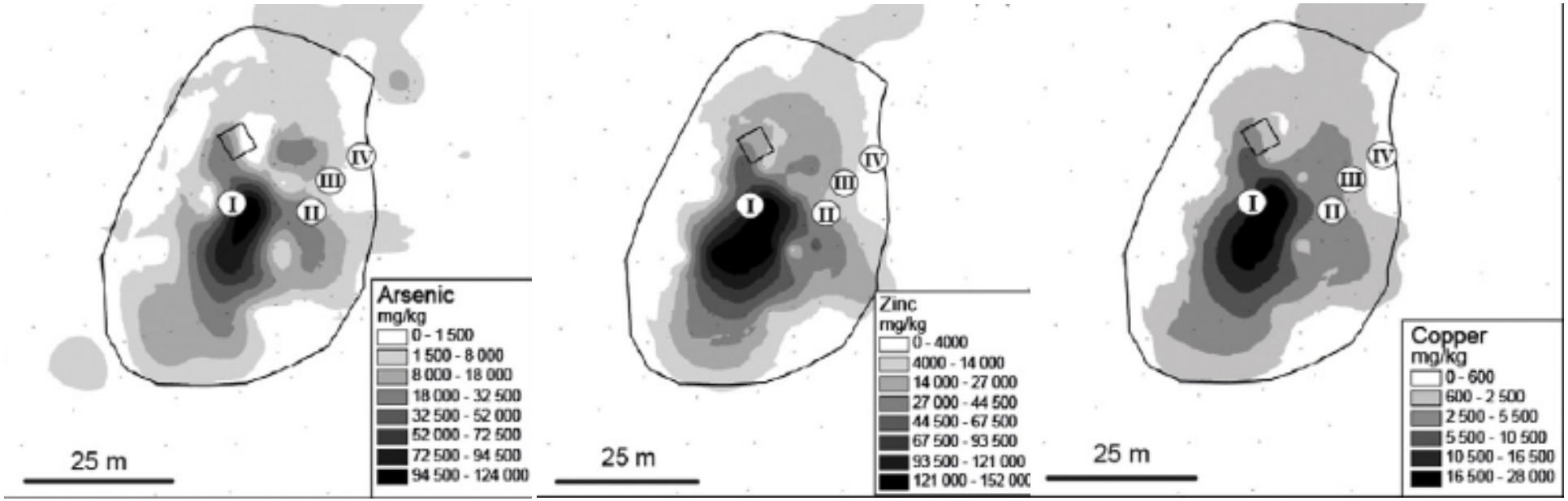
Arsenic Speciation

- Oxidation of As(III) to As(V)
- Ion exchange separation
  - As(III) is uncharged while As(V) is charged at pH 5-6
- 2% As(III) and 98% As(V)



Contaminant Mobility

- Copper and Lead
  - Constant concentration over each sample
- Arsenic and Zinc
  - High conc. in Sample 1 decreasing through to Sample 4



Arsenic Contamination

- Arsenic adsorption to Hydrous Ferric Oxides (HFO)
  - Fe_3O_4, Magnetite
  - FeO(OH), Goethite
  - $Fe_2O_3 \cdot 0.5H_2O$, Ferrihydrite
- pH values of 5 and 8
- Temperature values of 10°C and 25°C

As	Ca	Cl	Cu	F	Fe	K	Mg	Na	P	Pb	Zn
7.67	0.83	1.16	0.30	0.05	3.89	0.26	0.29	0.85	0.72	0.31	10.3

Mineral Saturation

10°C

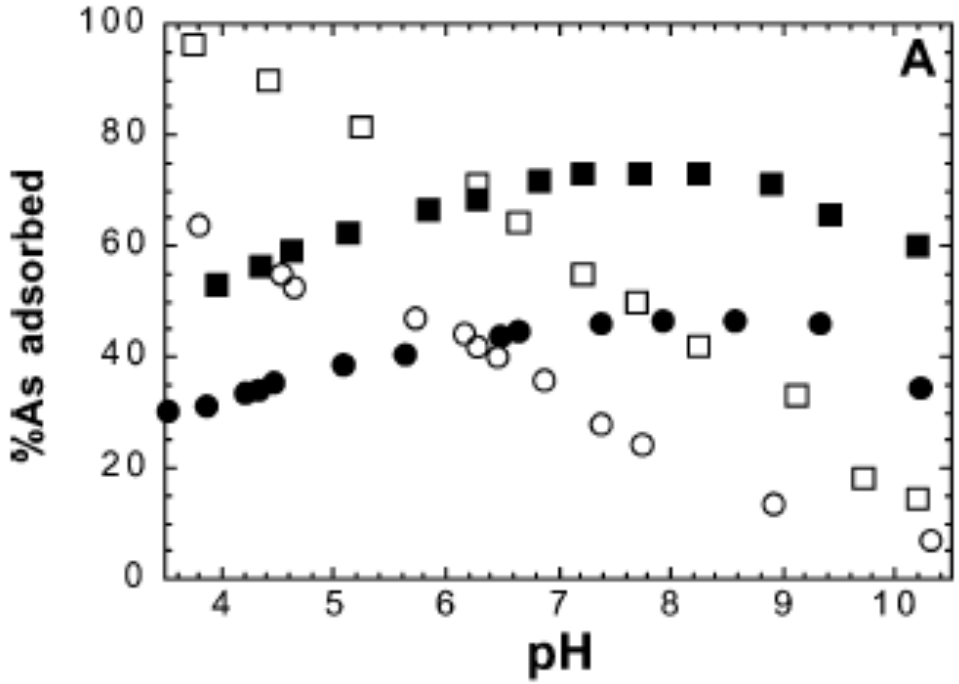
pH	Magnetite	Goethite	Ferrihydrite
5	-4.83	-3.69	-6.51
6	3.61	-0.70	-3.51
7	11.41	2.30	-0.52
8	19.08	5.28	2.46

25°C

pH	Magnetite	Goethite	Ferrihydrite
5	-2.11	-2.74	-5.44
6	5.88	0.26	-2.44
7	13.84	3.25	0.55
8	21.71	6.20	3.50

Arsenic Adsorption

- As(III) neutral at pH 5-6
  - Adsorbs better at higher pH
- As(V) charged at pH 5-6
  - Adsorbs better at lower pH
- As(III) and As(V) adsorb at similar rates at pH 6
- Higher pH limits movement of arsenic



Boxes = 100 μM
Circles = 50 μM

Solid = As(III)
Open = As(V)

Summary

- Verdun Battlefield is highly contaminated
- Water contamination
- Arsenic and Zinc runoff
- Higher pH causes less mobility of Arsenic

References

Thouin, H.; Forsteir, L. L.; Gautret, P. Battaglia-Brunet, F. Characterization and mobility of arsenic and heavy metals in soils polluted by the destruction of arsenic-containing shells from the Great War. Science of the total environment. 550. (2016) 658-669.

Ngai, K. K. Arsenic Speciation and Evaluation Of An Adsorption Media In Rupandehi And Nawalparasi Districts Of Nepal. MIT. June 2002.

Dixit, S.; Hering, J. Comparison of Arsenic(V) and Arsenic(III) Sorption onto Iron Oxide Minerals: Implications for Arsenic Mobility. Environ. Sci. Technol. 2003, 37, 4182-4189

World Health Organization. Guidlines for Drinking-water Quality. 3rd edition. Volume 1. 2008.