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

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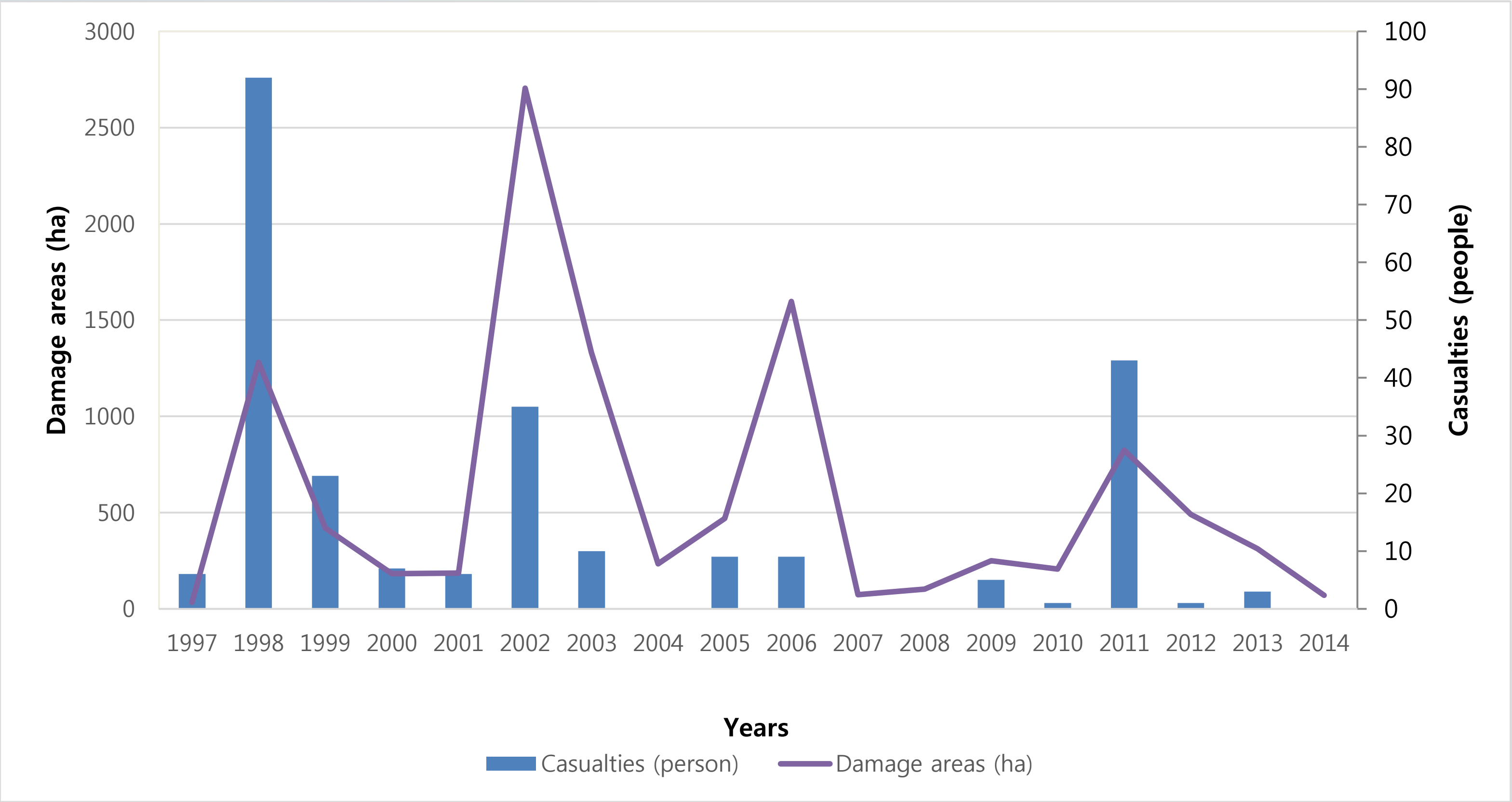
- *Conclusion*

What we are doing at KIGAM?

Landslide cases in Korea

Damages induced by landslides



(Statistics Korea, 2016)

Landslides in Gangneung city ('02)

Landslides on the highway ('06)

Destruction of a house by landslide('11)

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Landslides at Mt. Woomyeon in Seoul ('11)

(Courtesy : Korea Forest Service)

Landslides at Mt. Woomyeon in Seoul ('11)

(Courtesy; KBS)

Landslides at Mt. Woomyeon in Seoul ('11)

(Courtesy; SBS)

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

Courtesy ; E-daily news

Debris flows in a mountain valley('13)

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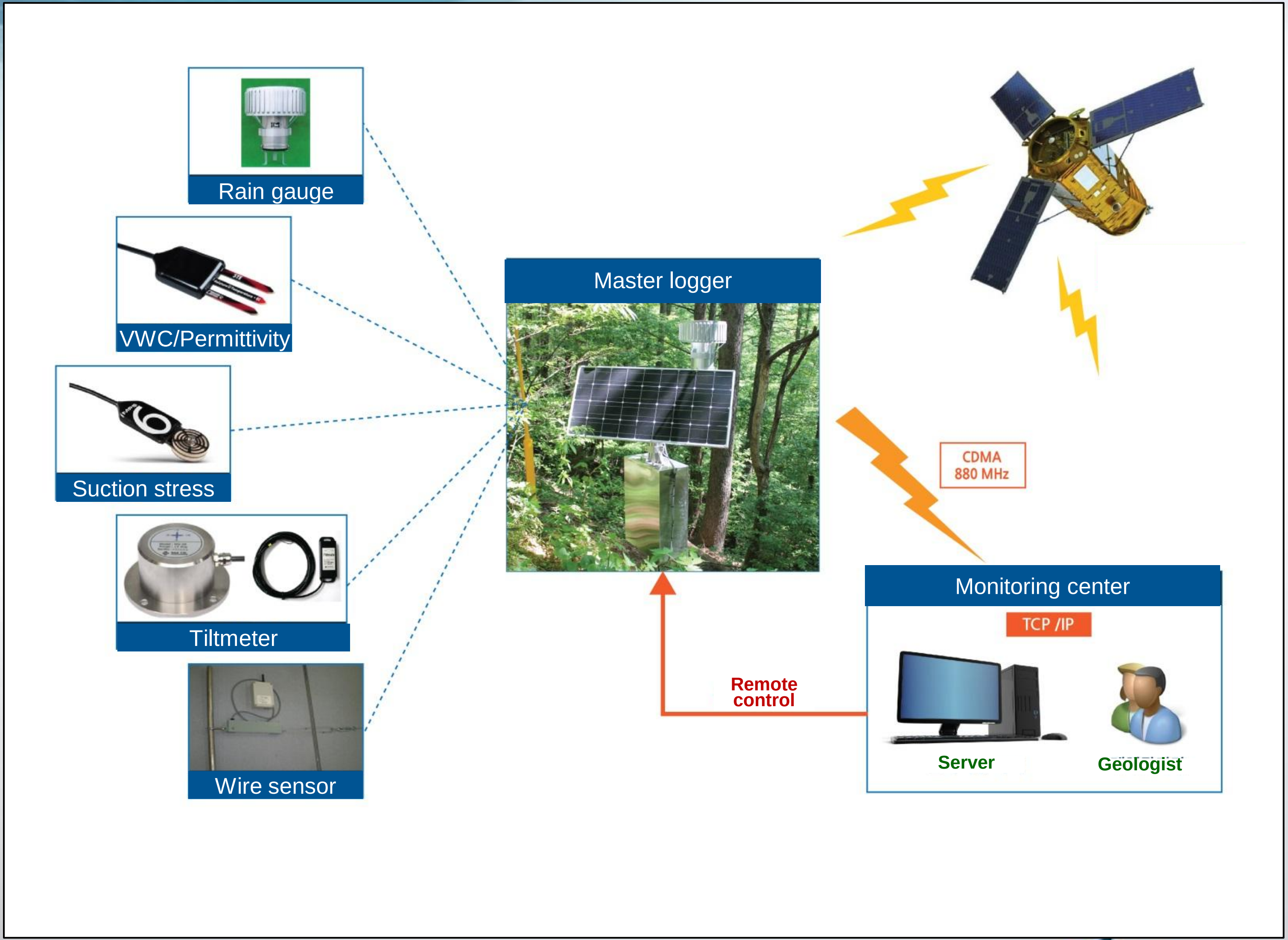
Methods of landslide monitoring & warning

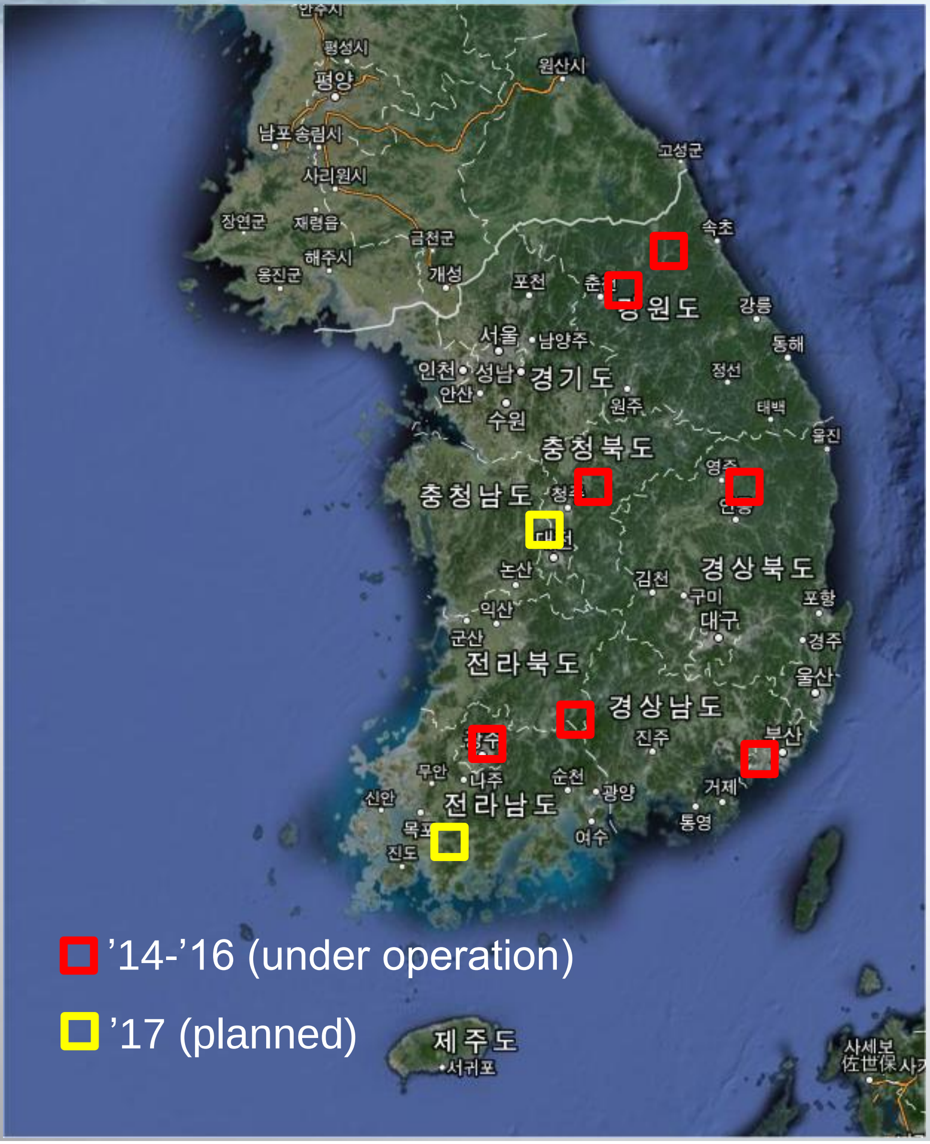
Monitoring of soil property change

- **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

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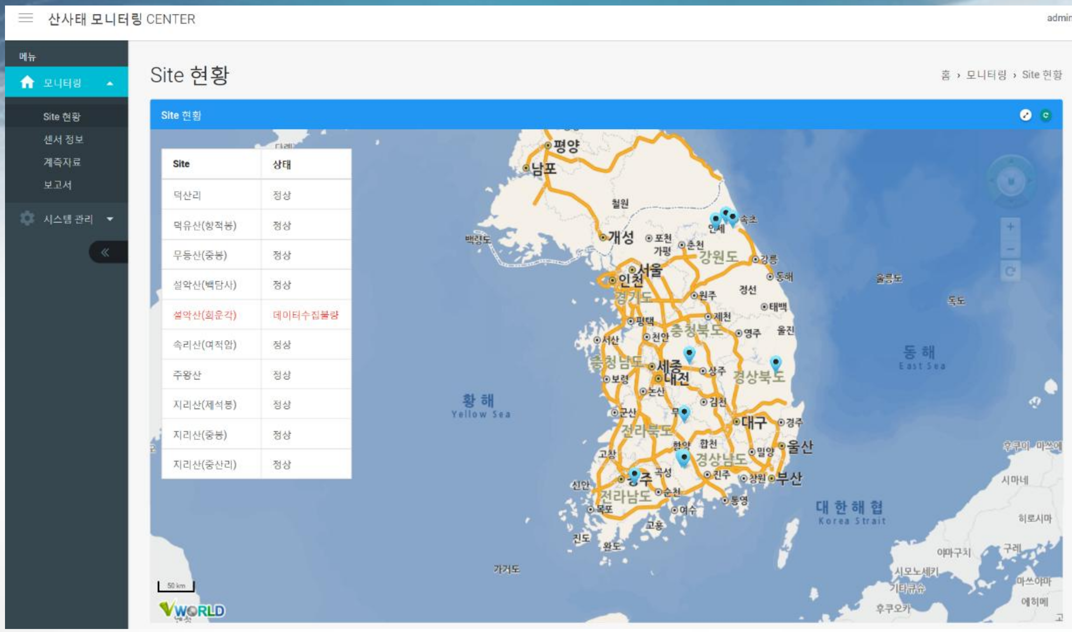
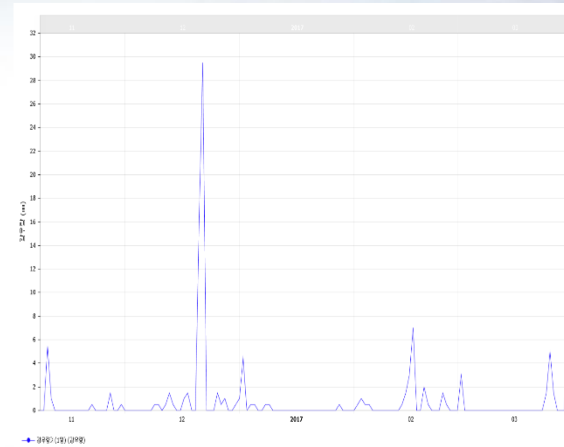
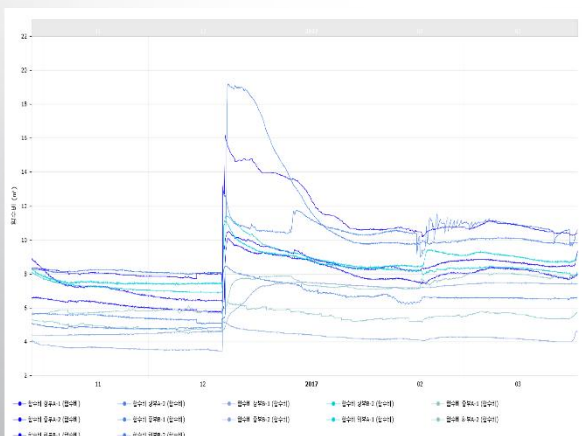
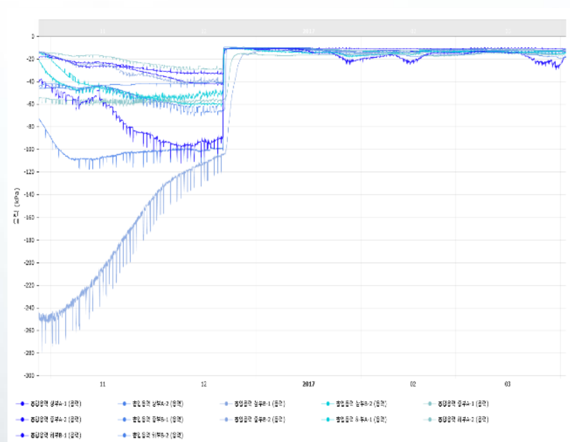
Monitoring of soil property change

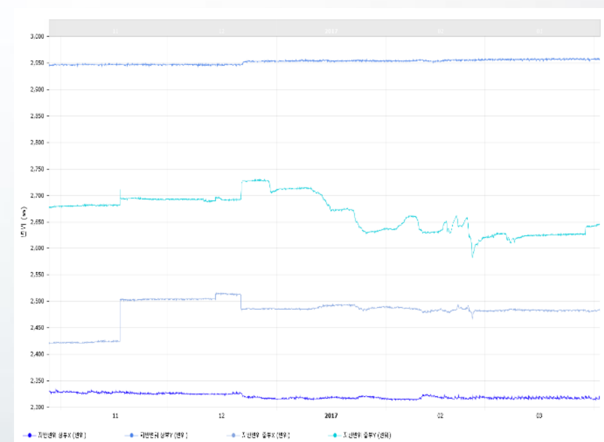




Rainfall







VWC / Dielectric Permittivity / Temp.

Suction stress

Slope displacement

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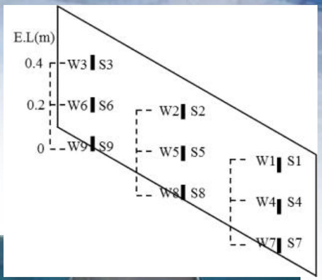
Monitoring of soil property change

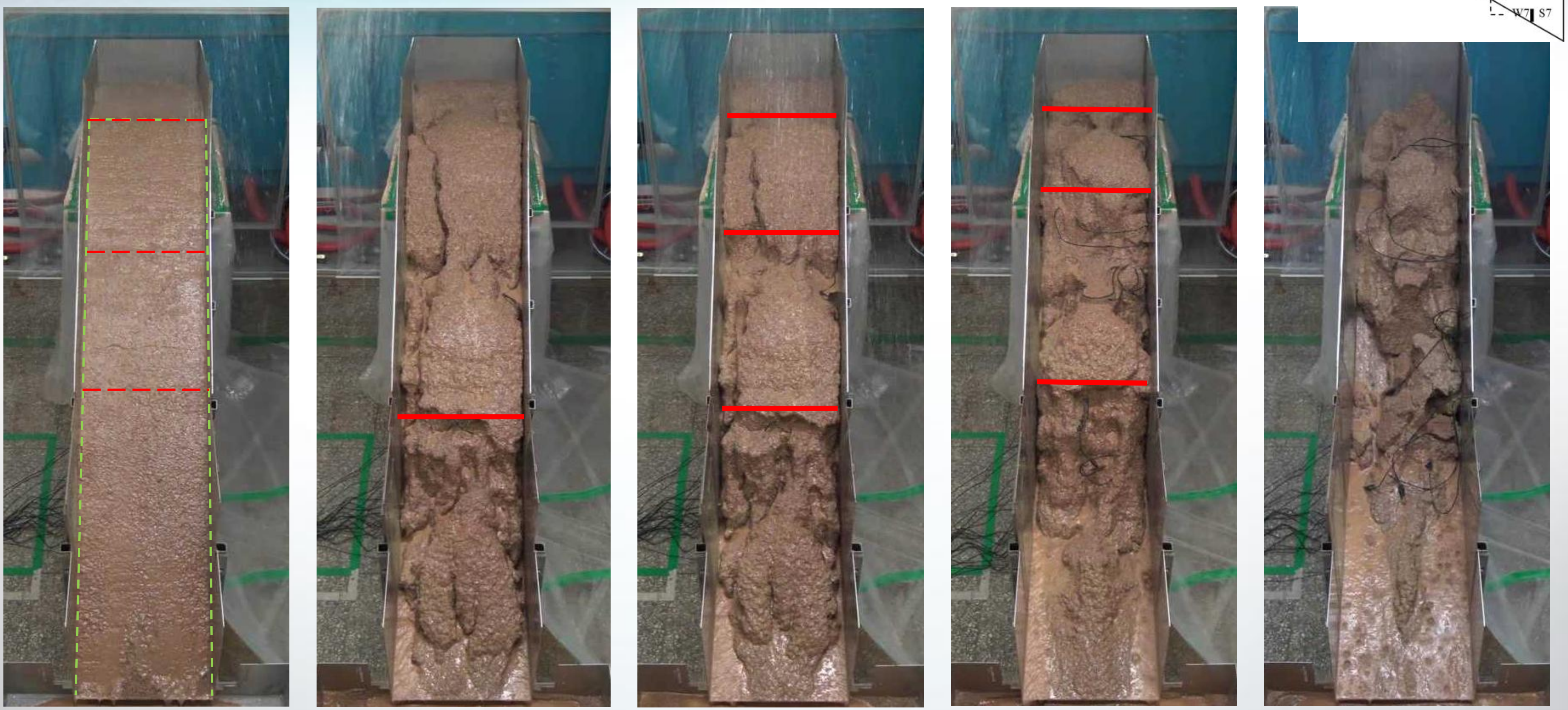
Gradient of the VWC change

- ✓ 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.

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  - Brief introduction of As/Sb pollution
  - Behavior of As/Sb in sulfide rich environment
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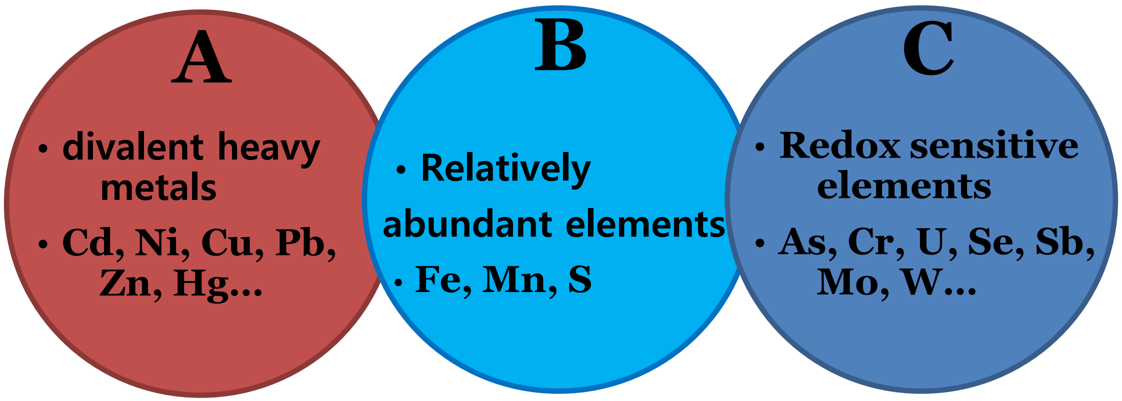
Toxic trace elements

Heavy metals

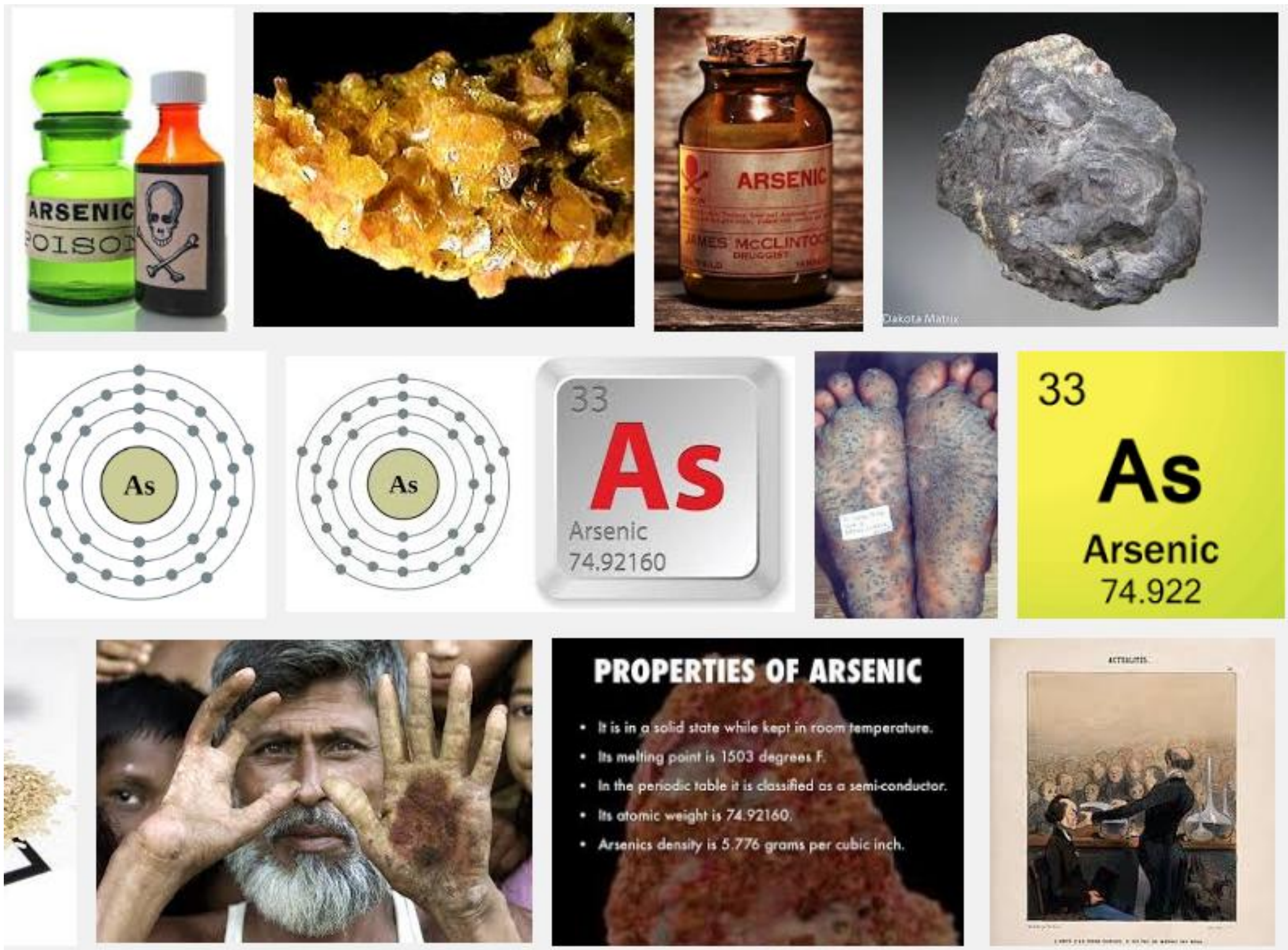
- Any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations
- Atomic density > 4~5 g/cm^3
- eg) Cd, Cr, Ni, Cu, Pb, Mn, Co, Hg, Zn, U, Mo, V, Sb, …

<Target elements in geochemistry>

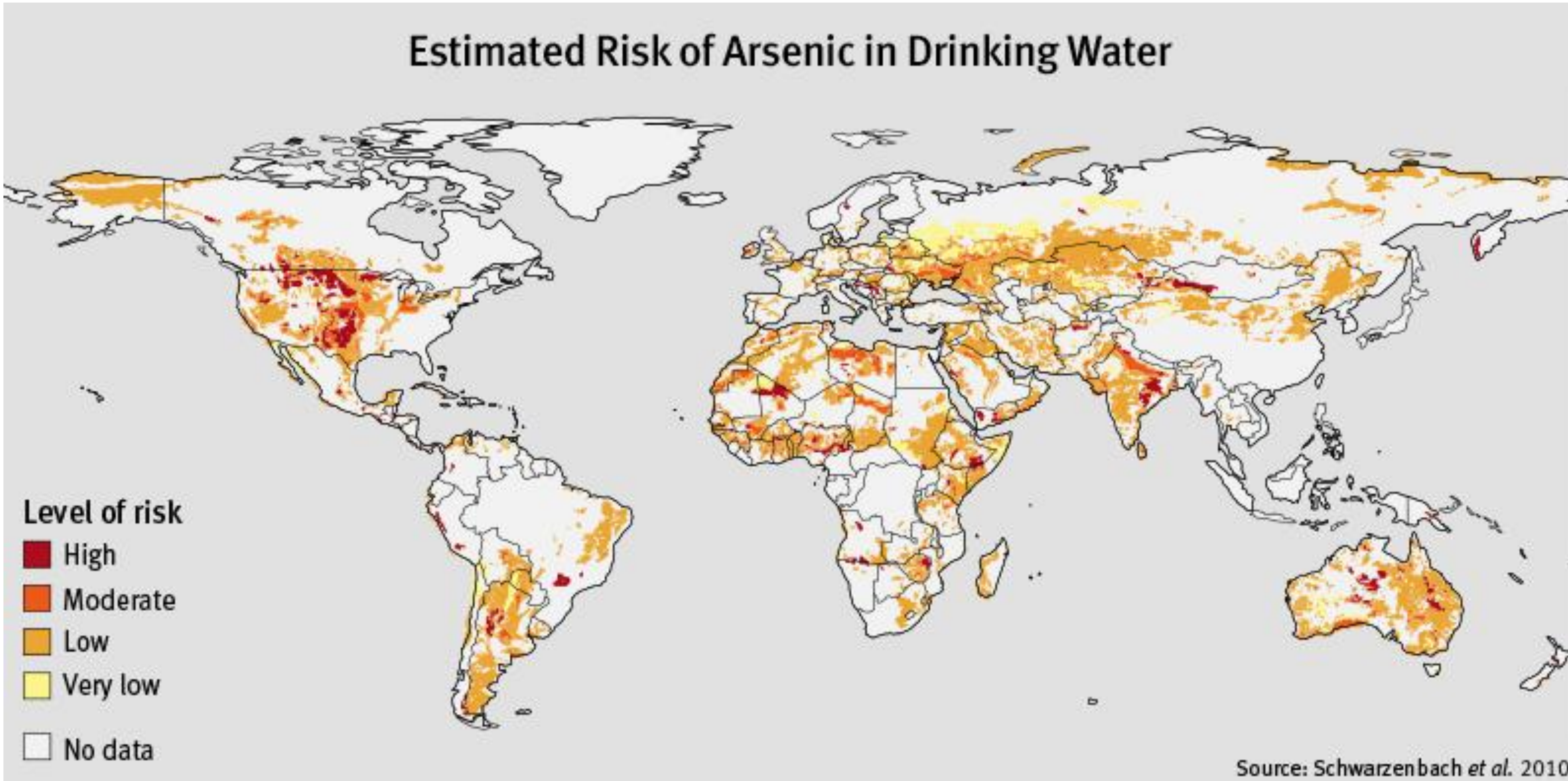


- Group C elements: Redox sensitive and existing in varous forms
- Element of interest: As, Sb

What is arsenic?



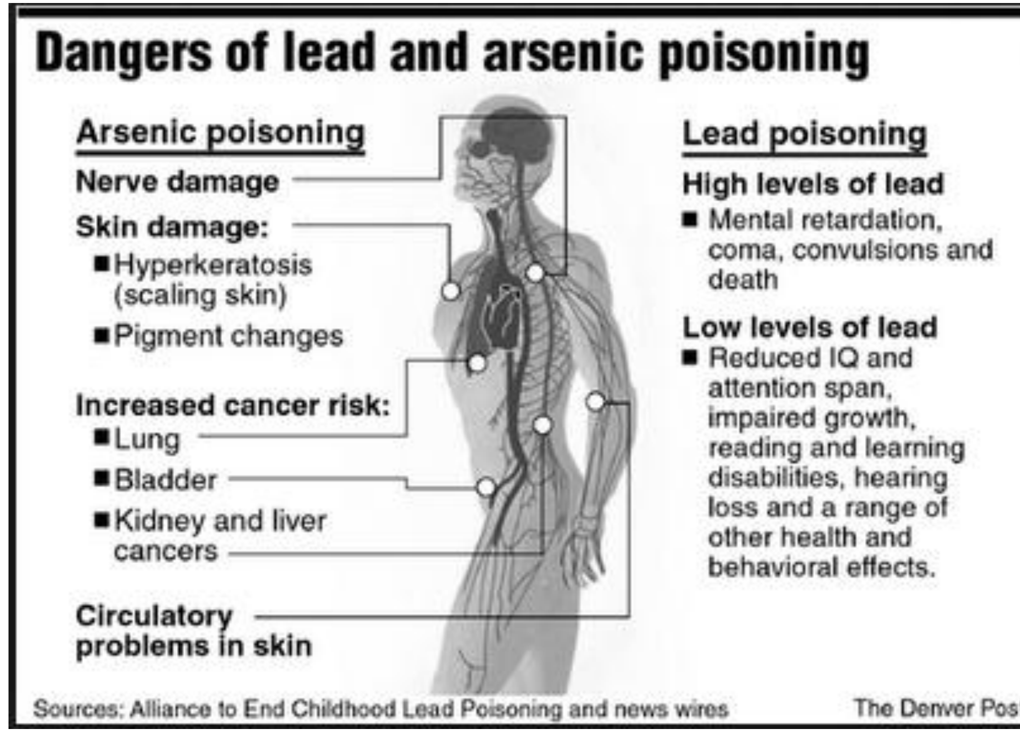
Arsenic contamination around the world



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

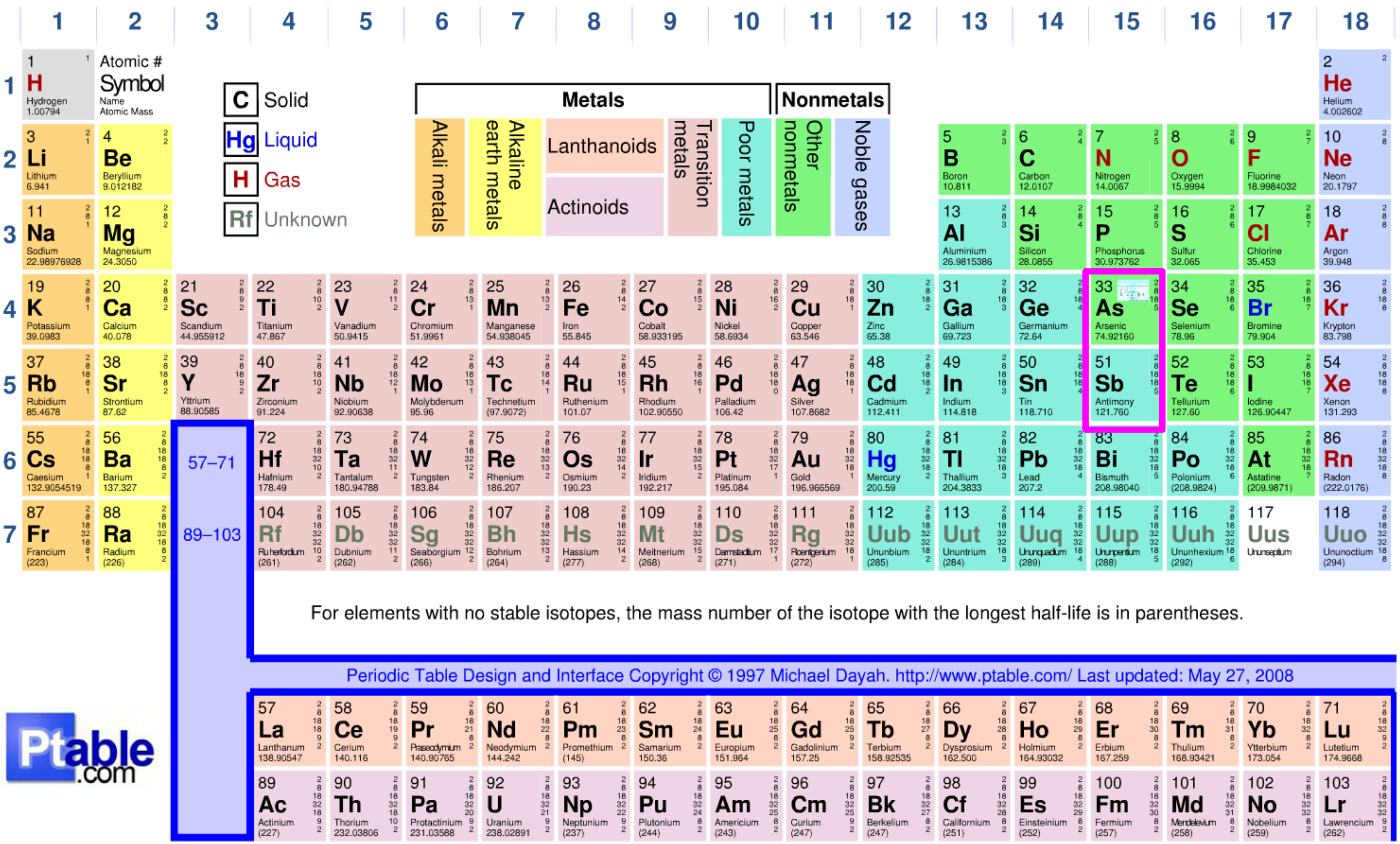
Population in risk of arsenic poisoning (India and West Bengal)

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



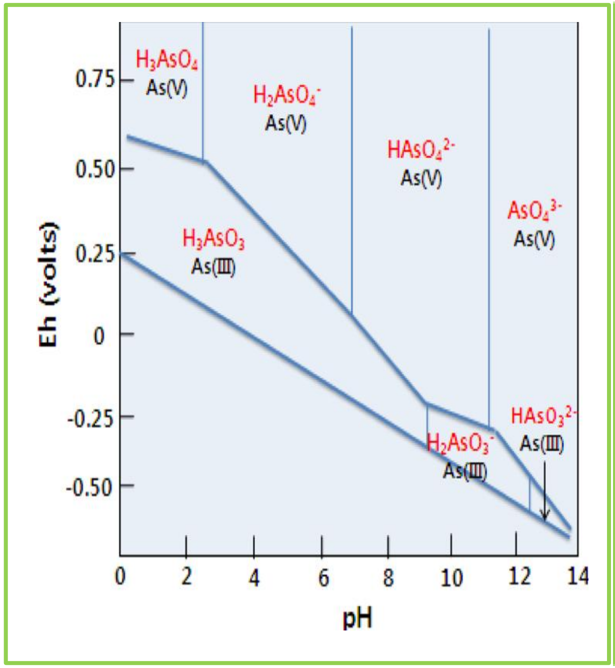
www.youtube.com/watch?v=pyevjRiz1UI

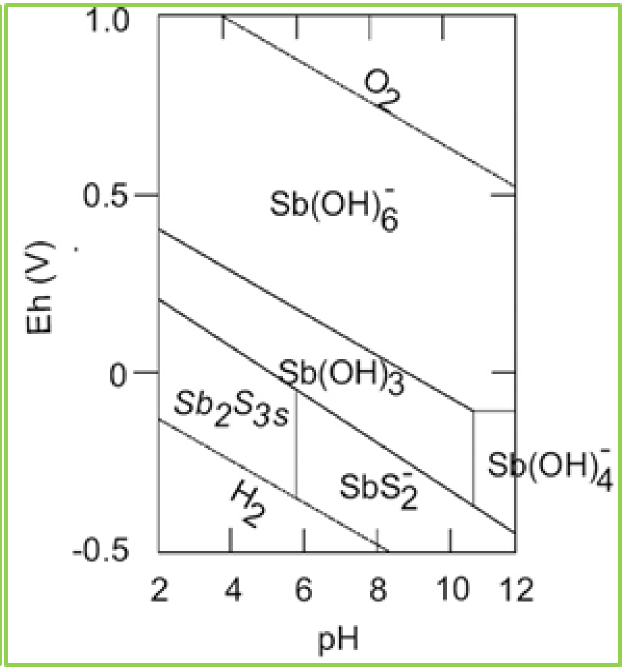
산화환원 환경조성에 의한 지화학적 거동특성 평가



Geochemical properties of Sb

- Oxidation state: Sb^{-3} ~ 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

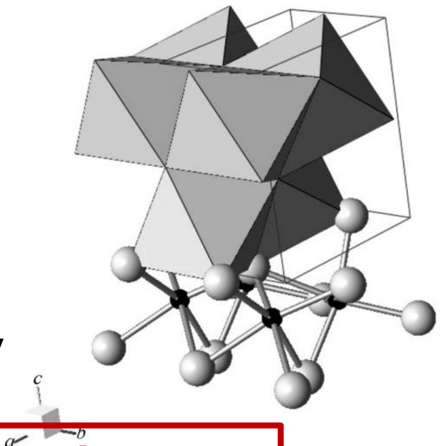
child (300 mg), adult (1,200 mg)

unit: ㎍/L	USA	canada	UK	Germany	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 → High surface area (~ 300m^2/g) → High reactiv**



Need to control size of the FeS → 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

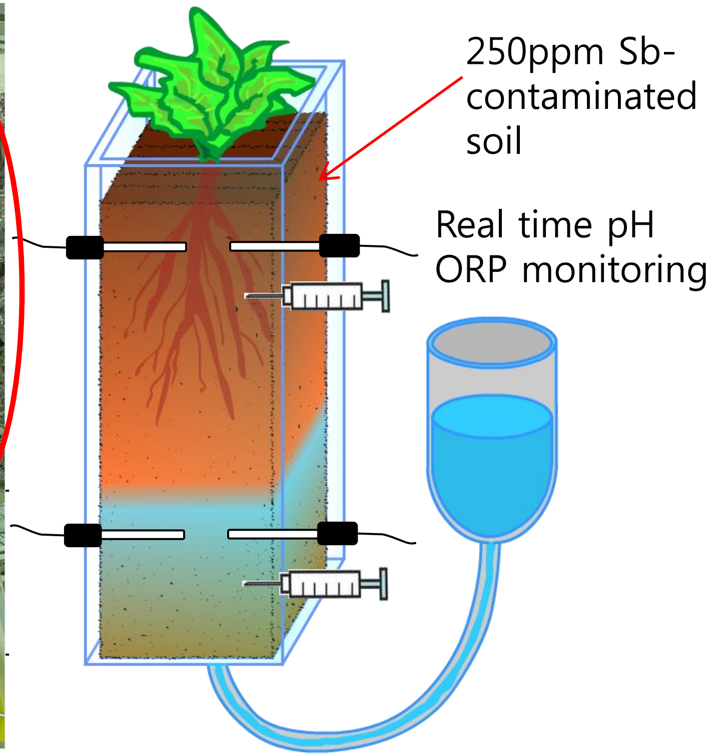
- **Simulate the Sb reaction in contaminated soil column**
- Geochemical reaction in various redox environment
- Observe the change of oxidation state of Sb

Expected results

- The geochemical reaction mechanisms of Sb under S-rich environment
- How to utilized 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

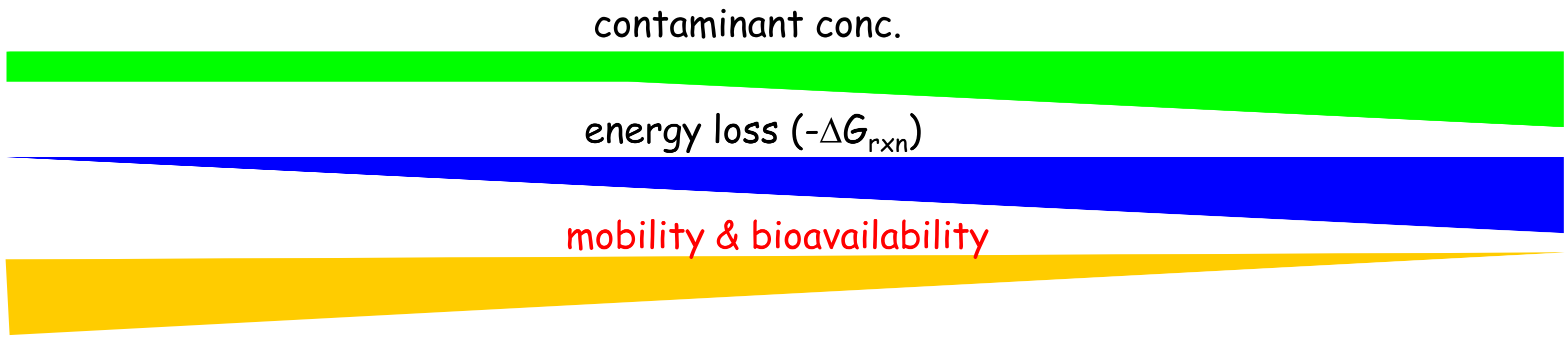
1. Simulating and Observing plant-soil-water interaction
2. Effect of redox condition on Sb behavoir
3. Solid phase Sb speciation using a synchrotron X-ray absorption spectroscopy

Spectroscopic methods as an useful tool

Key note: which technique should be employed?

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

ion exchange	surface complexation	surface ppt.	bulk-phase ppt.



analysis of sorption phases using x-ray tools

x-ray diffraction (XRD) ⟷

x-ray photoelectron spectroscopy (XPS) ⟷

← x-ray reflectivity (XR) →

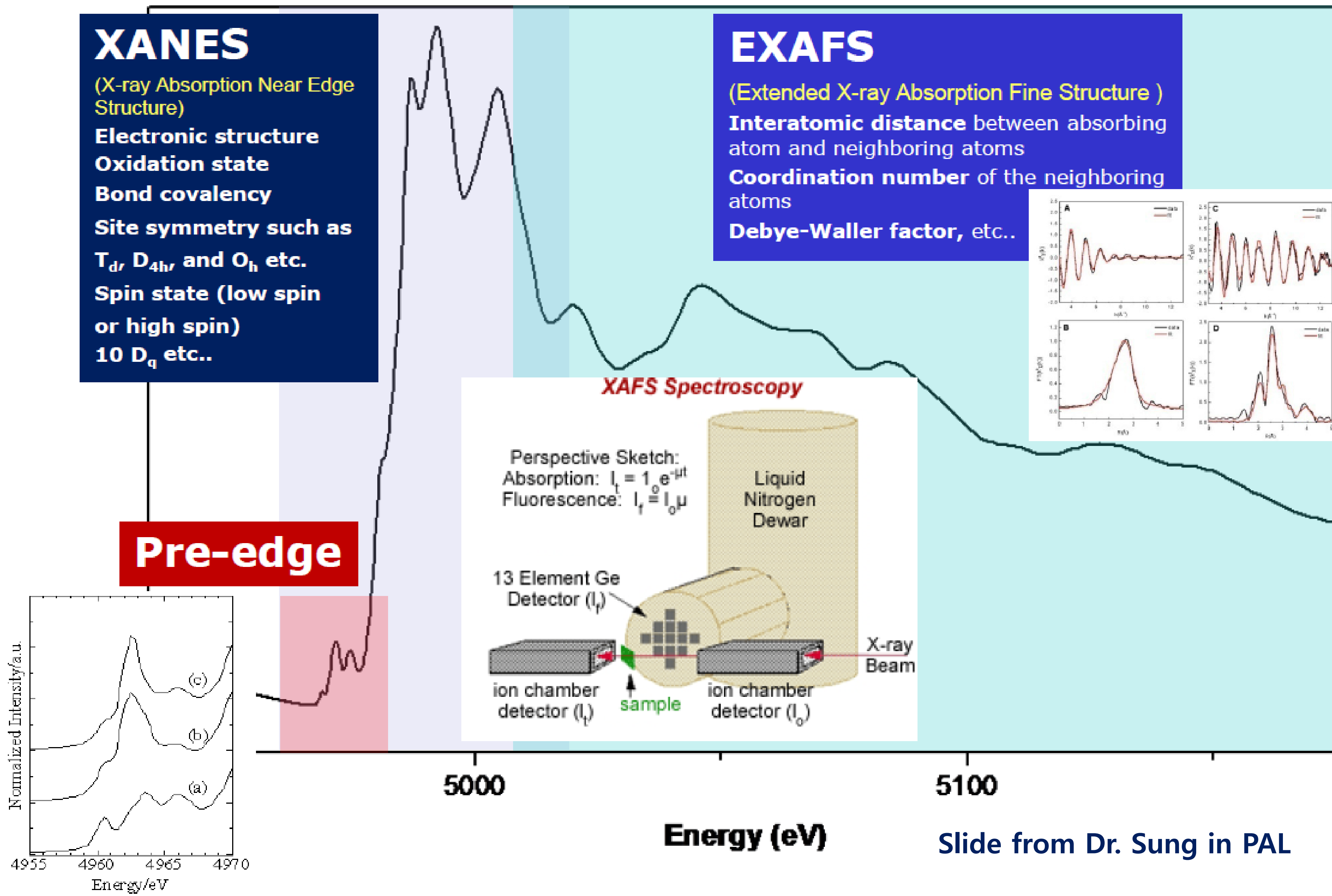
← x-ray absorption spectroscopy (XAS) →

Worldwide Synchrotron Facilities

Synchrotron facilities worldwide

http://www.veqter.co.uk/residual-stress_measurement/synchrotron-diffraction

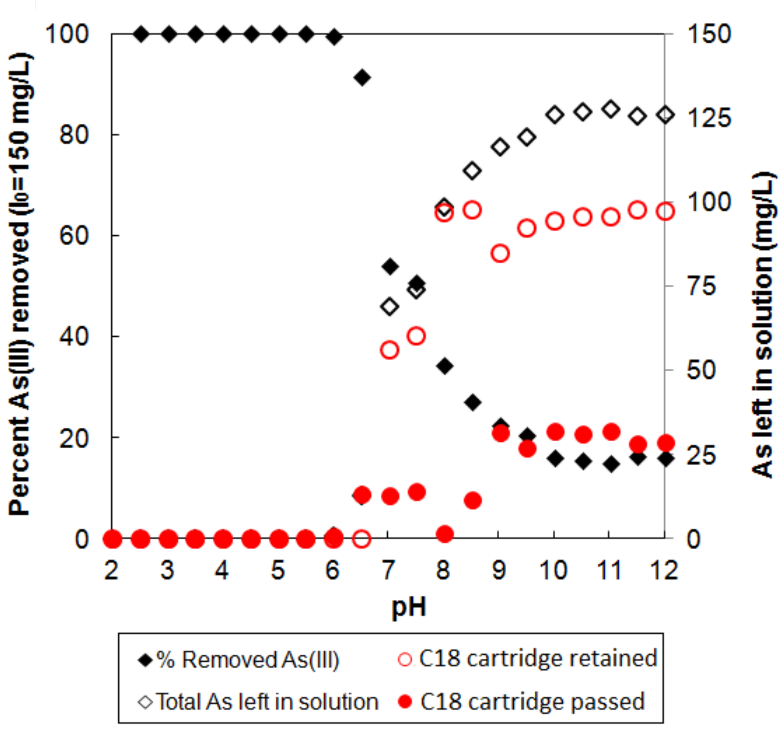
Division of the X-ray absorption spectroscopy in energy regions



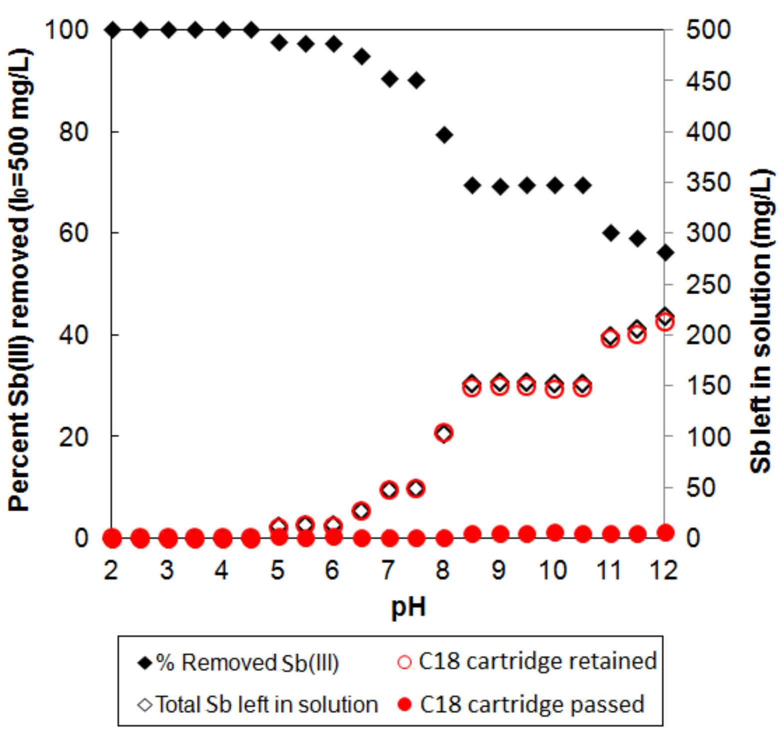
Slide from Dr. Sung in PAL

As/Sb removal under varying pH conditions

As(III)

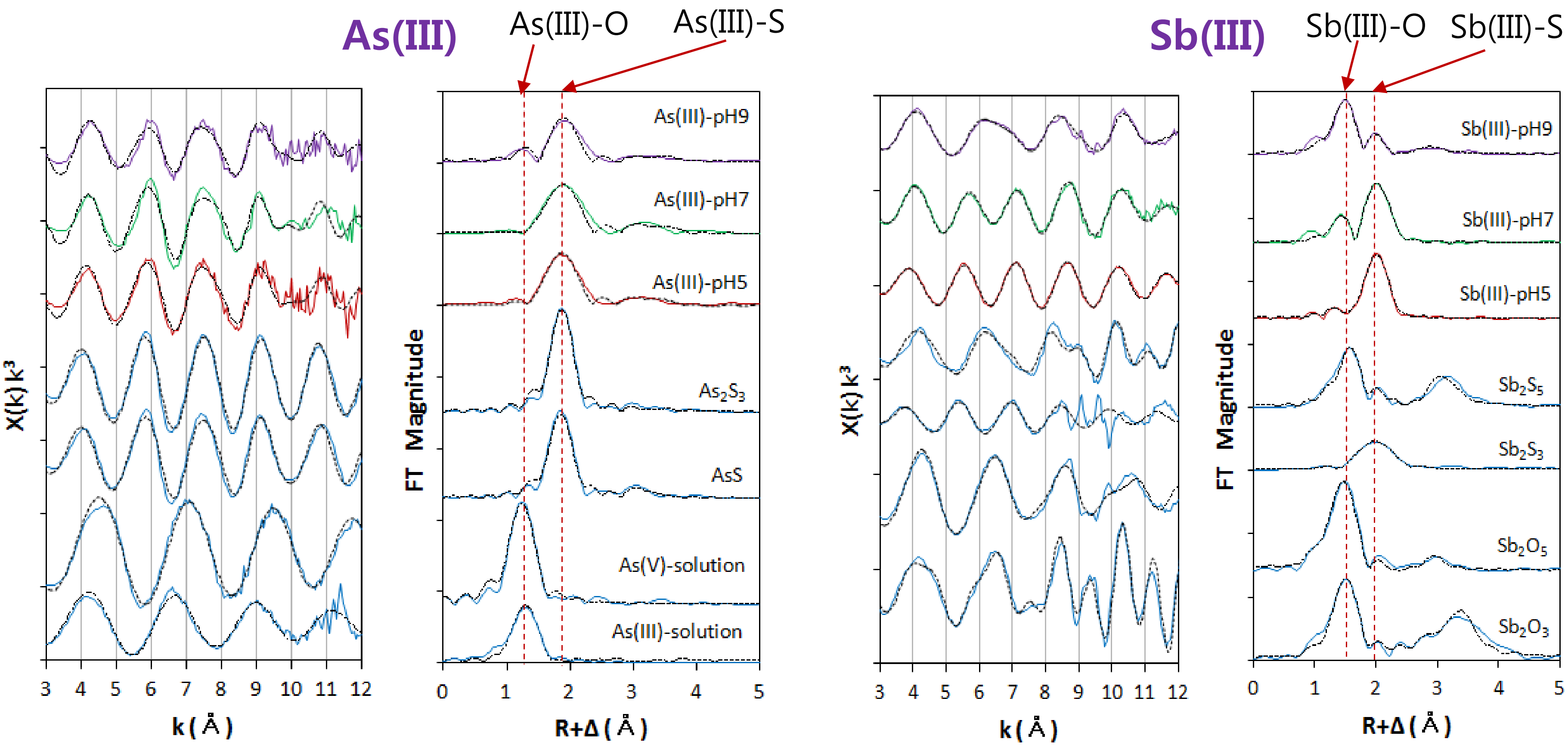


Sb(III)



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.

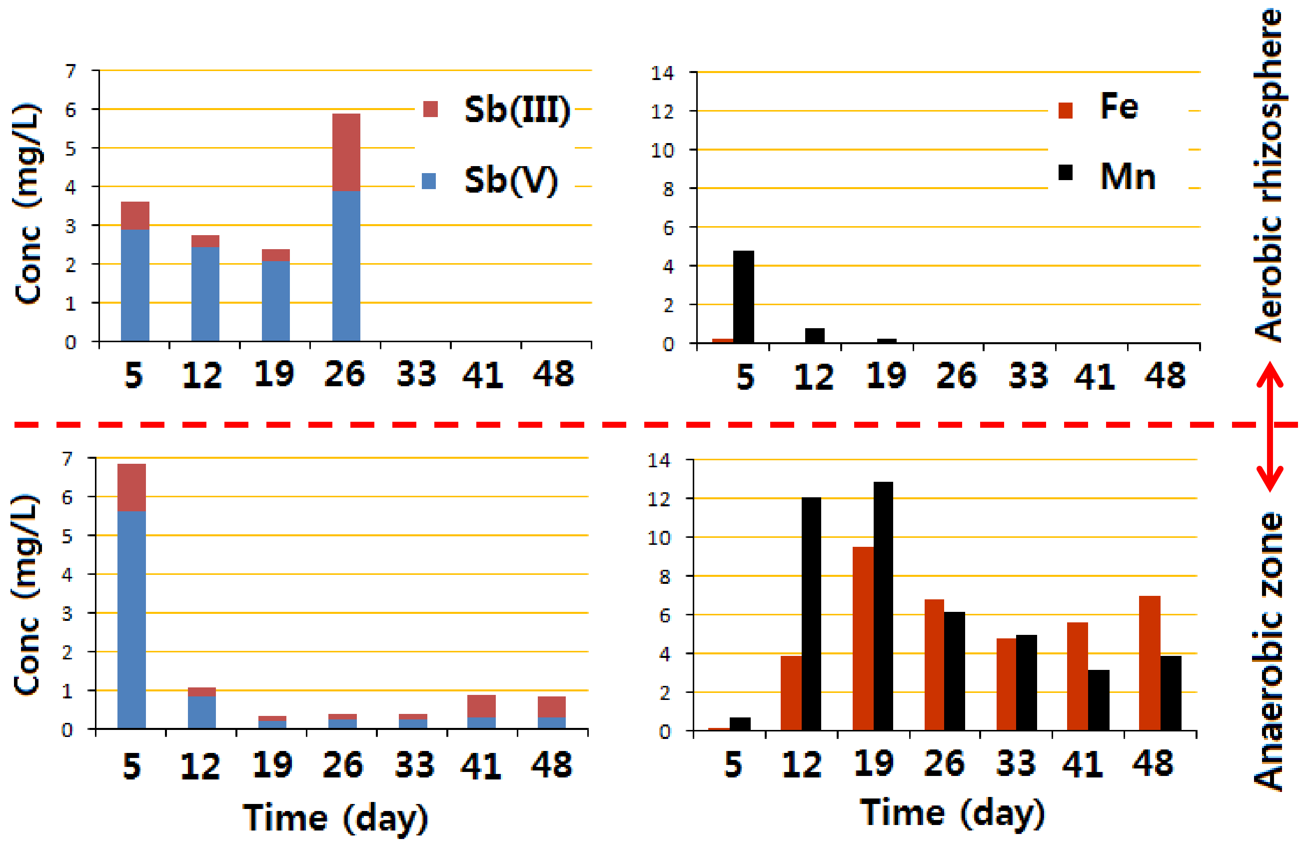
EXAFS results of FeS reacted with As/Sb



As-FeS reaction		Sb-FeS reaction	
pH5	As_2S_3 ppt	pH5	Sb_2S_3 ppt
pH7	As_2S_3 ppt	pH7	Sb_2S_3 ppt
pH9	Thioarsenite adsorption	pH9	Thioantimonite adsorption

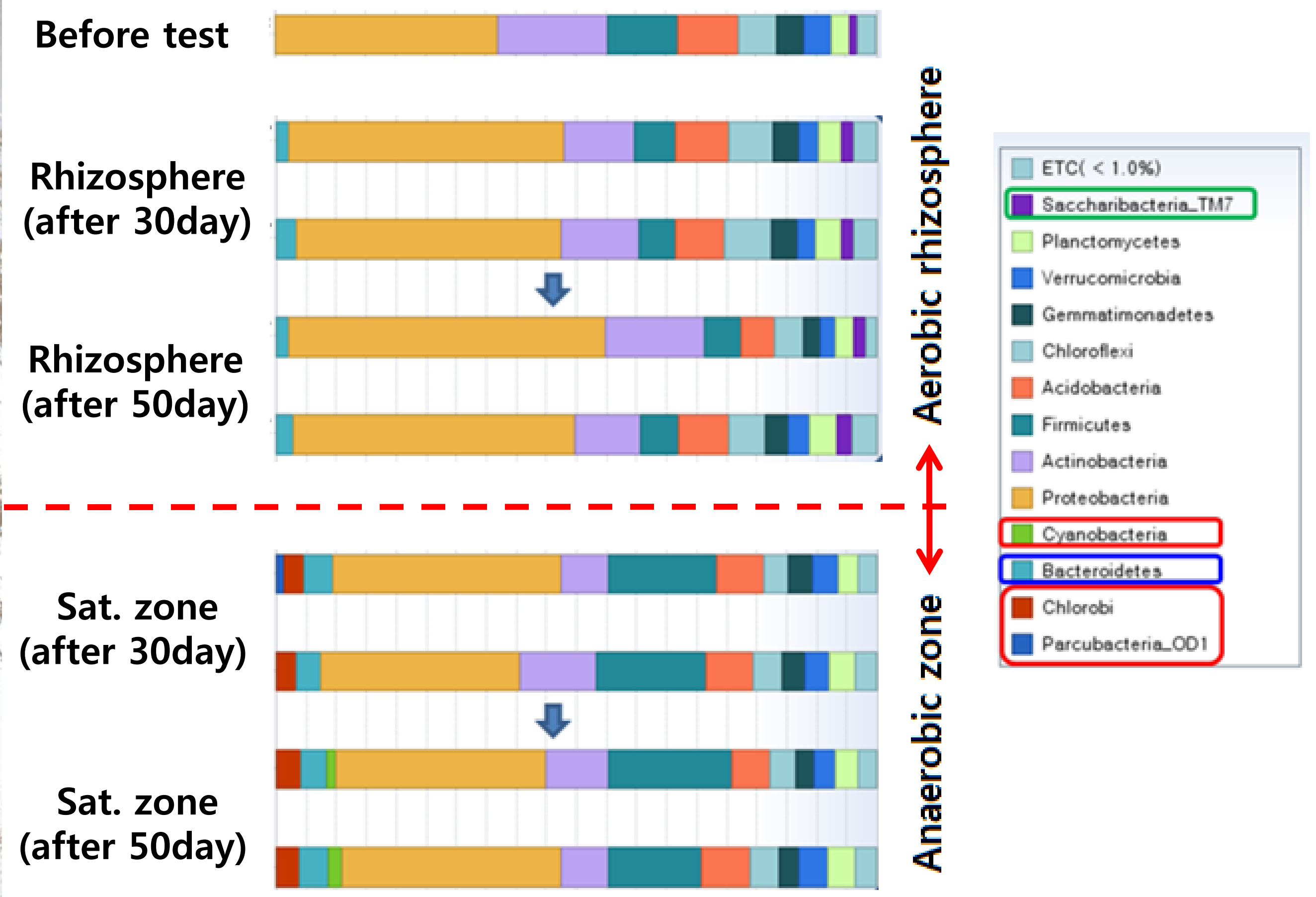
Sb(V)-cont. soil column test results(I)

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?



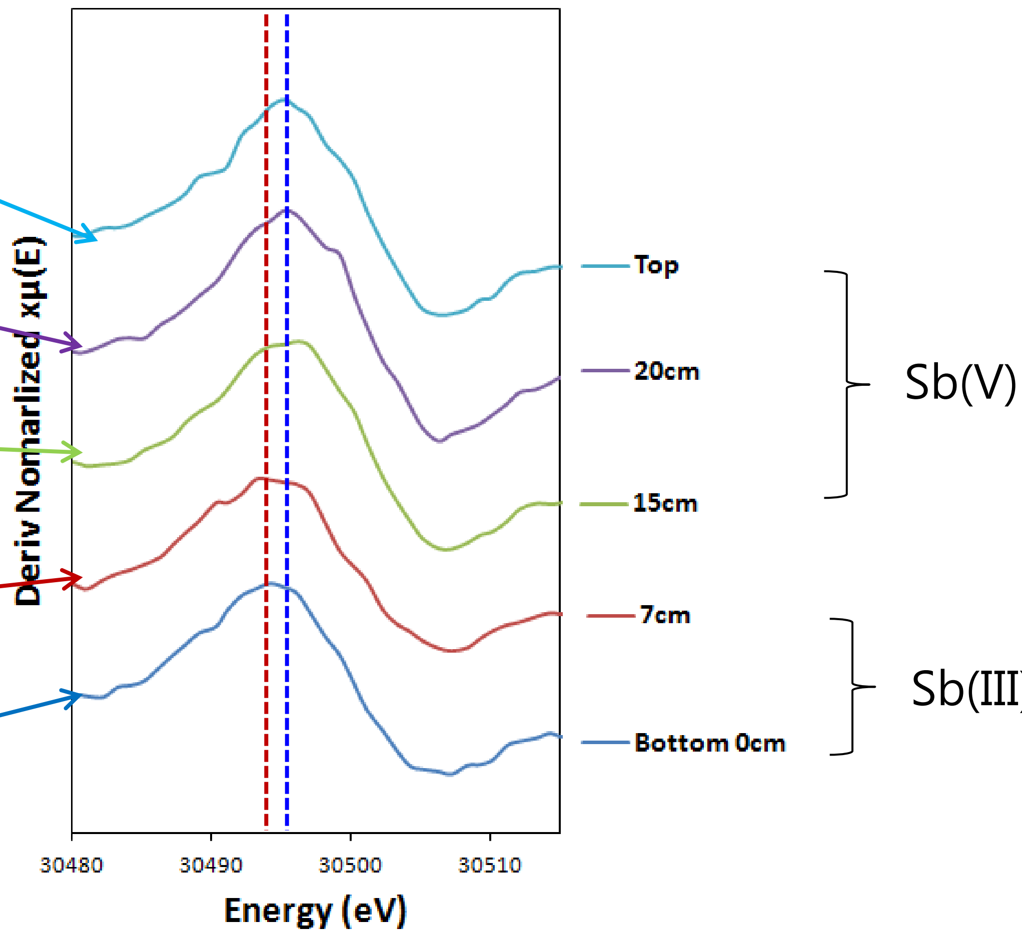
Sb(V)-cont. soil column test results(III)

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