

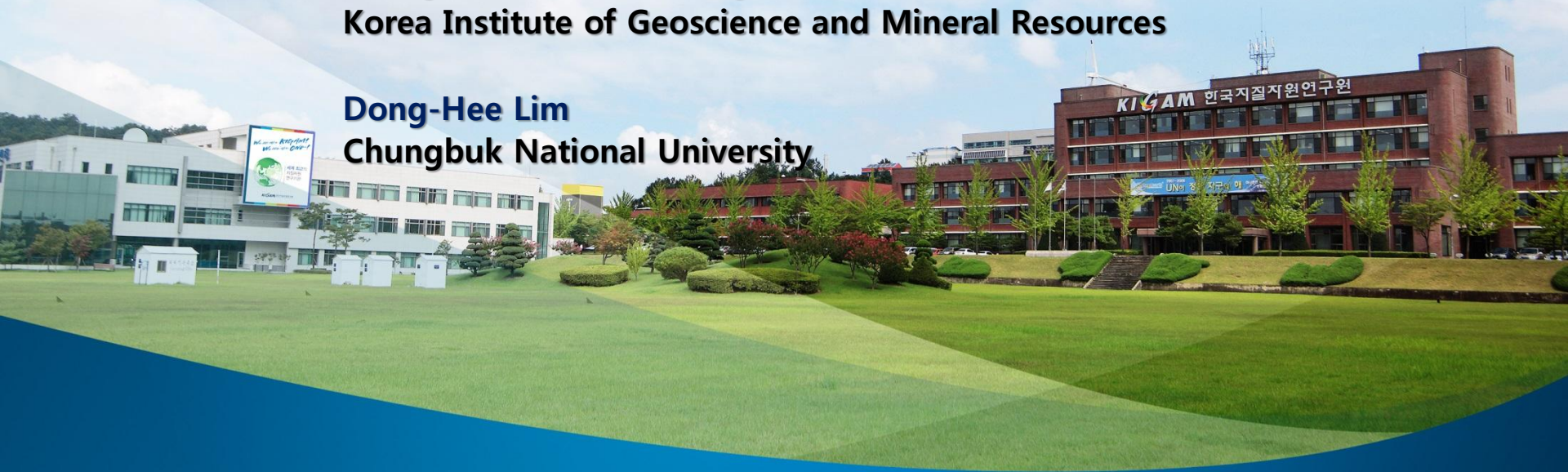
Interaction of Sb(III) under sulfide-rich reducing environment and brief introduction of landslide research in Korea

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Korea Institute of Geoscience and Mineral Resources

Dong-Hee Lim

Chungbuk National University



Contents

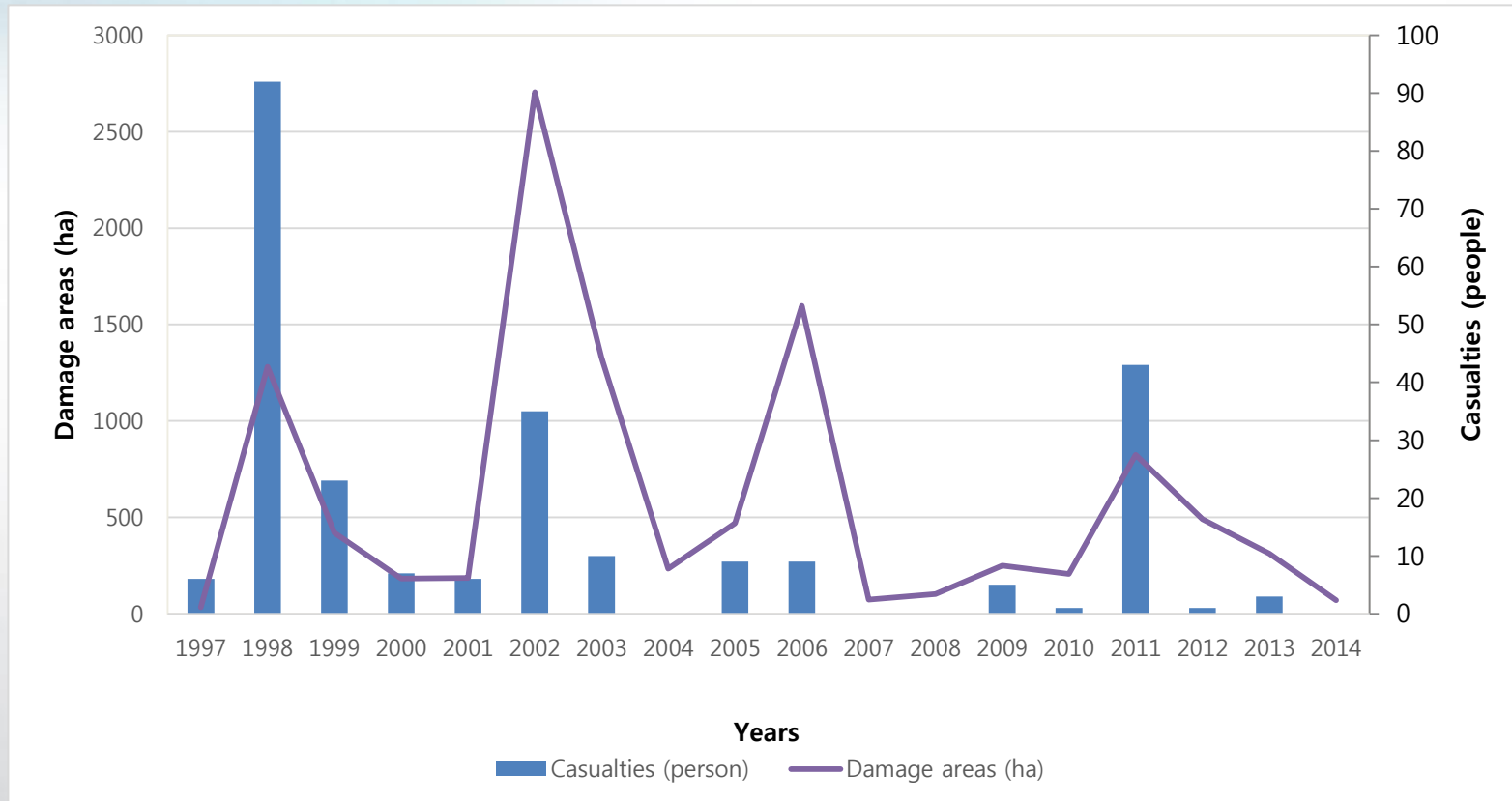
- ***Institution introduction***
 - ***Major landslide cases in Korea***
 - ***Landslide research in KIGAM***
- ***Sb(III) geochemistry compared with As(III)***
 - ***Brief introduction of As/Sb pollution***
 - ***Behavior of As/Sb in sulfide rich environment***
- ***Conclusion***

What we are doing at KIGAM?



Landslide cases in Korea

Damages induced by landslides



(Statistics Korea, 2016)

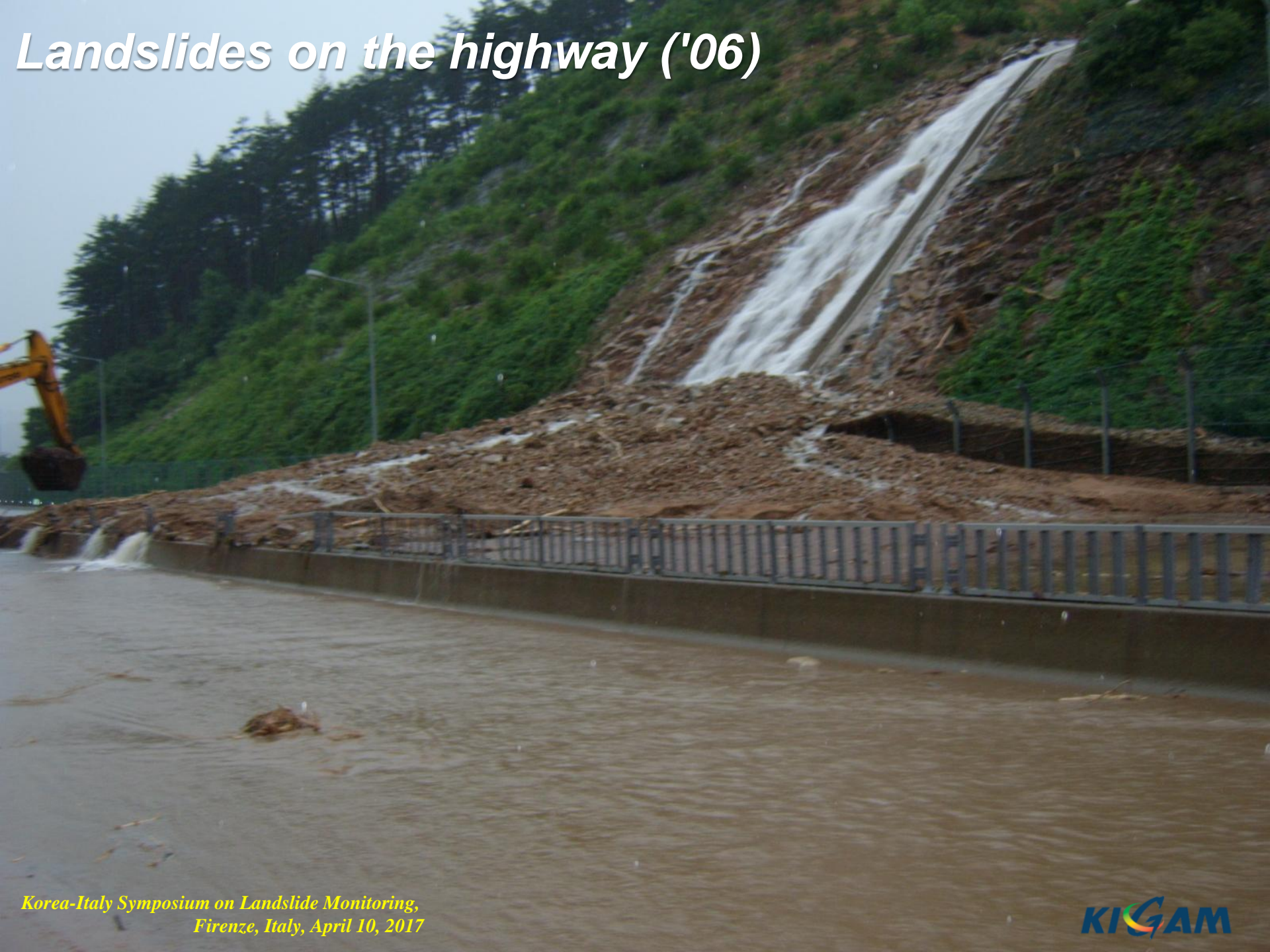
Landslides in Gangneung city ('02)



9 10:22 AM

KIGAM

Landslides on the highway ('06)



Destruction of a house by landslide('11)



Landslides at Mt. Woomyeon in Seoul ('11)



(Courtesy : Korea Forest Service)

*Korea-Italy Symposium on Landslide Monitoring,
Firenze, Italy, April 10, 2017*

Landslides at Mt. Woomyeon in Seoul ('11)



(Courtesy; KBS)

*Korea-Italy Symposium on Landslide Monitoring,
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Landslides at Mt. Woomyeon in Seoul ('11)



정치 광복회, 日 의원 울릉도 방문 반대 집회

(Courtesy; SBS)

*Korea-Italy Symposium on Landslide Monitoring,
Firenze, Italy, April 10, 2017*

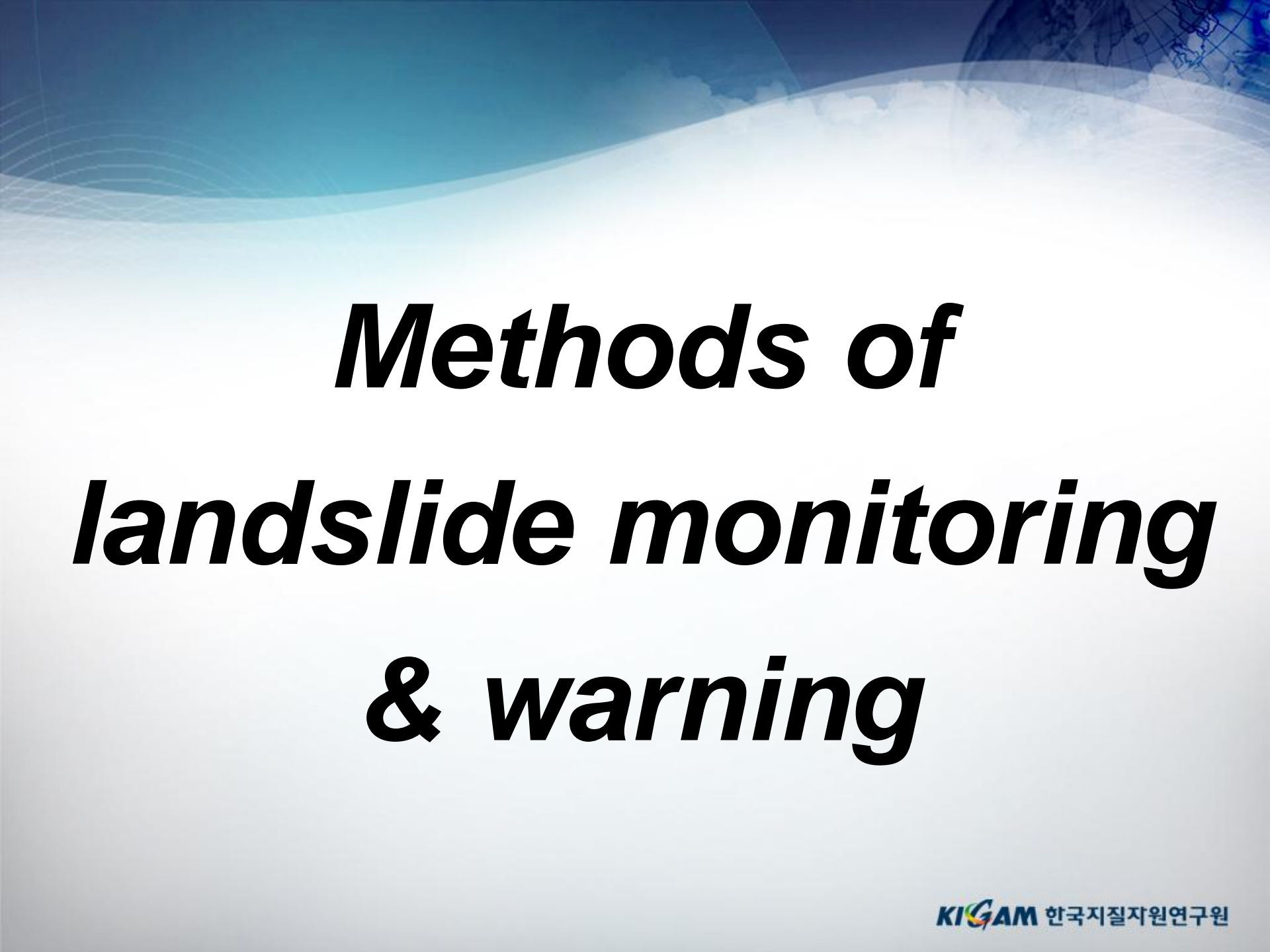
Damage by the landslide at Mt. Woomyeon ('11)



Courtesy ; E-daily news

Debris flows in a mountain valley('13)

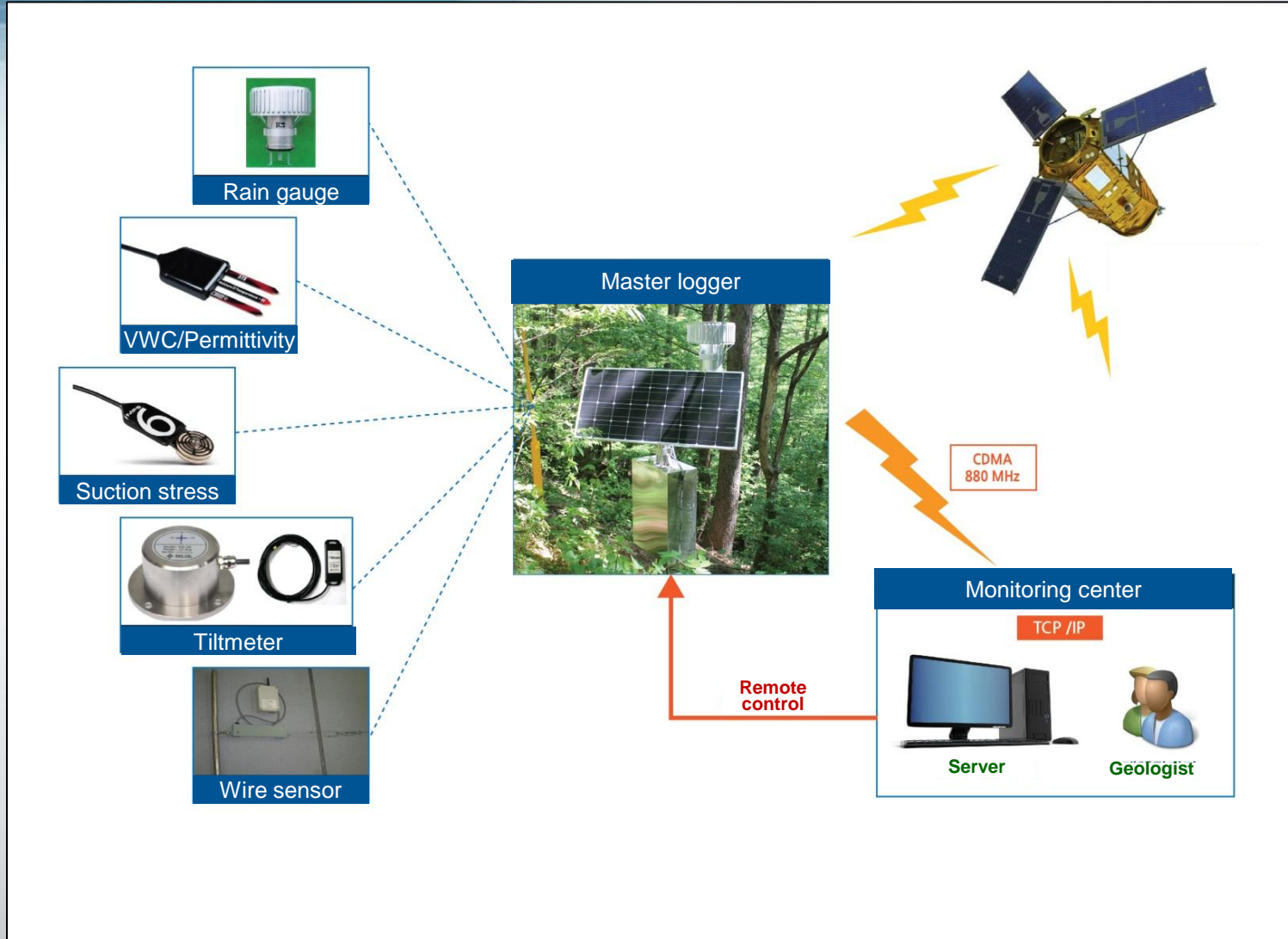


The background features a stylized globe in the upper right corner, partially obscured by a blue and white wavy pattern that resembles a landscape or a data visualization. The overall color scheme is light blue and white.

Methods of landslide monitoring & warning

Monitoring of soil property change

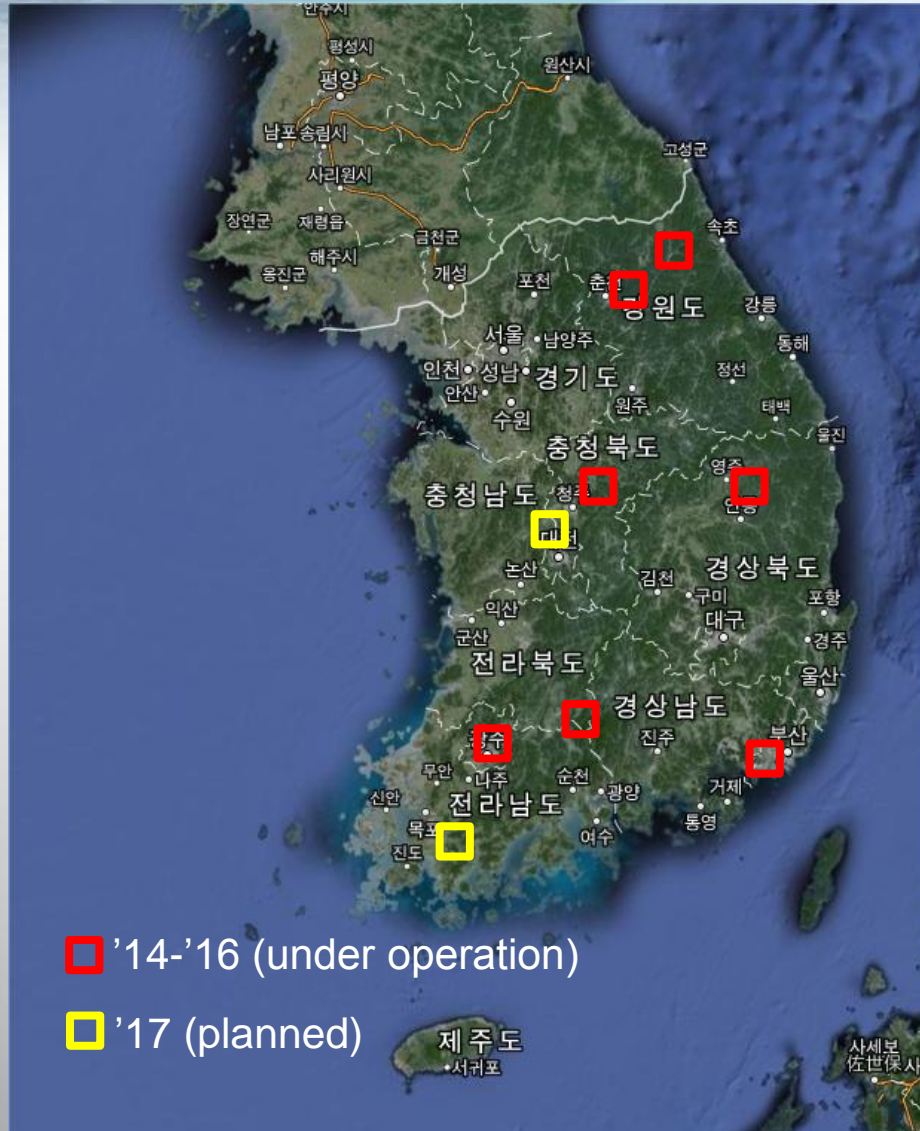
Components of landslide monitoring



Monitoring of soil property change

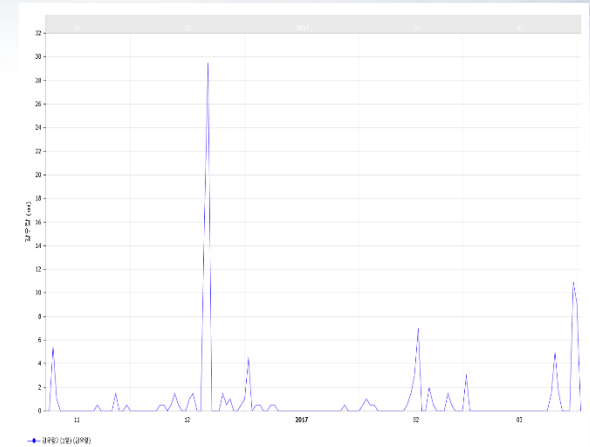
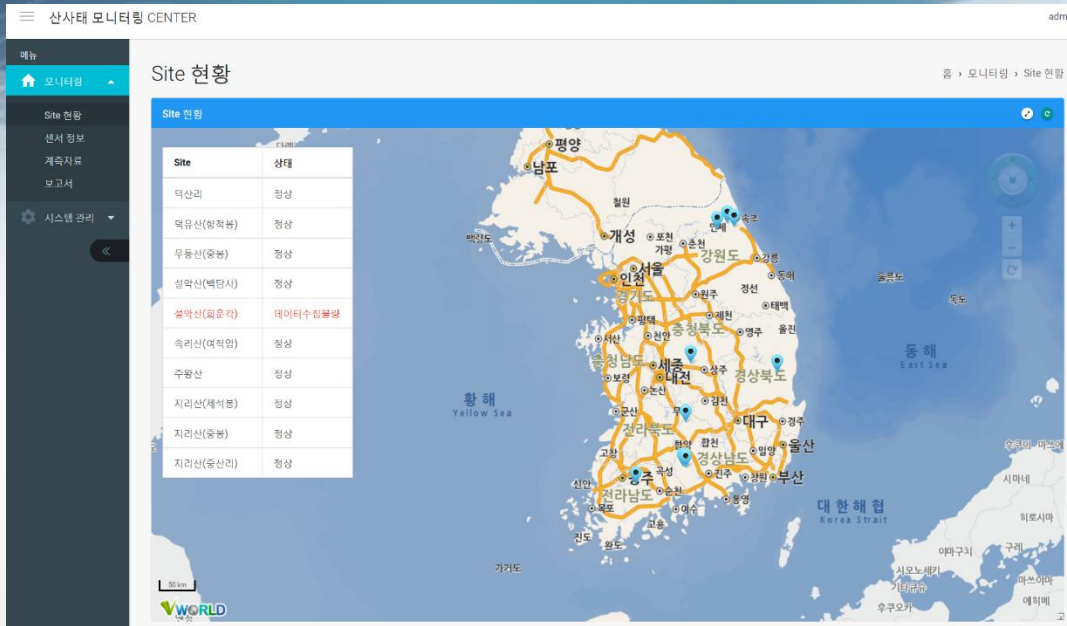
Locations of landslide field monitoring sites

- Monitoring systems at 11 sites in 6 National Parks and 1 metropolitan city (as of 2016)
- 2 additional sites to be installed in 2017
- Monitoring and analysis of data to decide warning threshold

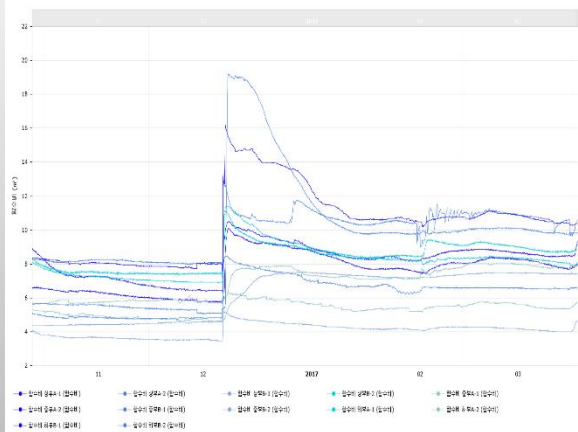


Monitoring of soil property change

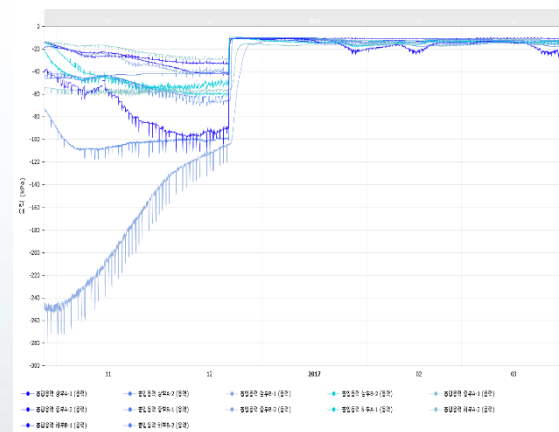
Korea-Italy Symposium on Landslide Monitoring,
Firenze, Italy, April 10, 2017



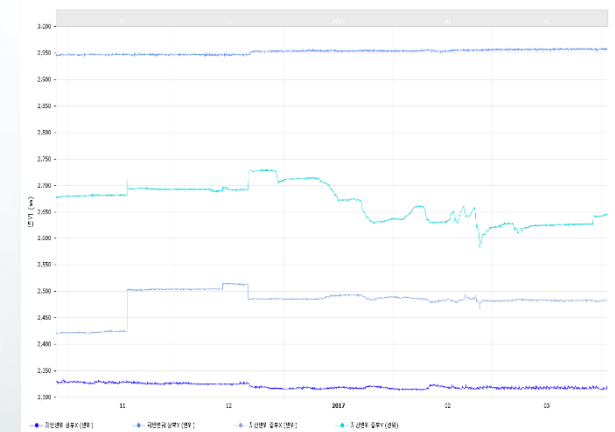
Rainfall



Wc / Dielectric Permittivity / Temp.



Suction stress



Slope displacement

Monitoring of soil property change

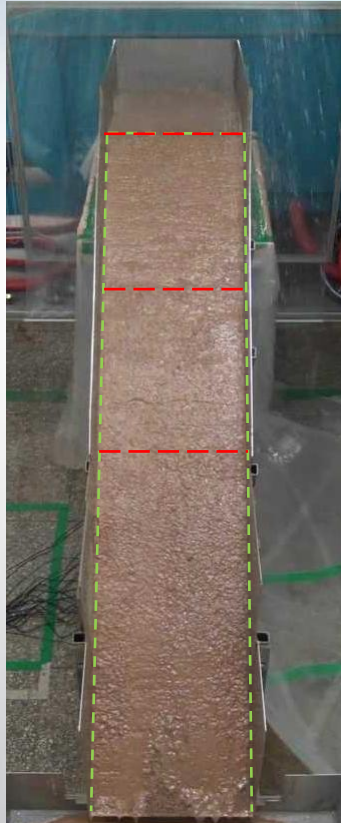
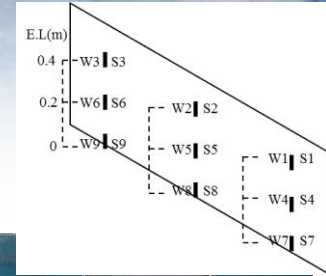
■ Gradient of the VWC change

- ✓ Warning threshold based on gradient of the VWC change by rainfall infiltration
- ✓ The gradient is decided by the rainfall infiltration velocity into the soil



Monitoring of soil property change

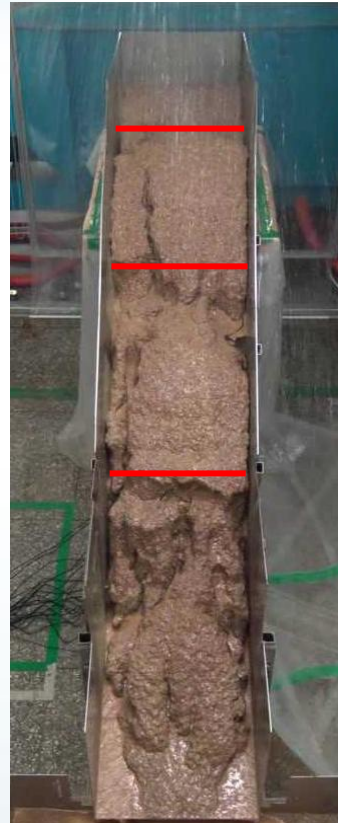
- Gradient of the VWC change



0 Sec



After 1,954 secs.



After 2,374 secs.



After 4,804 secs.



After 9,040 secs.

Contents

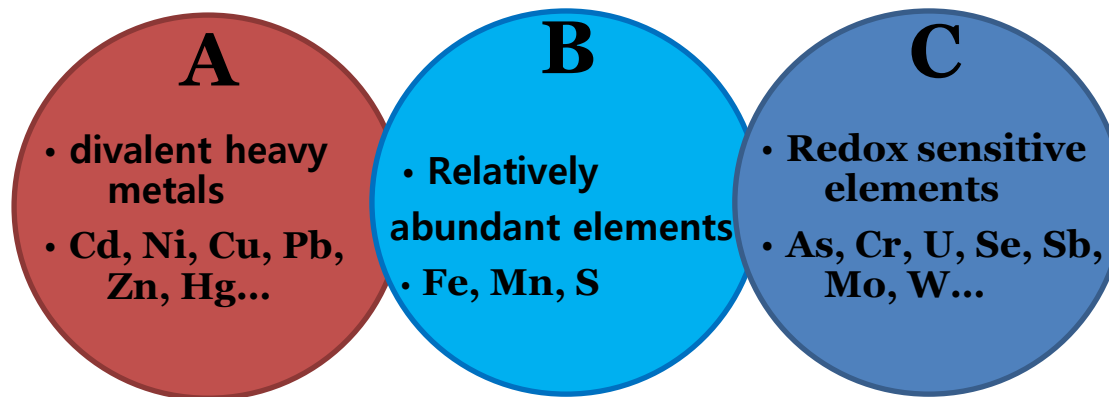
- *Institution introduction*
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Toxic trace elements

Heavy metals

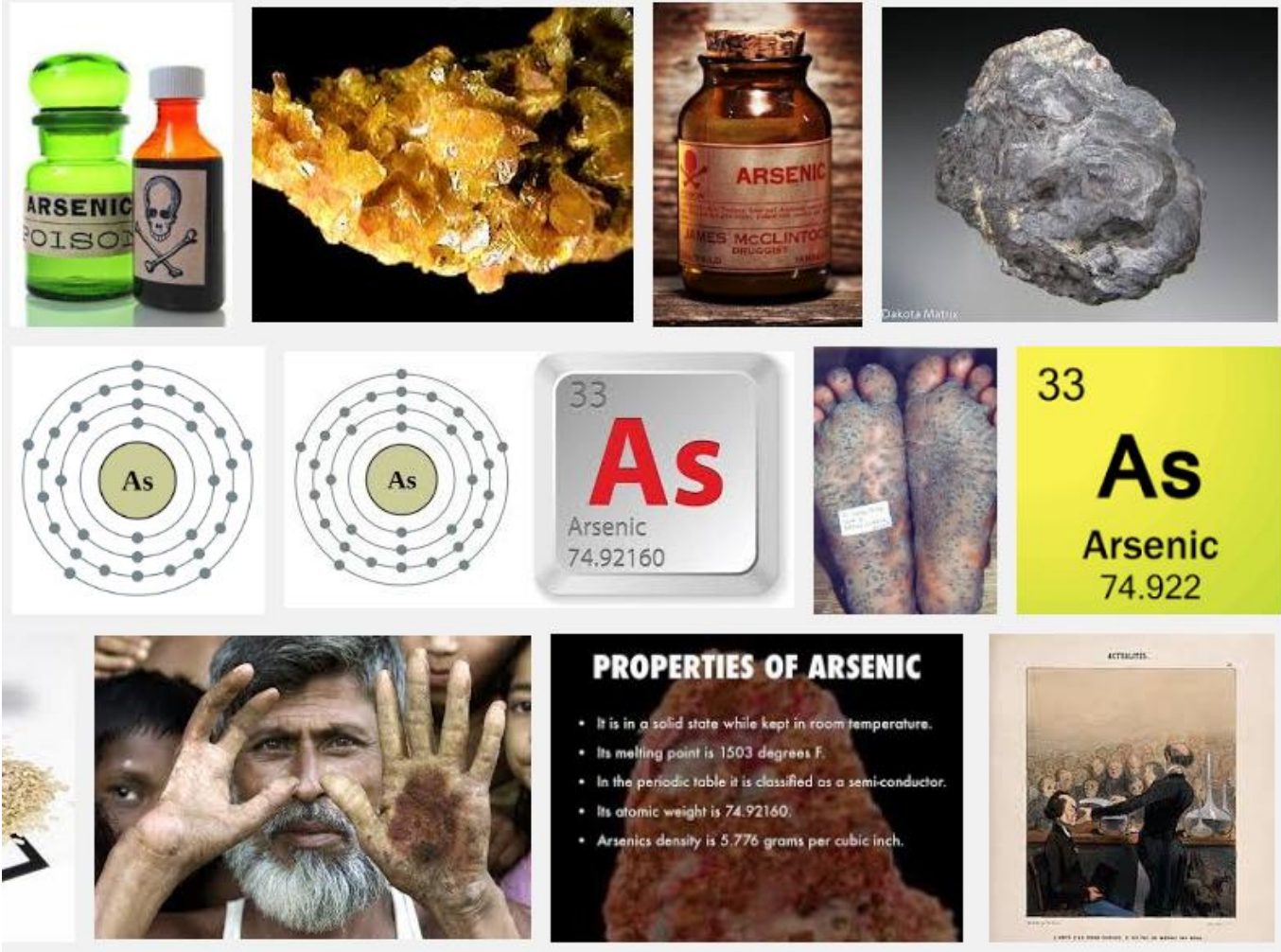
- Any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations
- Atomic density $> 4\sim 5 \text{ g/cm}^3$
- eg) Cd, Cr, Ni, Cu, Pb, Mn, Co, Hg, Zn, U, Mo, V, Sb, ...

<Target elements in geochemistry>



- Group C elements: Redox sensitive and existing in various forms
- Element of interest: As, Sb

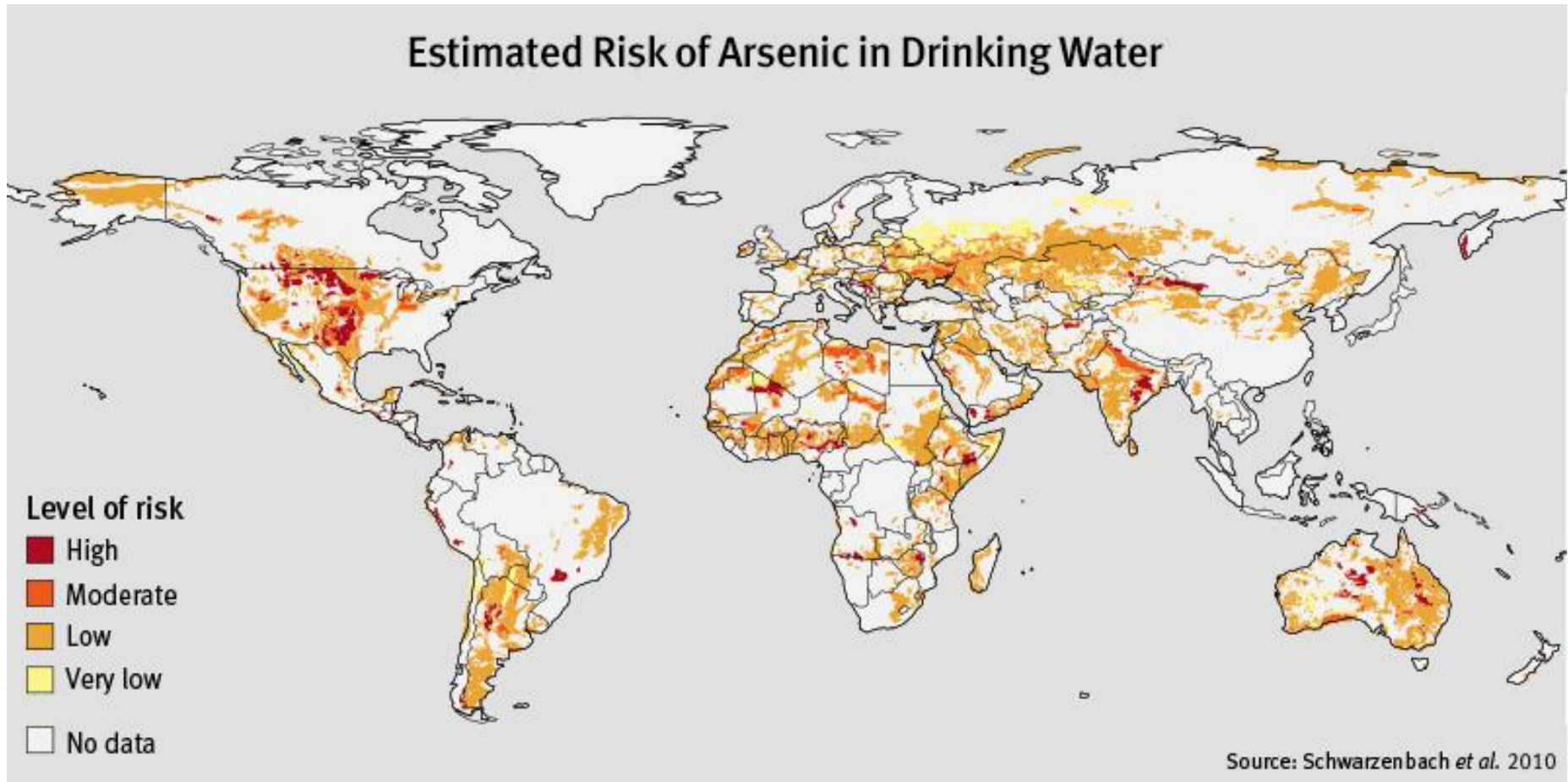
What is arsenic?



The collage consists of several panels:

- Top Left:** Two glass bottles. The one on the left is green with a label that says "ARSENIC POISON" and a skull and crossbones symbol. The one on the right is orange with a similar skull and crossbones symbol.
- Top Middle-Left:** A close-up photograph of a bright yellow, crystalline mineral sample.
- Top Middle-Right:** A brown glass bottle with a label that says "ARSENIC" and "JAMES MCCLINTOCK DRUGGIST".
- Top Far Right:** A large, dark, metallic-looking mineral specimen.
- Middle Left:** Two Bohr-style atomic models of an arsenic atom (As), showing a central nucleus and several concentric electron shells.
- Middle Middle-Left:** A periodic table entry for Arsenic (As) with atomic number 33 and atomic weight 74.92160.
- Middle Middle-Right:** A photograph of a person's feet showing characteristic blue-gray skin discoloration (arsenicosis).
- Middle Far Right:** A yellow background with the text "33 As Arsenic 74.922".
- Bottom Left:** A photograph of a man with a grey beard and mustache, with his hands raised to his face. His hands are heavily stained with a dark, reddish-brown substance, likely arsenic.
- Bottom Middle:** A black box with the title "PROPERTIES OF ARSENIC" and a list of properties:
 - It is in a solid state while kept in room temperature.
 - Its melting point is 1503 degrees F.
 - In the periodic table it is classified as a semi-conductor.
 - Its atomic weight is 74.92160.
 - Arsenics density is 5.776 grams per cubic inch.
- Bottom Right:** A historical illustration of a laboratory or pharmacy setting, showing a person in a white coat interacting with another person.

Arsenic contamination around the world



Maximum Contaminant Level for drinking water = 10 ppb (microgram/liter)

Population in risk of arsenic poisoning (India and West Bengal)

Country	Number affected
Taiwan	20 000
Inner Mongolia	50 000
Obuasi Ghana	Unknown
Cordoba Argentina	10 000
Antofagasta Chile	20 000
Lagunera Mexico	20 000
Cornwall Britain	Effect unknown
W. Bengal, India	38, 000 000
Bangladesh	50, 000 000



산화환원 환경조성에 의한 지화학적 거동특성 평가

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																																																																				
1 H Hydrogen 1.00794	<table border="1"> <tr> <td>C Solid</td> <td colspan="10">Metals</td> <td colspan="6">Nonmetals</td> </tr> <tr> <td>Hg Liquid</td> <td>Alkali metals</td> <td>Alkaline earth metals</td> <td>Lanthanoids</td> <td>Actinoids</td> <td>Transition metals</td> <td>Poor metals</td> <td>Other nonmetals</td> <td colspan="3">Noble gases</td> <td colspan="6"></td> </tr> <tr> <td>H Gas</td> <td colspan="16"></td> </tr> <tr> <td>Rf Unknown</td> <td colspan="16"></td> </tr> </table>																C Solid	Metals										Nonmetals						Hg Liquid	Alkali metals	Alkaline earth metals	Lanthanoids	Actinoids	Transition metals	Poor metals	Other nonmetals	Noble gases									H Gas																	Rf Unknown																	2 He Helium 4.002602
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3 Li Lithium 6.941	4 Be Beryllium 9.012182																	5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797																																																														
11 Na Sodium 22.98976928	12 Mg Magnesium 24.3050																	13 Al Aluminum 26.9815386	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948																																																														
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955912	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938045	26 Fe Iron 55.845	27 Co Cobalt 58.933195	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798																																																																				
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.96	43 Tc Technetium (97.9072)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293																																																																				
55 Cs Caesium 132.9054519	56 Ba Barium 137.327	57-71		72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (208.9824)	85 At Astatine (208.9871)	86 Rn Radon (222.0176)																																																																			
87 Fr Francium (223)	88 Ra Radium (226)	89-103		104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (271)	111 Rg Roentgenium (272)	112 Uub Ununbium (285)	113 Uut Ununtrium (284)	114 Uuq Ununquadium (289)	115 Uup Ununpentium (288)	116 Uuh Ununhexium (292)	117 Uus Ununseptium	118 Uuo Ununoctium (294)																																																																			

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

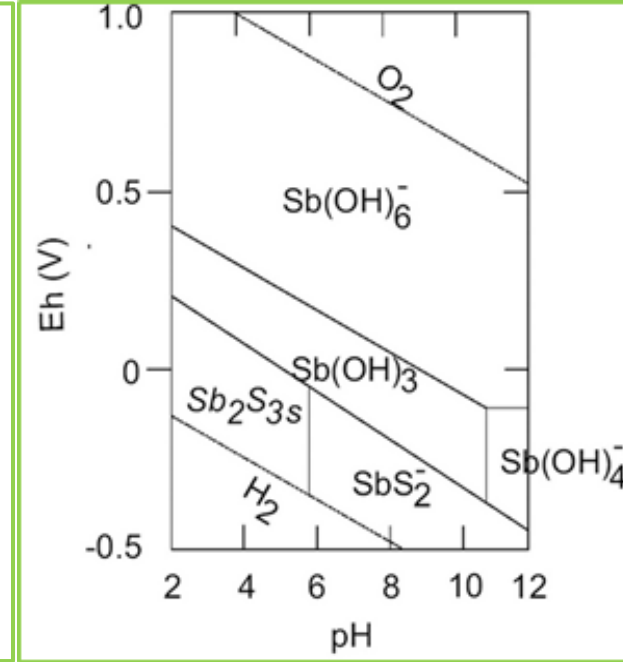
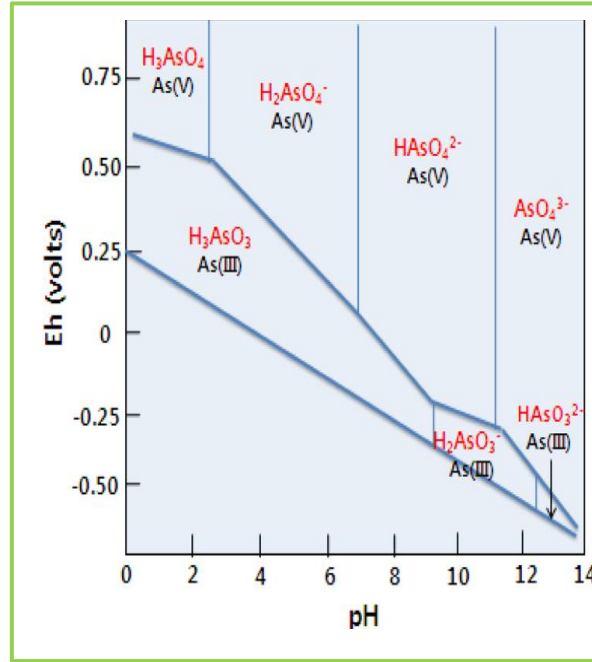
Periodic Table Design and Interface Copyright © 1997 Michael Dayah. <http://www.ptable.com/> Last updated: May 27, 2008



57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93032	68 Er Erbium 167.259	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.9668
89 Ac Actinium (227)	90 Th Thorium 232.03806	91 Pa Protactinium 231.03588	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

Geochemical properties of Sb

- Oxidation state: $Sb^{-3} \sim Sb^{+5}$
- Oxidizing condition: +5
- Reducing condition: +3
- Aqueous oxyanion
- Similar to As in chemical properties



Sb: oral ingestion

Gastrointestinal mucous membrane irritation, vomiting, Abdominal pain, diarrhea, cardiac toxicity

Sb: inhalation

Myocardial damage, liver damage, poor reproductive function (miscarriage, premature birth, etc.)

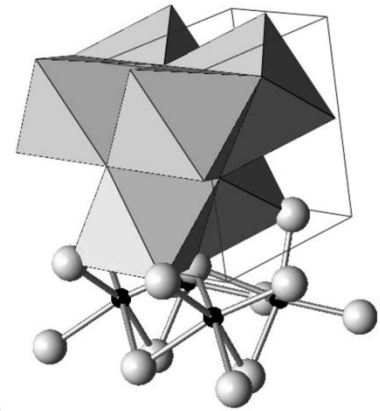
Sb: lethal dose

**child (300 mg),
adult (1,200 mg)**

unit: $\mu\text{g/L}$	USA	canada	UK	German y	France	Australia	Japan	WHO
먹는 물 수질기준	6	6	5	5	10	3	2	5

Iron sulfide for Arsenic(III) removal

- Sulfide minerals can be used to control arsenic concentration.
 - **Pyrite** : inner-sphere adsorption (Zouboulis et al.,1993)
 - **Mackinawite** : outer-sphere arsenic surface complex and coprecipitation of poorly crystalline arsenic sulfide (Farquhar et al., 2002)
 - **Troilite and pyrite** : a mononuclear, bidentate surface complex, arsenopyrite-like surface precipitation (Bostick and Fendorf, 2003)
 - **Disordered mackinawite** : outer-sphere complexes (Wolthers et al., 2005)
 - **Mackinawite** : realgar-like precipitation and adsorption (Gallegos et al., 2008)
- Mackinawite (FeS) for As(III) sequestrator
 - **First mineral product when Fe^{2+} and S^{2-} react**
 - **S^{2-} : Sulfide has a strong affinity for heavy metals**
 - **Commonly found mineral**
 - **Nano size \rightarrow High surface area ($\sim 300\text{m}^2/\text{g}$) \rightarrow High reactiv**



Need to control size of the FeS \rightarrow FeS-coated sand

Objectives

Sb-FeS

- **Understand geochemical behavior of Sb with FeS**
- Batch and spectroscopic study
- Compare its results with those with As-FeS

Sb-column

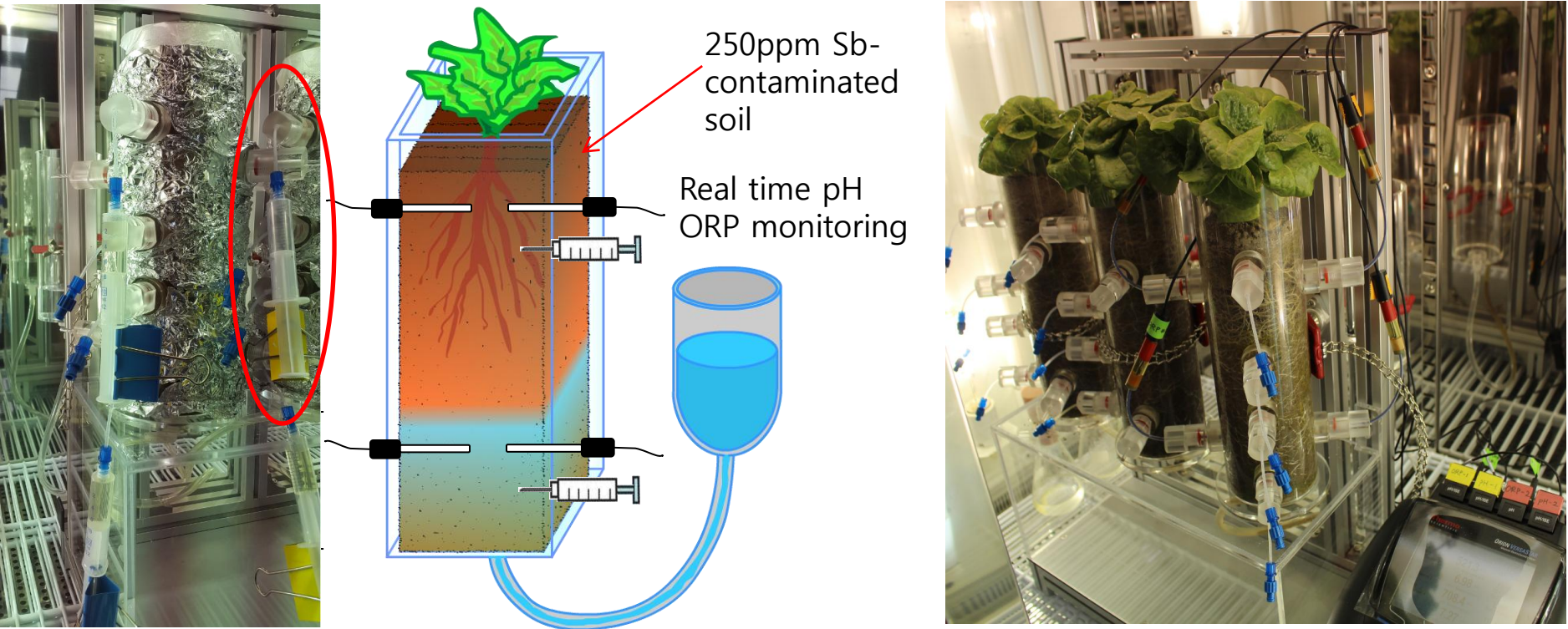
- **Simulate the Sb reaction in contaminated soil column**
- Geochemical reaction in various redox environment
- Observe the change of oxidation state of Sb

Expected results

- The geochemical reaction mechanisms of Sb under S-rich environment
- How to utilize well-investigated As chemistry to understand that of Sb

Rhizosphere/vadose zone column test

Column study simulating plant rhizosphere and saturated zone



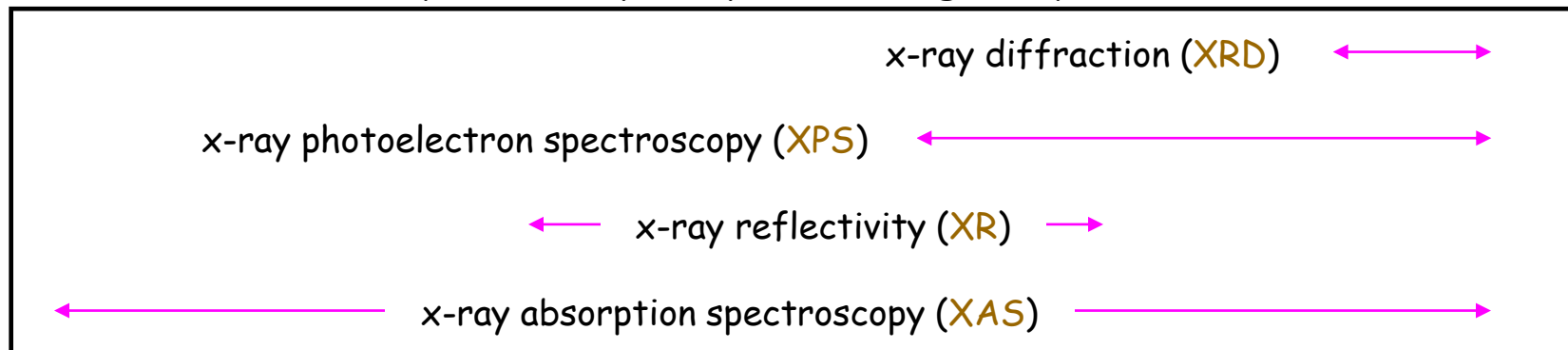
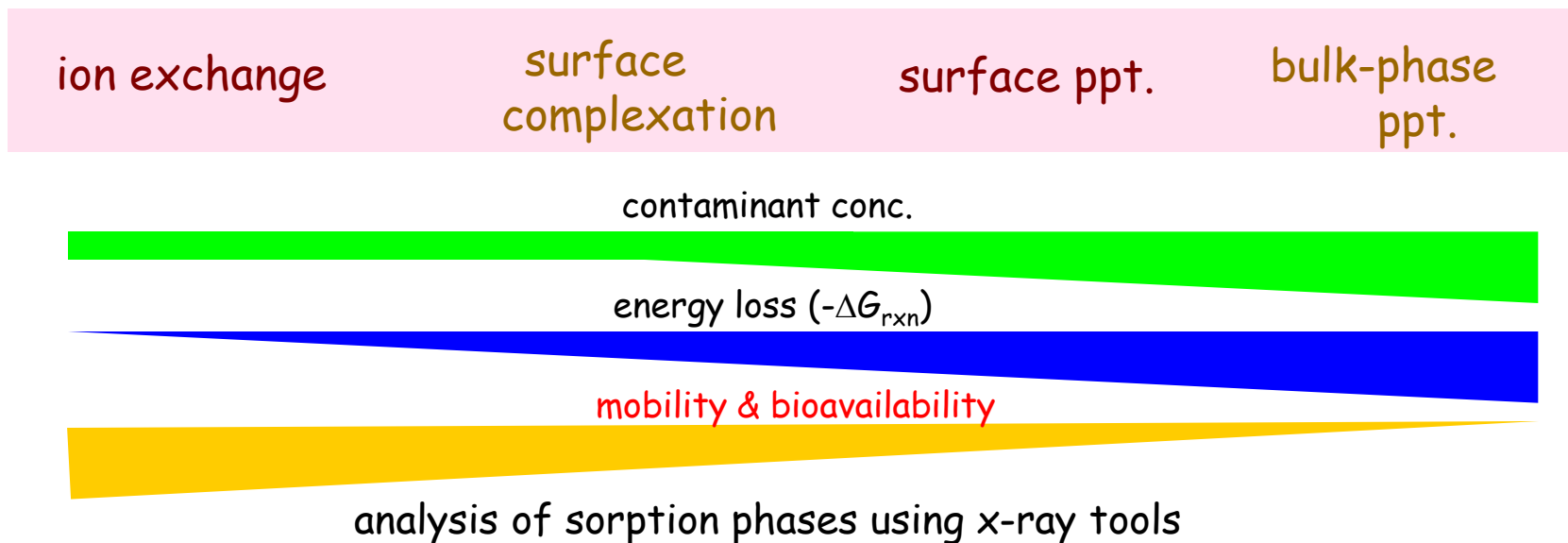
Objective of column study

1. Simulating and Observing plant-soil-water interaction
2. Effect of redox condition on Sb behavior
3. Solid phase Sb speciation using a synchrotron X-ray absorption spectroscopy

Spectroscopic methods as an useful tool

Key note: which technique should be employed?

Minerals can "sorb" ("sequester," "immobilize") inorganics:



Worldwide Synchrotron Facilities



Synchrotron facilities worldwide

[http://www.veqter.co.uk/residual-stress measurement/synchrotron-diffraction](http://www.veqter.co.uk/residual-stress%20measurement/synchrotron-diffraction)

XANES

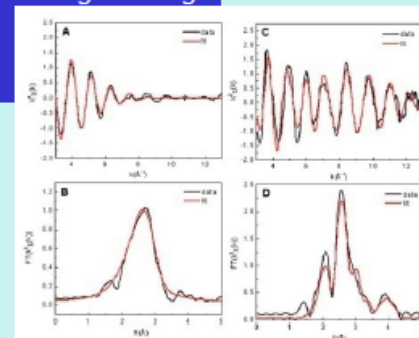
(X-ray Absorption Near Edge Structure)

- Electronic structure
- Oxidation state
- Bond covalency
- Site symmetry such as T_d , D_{4h} and O_h etc.
- Spin state (low spin or high spin)
- $10 D_q$ etc..

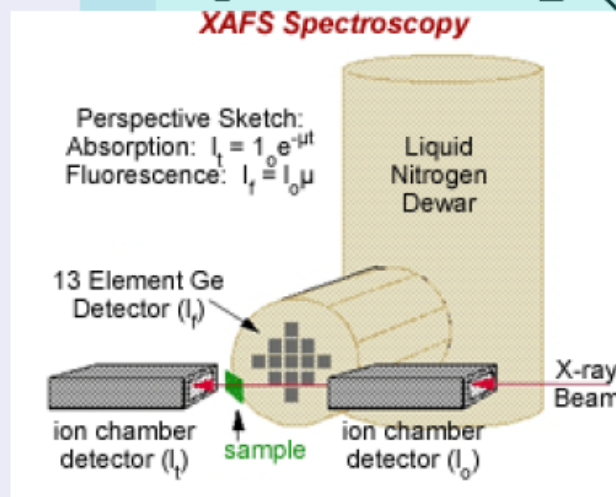
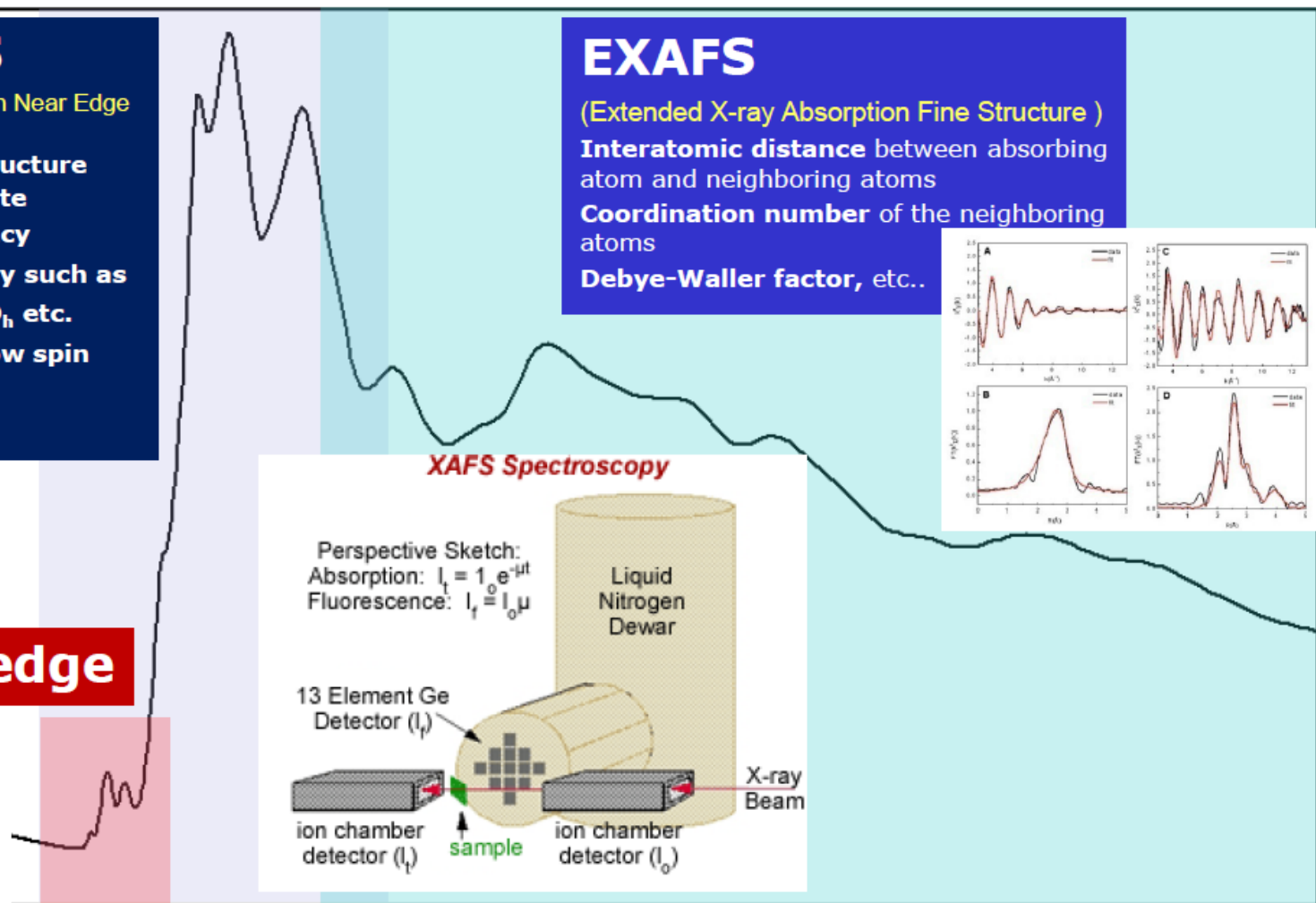
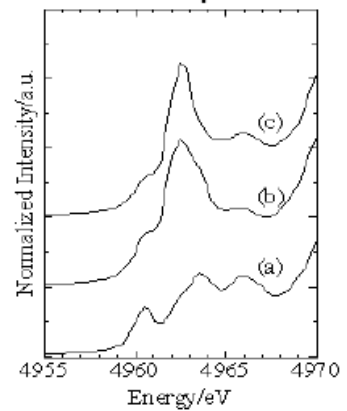
EXAFS

(Extended X-ray Absorption Fine Structure)

- Interatomic distance between absorbing atom and neighboring atoms
- Coordination number of the neighboring atoms
- Debye-Waller factor, etc..

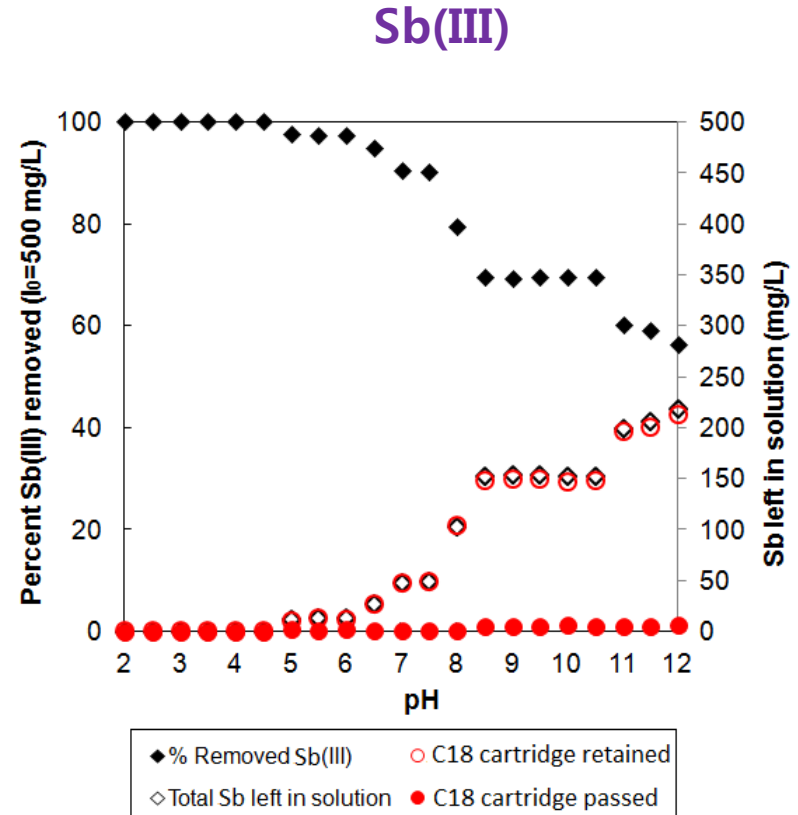
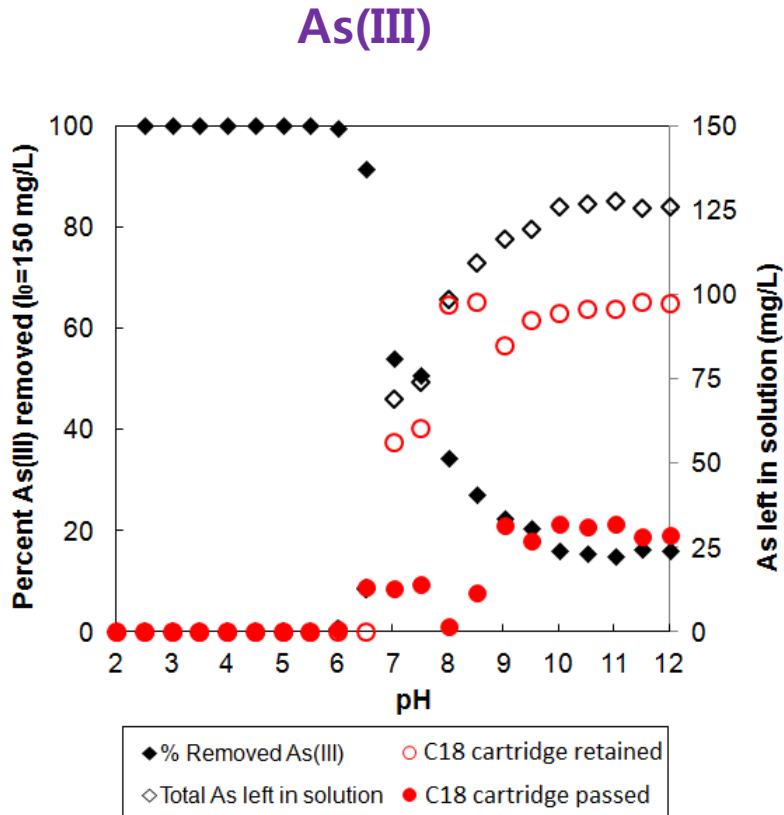


Pre-edge



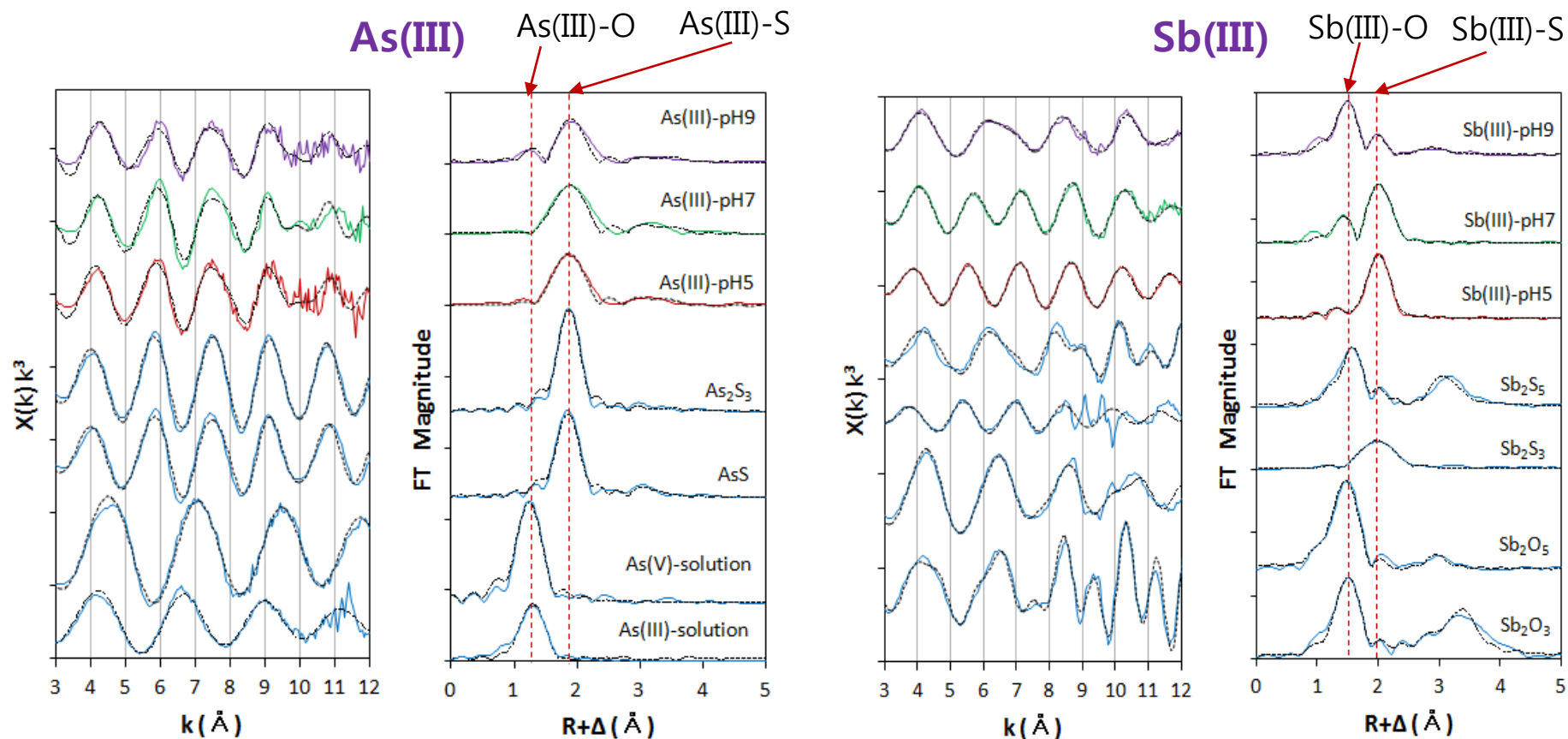
Energy (eV)

As/Sb removal under varying pH conditions



As(III) and Sb(III) removal efficiency under pH 2 to 12 conditions with the amount of dissolved As or Sb left in solution and its speciation ($I_0 = 150$ mg/L for As(III) and 500 mg/L for Sb(III)). Aqueous speciation was conducted using a Bond Elut C18 cartridge.

EXAFS results of FeS reacted with As/Sb

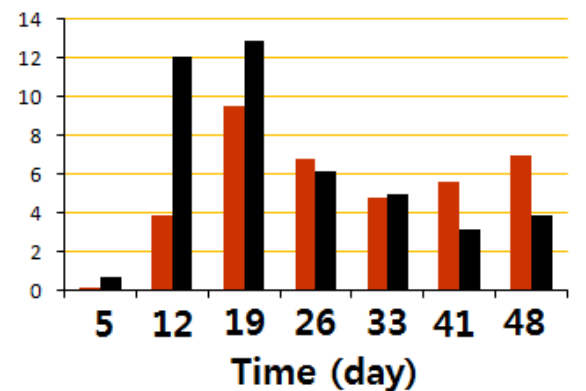
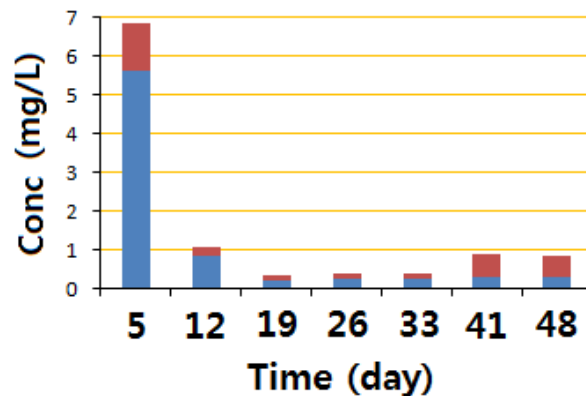
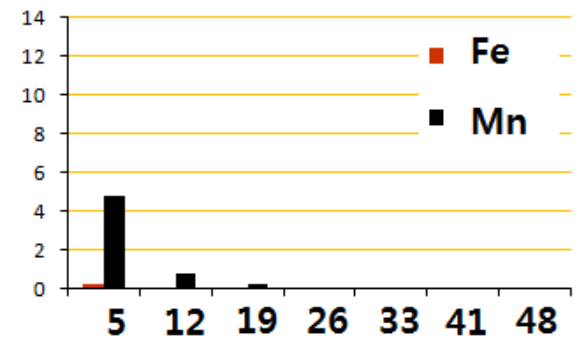
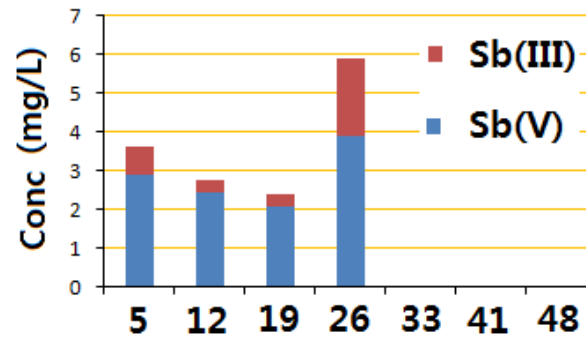


As-FeS reaction		Sb-FeS reaction	
pH5	As ₂ S ₃ ppt	pH5	Sb ₂ S ₃ ppt
pH7	As ₂ S ₃ ppt	pH7	Sb ₂ S ₃ ppt
pH9	Thioarsenite adsorption	pH9	Thioantimonite adsorption

Sb(V)-cont. soil column test results(I)



1. After the initial weakly-bound Sb outflow, the Sb efflux of the rhizosphere zone is more prominent
2. In the anaerobic zone, the reductive dissolution of iron in natural soil was observed
3. The ratio of Sb (III) / Sb (V) increases as the reaction time increases in anaerobic zone. The role of Sb reduction bacteria?



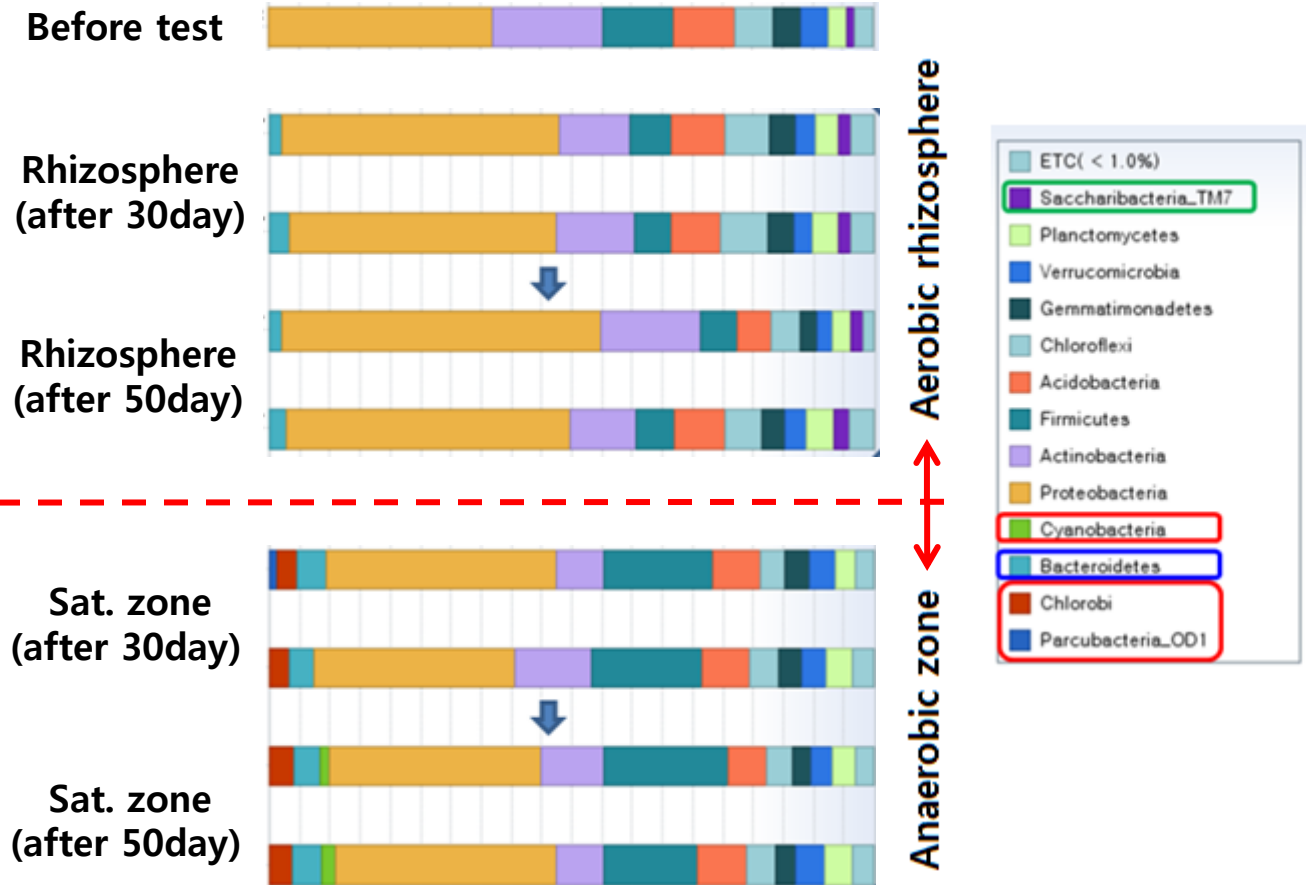
Aerobic rhizosphere

Anaerobic zone

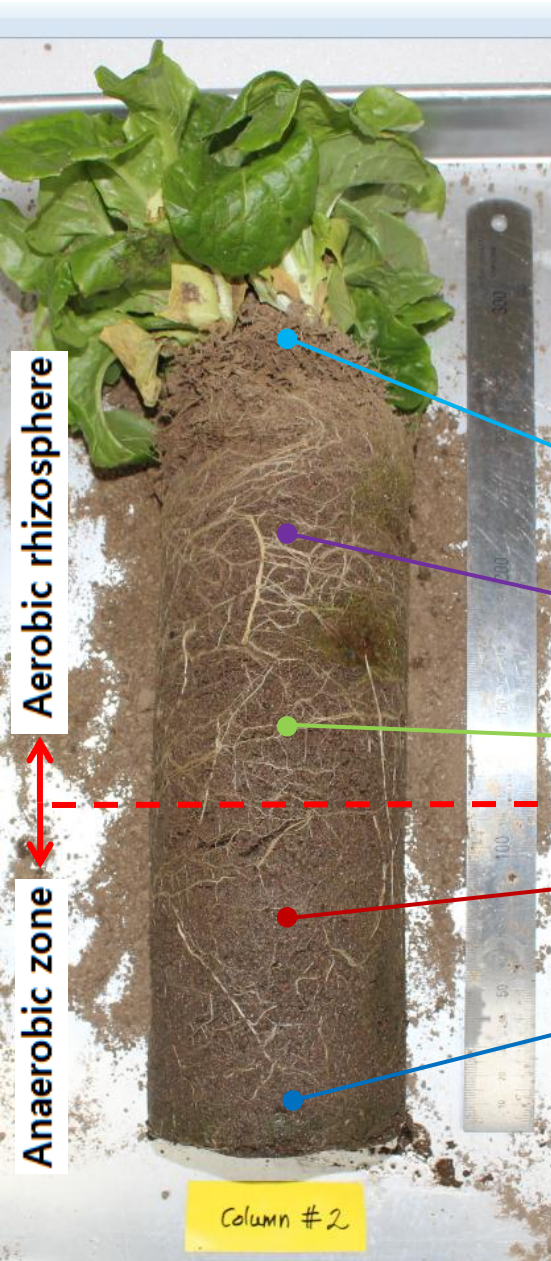
Sb(V)-cont. soil column test results(III)



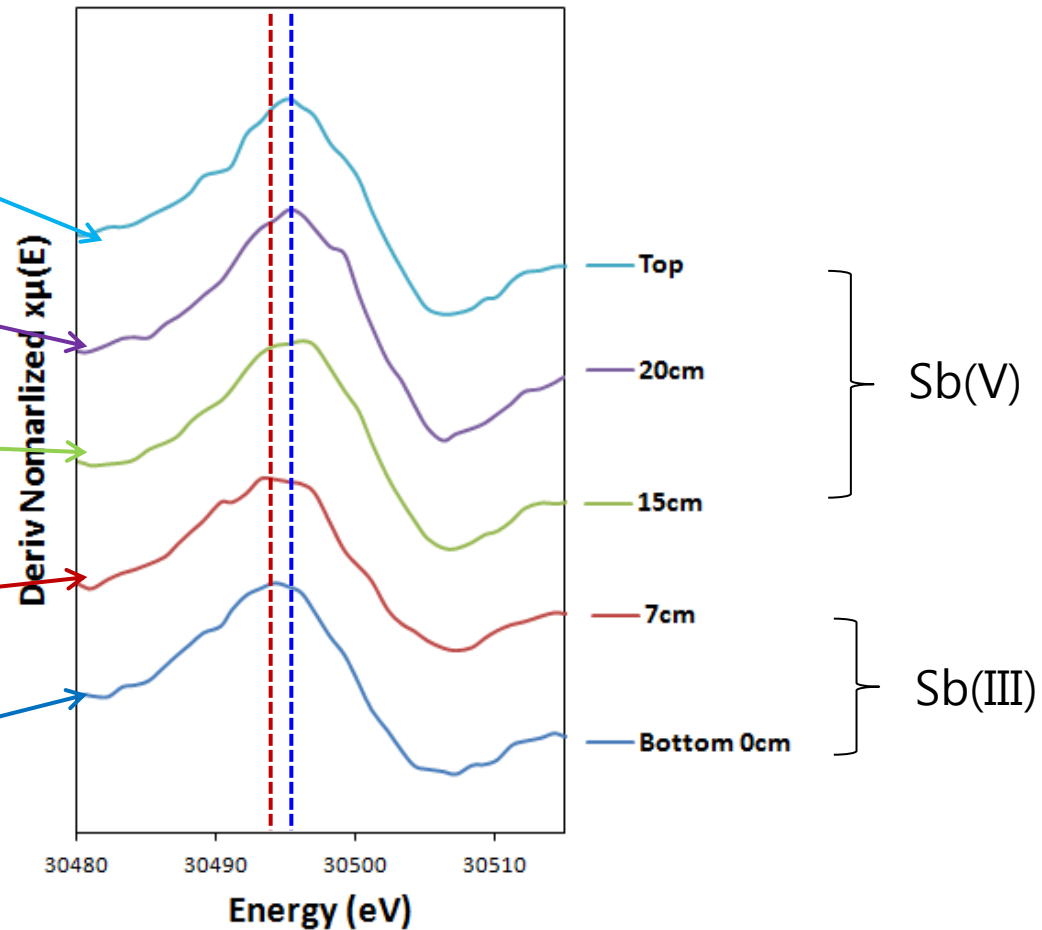
1. Distribution of microbial communities in the plant rhizosphere and column lower saturation zone
2. The redox state of antimony may be changed by microorganisms.



Sb(V)-cont. soil column test results(IV)



1. Sb K-edge XANES measured on soil samples from the upper part of the column and the lower column saturation zone
2. Sb is more reduced in anaerobic soil than in upper soil. → Reduction of Sb (V) to Sb (III)



Conclusion

- Interaction of Sb(III) with mackinawite was tested under acidic and basic pH conditions and the reaction mechanisms of Sb(III)-FeS and As(III)-FeS were compared.
- In both Sb(III)- and As(III)-FeS systems, pH was revealed as an important controlling parameter.
- Under acidic conditions the dominant reaction process was precipitation of as sulfide minerals.
- Surface complexation was the dominant reaction process under basic pH conditions.
- The redox condition of soil environment seems to be an important control of Sb redox states