FLOWPATH 2012

"Percorsi di Idrogeologia"

Bologna, 20-22 June 2012

ARSENIC MOBILITY UNDER ANAEROBIC CONDITIONS

A laboratory study

Presenting author: **Sabrina Piccolo**

Authors: Accoto Valentina (1), Bullo Pierluigi (1), Piccolo Sabrina (2)

(1) Sinergeo srl, Vicenza, Italy, info@sinergeo.it; (2) Dep. of Agricultural Biotechnology, University of Padua, Italy, sabrina.piccolo@unipd.it

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INTRODUCTION

Arsenic in the environment

- The main mineral sources of arsenic (As) are: arsenopyrite (FeAsS) and pyrite (FeS_2)
- The oxidation of arsenopyrite and pyrite is a process that releases As and Fe in the oxidizing state [As(V) and Fe(III)] into the environment
- In oxidizing conditions, Fe(III) precipitates as iron oxyhydroxyde while arsenic is absorbed and coprecipitates
- *«Arsenic-bearing precipitates are deposited as iron oxyhydroxyde coatings on aquifer soil particles..»* *(Farhana S. Islam – 2008 in Satinder Editor)*
- Under low redox conditions Fe(III) reduces to soluble Fe(II) and releases the segregated As

INTRODUCTION

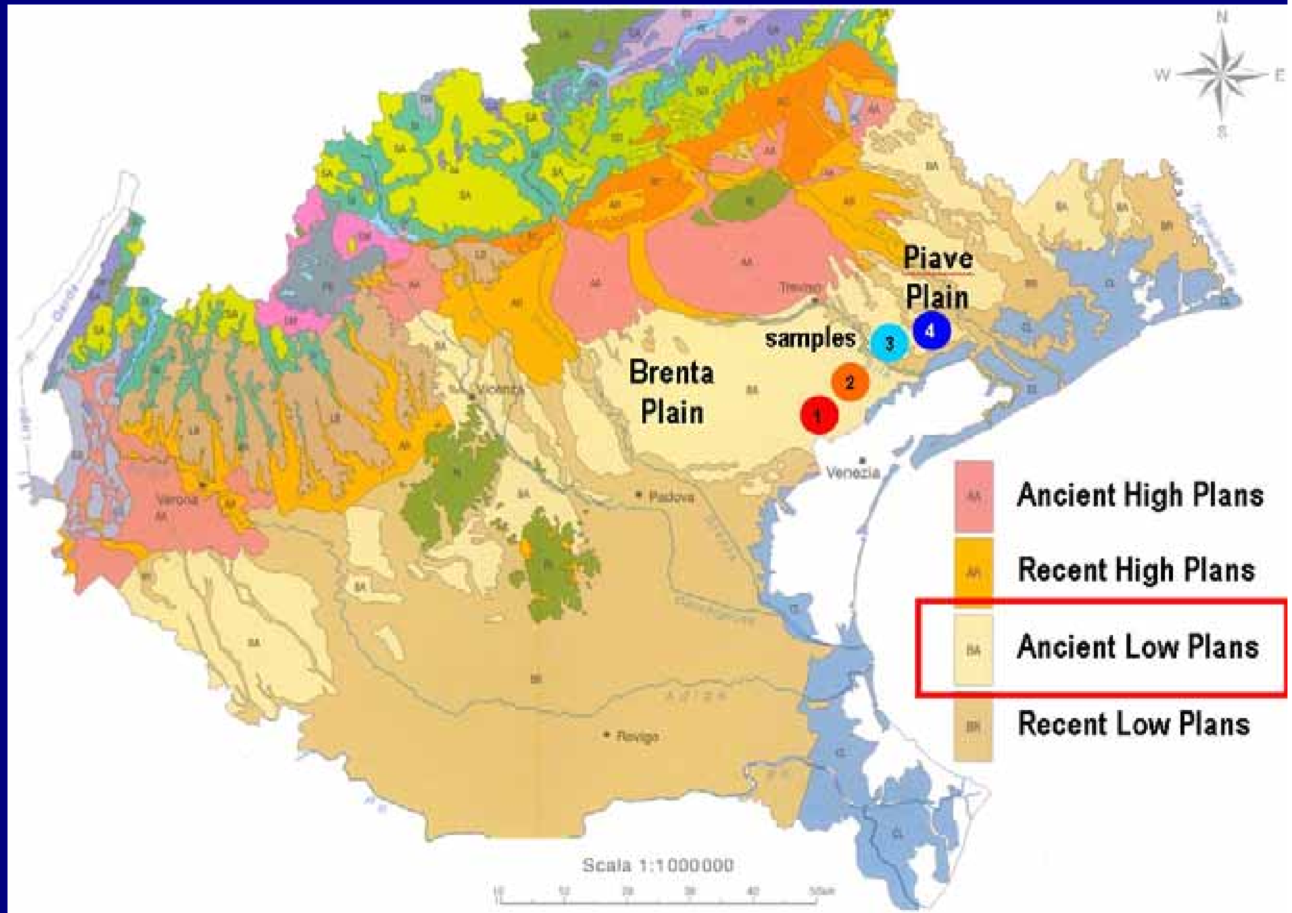
Arsenic in the environment

- In the environment, As(V) is present in oxidizing conditions, As(III) in reducing conditions
- As(III) is 100-200 times more toxic than As(V)
- As(III) is considered more mobile than As(V)
- In fact As(V) is generally segregated into iron oxyhydroxyde
- However As(III) is not mobile in presence of sulfides
- The presence of different solutes and the eH-ph conditions determine the mobility of As

MATERIALS AND METHOD

Soil samples collection

Four soil samples were collected in the Venetian Plain (Veneto, Italy) at 1,5 m bgl from two different sedimentary basins:



Brenta plain: samples 1-2 ancient low plain

Piave plain: samples 3-4 ancient low plain

MATERIALS AND METHOD

Soil analysis and standard leaching tests

- Granulometric distribution
- Organic carbon content
- XRD analysis
- Texture
- Soil As, Fe and Mn content:
  - total acid (HCl, HNO_3 e HF) digestion (EPA 3052 + EPA 6020A/98)
  - “environmentally available” extraction (HCl/HNO_3 = 3/1) (EPA 3050B/96 + EPA 6020A/98)
- Leachate As, Fe, Mn content:
  - leaching test (PR/SUO-TEC/151-2007 - APAT/ISS):
    - deionized water
    - soil/water ratio 1:2;
    - sample under continuous (24h) agitation
    - 30 minutes in centrifuge before analysis

MATERIALS AND METHOD

Modified leaching tests

- Leachate As, Fe, Mn content:
  - leaching test (PR/SUO-TEC/151-2007 - APAT/ISS modified):
    - deionized water
    - soil/water ratio 1:2
    - addition of Glucose (4% of soil weight)
    - closed vials
    - daily manual mixing
    - opening of vials at day 1, 2, 3, 4, 5, 7, 8, 10
    - measure of pH and Eh
    - 0,45 μm filtration
    - control sample (no addition of glucose)

RESULTS

Soil sample analysis

- Soil samples show chemical differences between the two basin deposits. As content varies from 23 (Brenta basin) to 6 (Piave basin) mg/kg.

- The different metal extractions lead to similar results indicating that these metals are not associated with silica minerals

Soil Sample Analysis

		1		2		3		4	
		A	B	A	B	A	B	A	B
Arsenic (as As)	mg/kg	23	24	26	21	6	6	6	3
Iron (as Fe)	mg/kg	23000	19968	38000	31878	12000	14671	12000	8371
Manganese (as Mn)	mg/kg	350	441	240	231	290	380	240	160
Organic Carbon	%	0,2		0,7		0,2		0,4	
Sand	%	11,4		7,9		3,7		29,7	
Silt	%	61,3		31		59,8		41,7	
Clay	%	27,3		61,1		36,6		28,6	
Total Organic Carbon	%	45		0		59		23	
Active Limestone	%	11		0		13		5	
pH	-	8,5		7,2		7,9		8,1	
Quartz	C	present		present		present		present	
Calcite	C	present		-		-		-	
Clinochlore	C	present		present		-		-	
Muscovite	C	present		present		-		-	
Dolomite	C	present		-		present		present	

A: Total Acid Digestion - EPA 3052 1996+EPA 6020A 1998

B: "Environmentally Available" Extraction - EPA 3050B 1996+EPA 6020A 1998

C: Qualitative XRF Analyses

RESULTS

Standard leaching test

- Standard test (ST) shows very low As concentration (≈ 1 µg/l).
- ST gives higher Fe and Mn concentrations in the leachate in comparison with modified test (MT)
- Both tests lead to a pH reduction (horizontal shifting into eH-pH diagram)

		Leaching Tests			
		1	2	3	4
Demineralized water test (1 day) PR/SUO-TEC/151-2007					
Arsenic (as As)	mg/l	0,001	0,001	<0,001	<0,001
Iron (as Fe)	mg/l	0,110	0,015	0,051	0,100
Manganese (as Mn)	mg/l	0,082	0,150	0,057	0,070
pH (at the beginning of test)	-	8,7	7,1	8,5	8,7
pH (at the end of test)	-	8,2	5,2	8,4	8,3
Demineralized water test (1 day) PR/SUO-TEC/151-2007_mod					
Arsenic (as As)	mg/l	<0,001	<0,001	<0,001	<0,001
Iron (as Fe)	mg/l	<0,010	<0,010	<0,010	<0,010
Manganese (as Mn)	mg/l	<0,001	0,003	<0,001	<0,001
pH (at the end of test)	-	8,5	7,2	7,9	8,1
Eh (at the end of test)	mV	352	452	360	416

- Fe concentration in sample 2, although less pH and high Fe concentration in the soil, is very low probably due to the high clay content
- The absence of continuous agitation in the MT, probably led to less metal desorbtion and solubilization

RESULTS

Anaerobic conditions leaching test

- The test in anaerobic conditions (MT) lead to **greater concentrations** of As, Fe and Mn in the leachate
- The **oxidation of glucose** by autochthonous microorganisms lead to a **decrease of redox potential**

		1	2	3	4
Demineralized water test (10 days)					
PR/SUO-TEC/151-2007_mod					
Arsenic (as As)	mg/l	<0,001	<0,001	<0,001	<0,001
Iron (as Fe)	mg/l	0,025	0,010	0,010	<0,010
Manganese (as Mn)	mg/l	<0,001	0,065	<0,001	<0,001
pH (at the end of test)	-	7.0	5,7	6,8	7.0
Eh (at the end of test)	mV	372	453	444	434
Anaerobic test (10 days)					
Arsenic (as As)	mg/l	0,140	0,006	0,013	0,013
Iron (as Fe)	mg/l	14	2,5	4.0	45
Manganese (as Mn)	mg/l	3,90	0,26	3,30	6,30
pH (at the end of test)	-	6,23	4,50	6,00	5,90
Eh (at the end of test)	mV	-158	-218	-228	-238

- In these conditions Fe oxides are reduced and mobilized causing As leaching
- The control batch (without glucose) showes a **very low metals concentration** in the leachate, **low pH** condition and **high redox potential**

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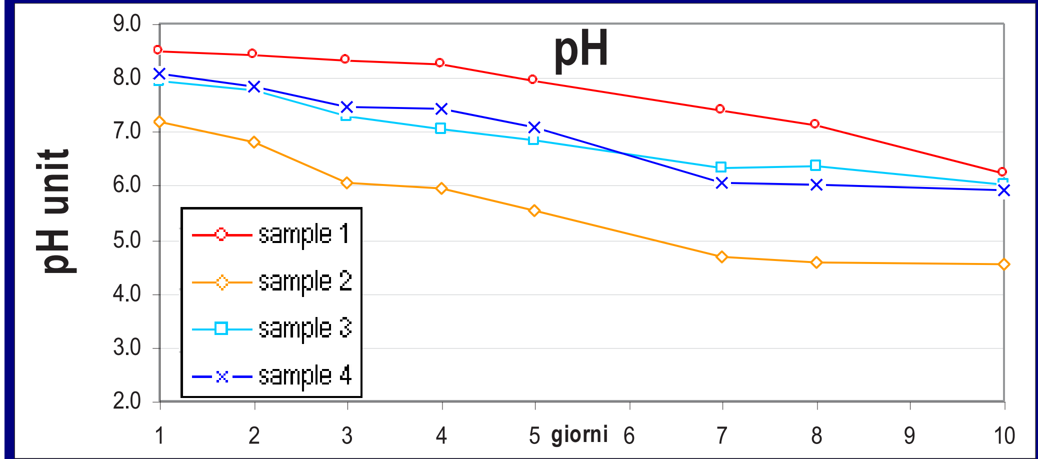
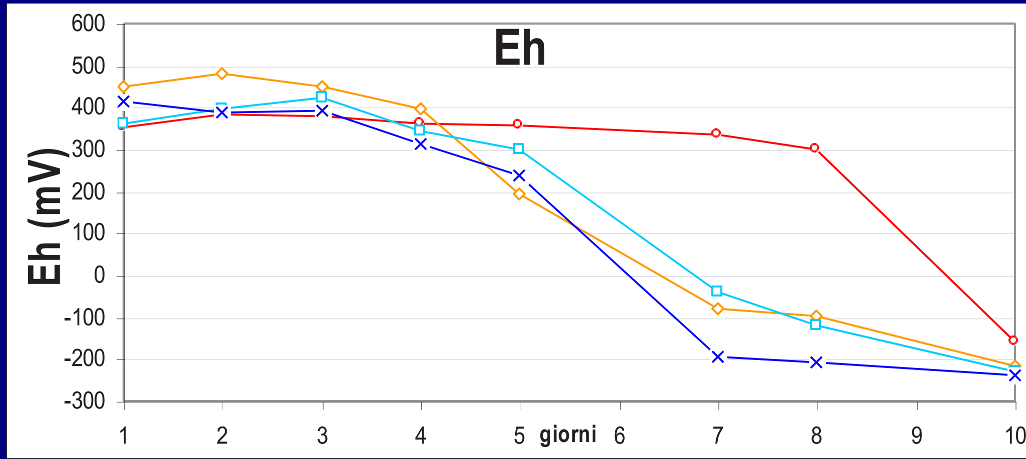
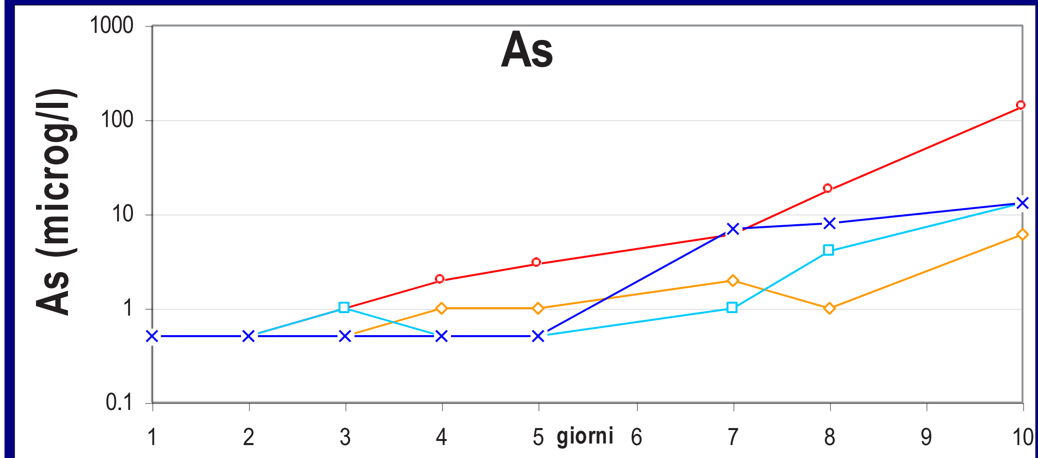
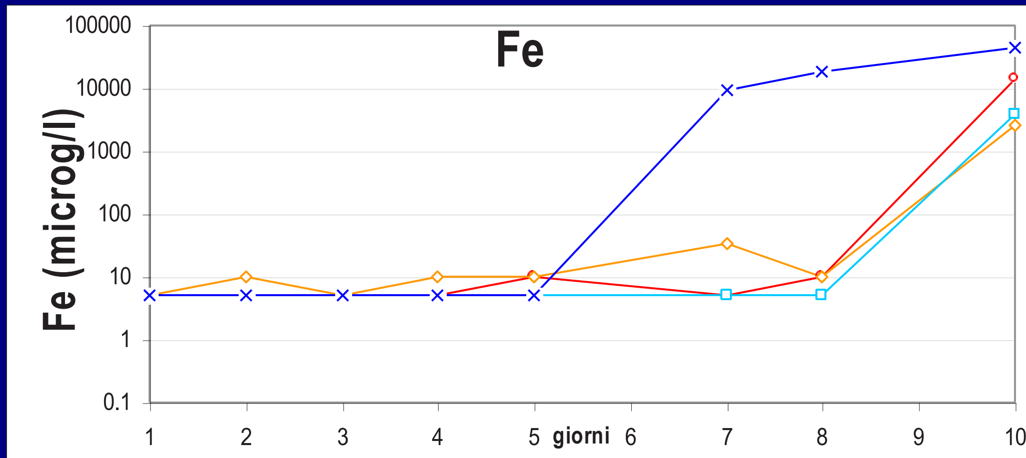
RESULTS

Anaerobic conditions leaching test









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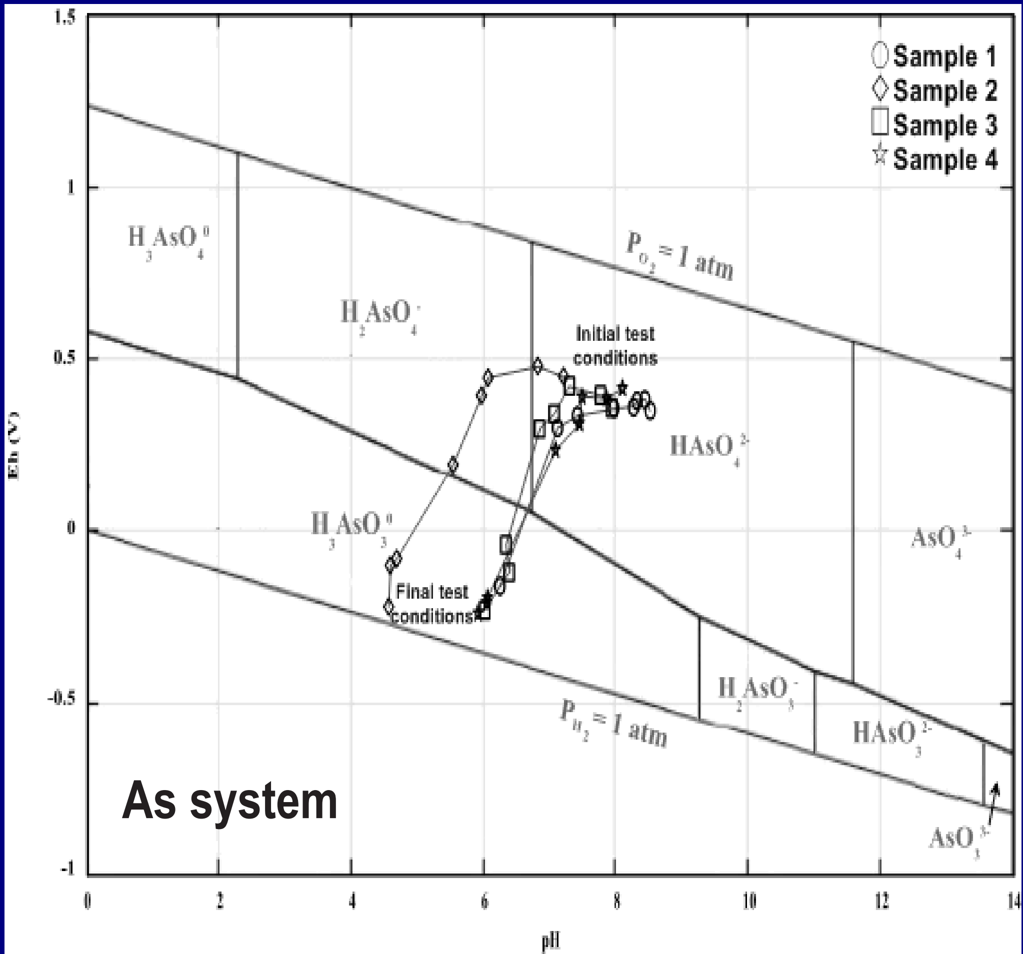
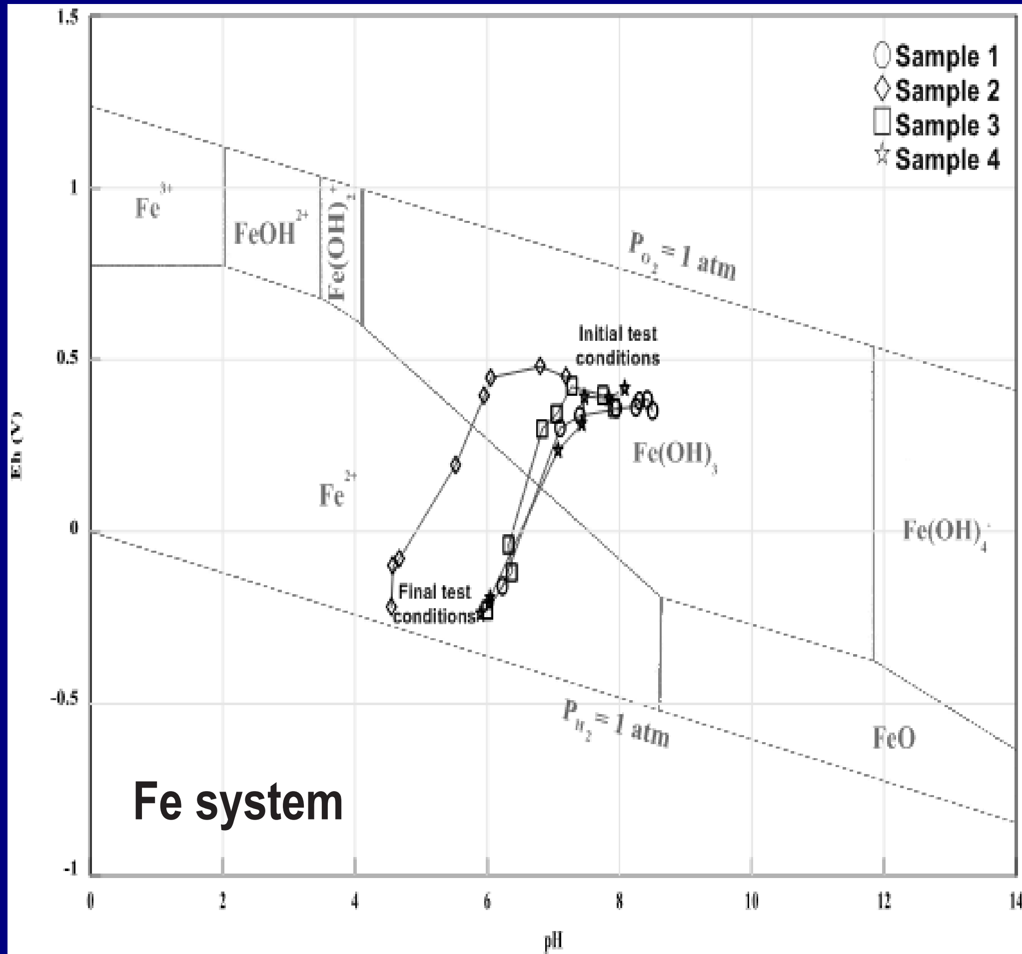
RESULTS

Anaerobic conditions leaching test





The trend of pH and Redox give evidence of variations of metals concentrations in leachate

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University of Padua, Italy

CONCLUSIONS

Arsenic mobility

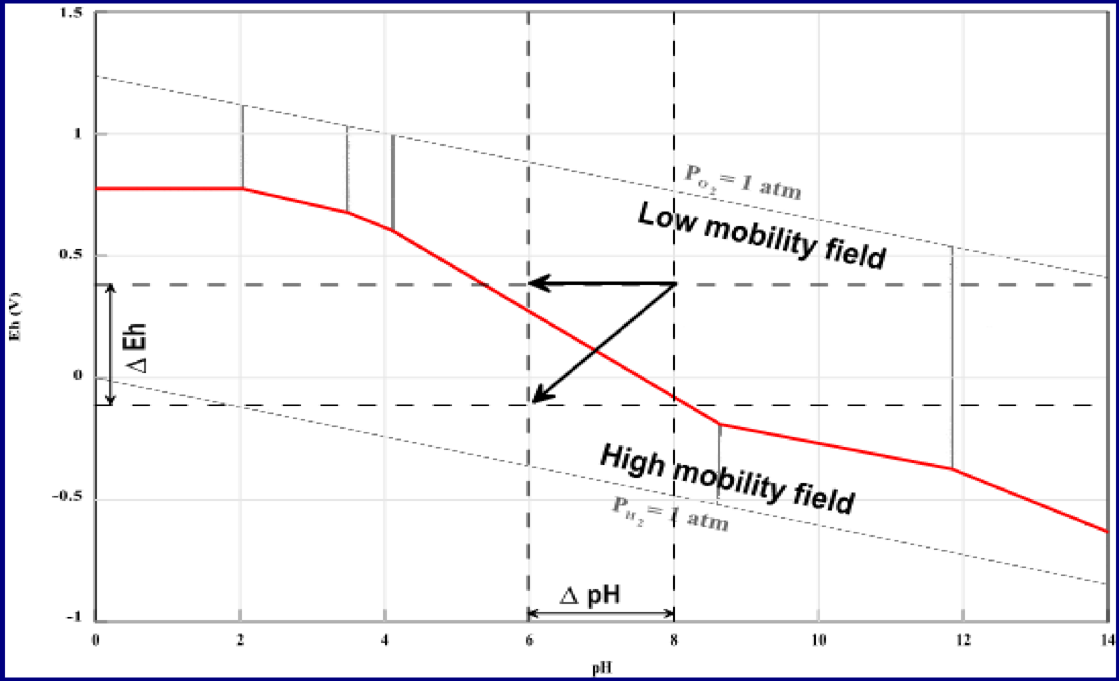
Leaching test in anaerobic conditions showed:

- Higher As concentrations in comparison with standard test
- High As correlation with Fe concentration in the leachate
- These results support the hypothesis that the source of As was the reduction of Fe oxides
- The mobility of arsenic appears also to be controlled by several soil sample parameters that regulate the reaction kinetic. In this study the main controlling parameter was the clay content

CONCLUSIONS

Conclusions

- In leaching tests the variation of Eh can lead to significant effects, instead usually only pH variation is considered
- All metal species that increase mobility at low Eh, should be tested also under anoxic conditions



- Partition coefficient under anoxic conditions can be 10-100 times smaller than in oxidizing conditions
- In groundwater modelling and in the risk analysis, smaller partition coefficients lead to worst case conditions

....THANKS for your attention....

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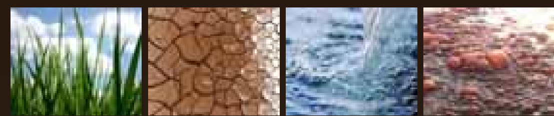

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Studio Associato di Geologia &
Società a Responsabilità limitata
Contrà del Pozzetto, 4
36100 – VICENZA
www.sinergeo.it
Tel. : +39.0444.321.168
Fax: +39.0444.543.641

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Bologna 2012
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iah aih

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