## Grand Challenges and Opportunities in Soil Chemistry in the 21<sup>st</sup> Century

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# **Global Environmental Challenges**

- Population Expansion and Food Production/Security
- Water Quantity and Quality
- Air Quality
- Soil Contamination
- Global Climate Change
- Energy Sustainability
   Biodiversity



Earth at Night More information available at: http://antwrp.gsfc.nasa.gov/apod/ap001127.html Astronomy Picture of the Day 2000 November 27 http://antwrp.gsfc.nasa.gov/apod/astropix.html



C. Mayhew R. Simmon (NASA/GSFC), NOAA/ NGDC, DMSP Digital Arch

Rapid Urbanization (Health, Water, Climate Nexus)

Increasing slums in magacities (>10 million)
 Lack of water or sanitation, health care, education

Climate change impacts (droughts, flooding, sanitation)





Fig. 1. (a) Global distribution of population living in slums. Credit: UN-HABITAT, http://www .unhabitat.org. (b) Map of slums in Dhaka according to surveys conducted a decade apart: Orange represents slums identified in 1995 survey, and green represents new slums identified in 2005 [Islam et al., 2006]. (c) Karail slum of Dhaka near a large water body (Gulshan Lake). (d) The Makoko slum of Lagos, Nigeria (photo by Rainer Wozny).



Akanda, EOS 93: (37) 11 Sept 2012

# The Earth is shrinking



YEAR Hectar of surface per person

Ecological footprint = the land we need to provide daily needs and take up the waste. Now we are using 1.5 Earths per year.





#### Global Water Sustainability

JANET G. HERING, CHEN ZHU, and ERIC H. OELKERS , Guest Editors

#### Is There a Crisis?

Water and Sanitation in Developing Countries

Hydrogeochemical Processes

Groundwater: A Resource in Decline

Water Management in Production of Shale Gas

Conservation, Efficiency, and Reuse



#### TABLE 1 MAJOR EARTH-SURFACE WATER RESERVOIRS (AFTER GLEICK 1996)

Water reservoir	Water volume (10 <sup>3</sup> km <sup>3</sup> )	Percent of total water	Percent of fresh water	Mean resi- dence time
Oceans, seas, bays	1,338,000	96.5	0	2500 years
Ice caps, glaciers	24,064	1.74	69	9700 years
Groundwater	23,400	1.69	-	1400 years
• fresh	10,530	0.76	30	-
• saline	12,870	0.93	0	-
Ground ice and permafrost	300	0.022	0.86	10,000 years
Lakes	176.4	0.013	-	17 years
• fresh	91	0.007	0.26	
• saline	85.4	0.007	0	
Atmosphere	12.9	0.001	0.04	8 days
Swamps	11.47	0.0008	0.03	5 years
Rivers	2.12	0.0002	0.002	16 days
Biological water	1.12	0.0001	0.003	4 hours



"Because many of the threats from climate change affect the land, soil scientists will need to be at the forefront of climate change research."



Janzen et. al, CSA News, April 2011



Figure 1. (top) Annual global total carbon dioxide emissions (mmt), 1958-2006; (bottom) Year-to-year change in atmospheric CO2 concentrations (ppm), 1959-2006. (Data source: Carbon Dioxide Information Analysis Center)





This graph, based on the comparison of atmospheric samples contained in ice cores and more recent direct measurements, provides evidence that atmospheric CO2 has increased since the Industrial Revolution. (Source: NOAA)

Table 1.	Estimated	mass of	carbon	in the	e world's	soils.
Source: U	ISDA.					

Soil orders	Area	Organic C
	10 <sup>3</sup> km <sup>2</sup>	Gt
Alfisols	13,159	90.8
Andisols	975	29.8
Aridisols	15,464	54.1
Entisols	23,432	232.0
Gelisols	11,869	237.5
Histosols	1,526	312.1
Inceptisols	19,854	323.6
Mollisols	9,161	120.0
Oxisols	9,811	99.1
Spodosols	4,596	67.1
Ultisols	10,550	98.1
Vertisols	3,160	18.3
Other soils	7,110	17.1
TOTALS	130,667	1,699.6



# Sea Level Rise Impacts

Australia USA Brazil Globally 

# Sea Level Rise Impacts

China, 60% of population live in 12 coastal provinces Asia, 60% live within 400 km of coast



Storm Barrels Through Region, Leaving Destructive Path, NY Times, Oct 29, 2012





Storm Barrels Through Region, Leaving Destructive Path, NY Times, Oct 29, 2012





Storm Barrels Through Region, Leaving Destructive Path, NY Times, Oct 29, 2012







# FIGHTING TIDES WHICH PROPERTIES TO PROTECT?





Mark Wells' farm field shows damage from salt water among his crops in Sussex County.







# Climate Change and National Security/ Military Response

 Humanitarian Relief and Conflict (food shortages, water crises, pollution, flooding)
 Sea Level Rise Impacts on Military Bases
 Arctic Melting (opening of shipping channels; undersea resources, e.g., oil, gas, rare minerals

What are the new relationships among resources, diplomacy, crises and conflict?





ANDREW TESTA FOR THE NEW YORK TIMES

#### **Greenland Weighs Peril and Potential of Climate Change**

In one Greenland town, climate change is threatening a fishing culture but also hinting at new opportunities in mining. Page A4.



New York Times, September 24, 2012

# **Global Food System Threats**

- Climate Change
- Soil and Ecological Degradation
- Population Growth
- Rising Energy Prices
- Increasing Demand for Meat and Dairy Products
- Urban Expansion
- Increasing Competition for Land from Biofuels, Industry and Urbanization
- Conflicts over Water



# **Food Security**

 925 million hungry people (2010, Food and Agr. Org. of U.N.)
 Food prices could more than double by 2030; climate change responsible for 50% of rise











# A Range of Scales



2. TEM

3. AFM

- Kinetic
   Studies
- Extractions

synchrotron

radiation.

#### Time Scales of Reactions in Natural Environments



# It's About Interfaces!



The microbe-mineral interface



#### The root-soil interface



# The Critical Zone



# **Molecular Environmental Science**

Study of the chemical and physical forms and distribution of contaminants in soils, sediments, waste materials, natural waters, and the atmosphere at the molecular level.



### Synchrotrons of the World – The Generations



Shanghai Synchrotron Radiation

Facility (SSRF)

#### NSLS -BNL Upton, NY USA



#### LBNL-ALS Berkeley, CA USA



#### Beijing Synchrotron Radiation Facility (BSRF)













#### Principal Synchrotron Techniques Used in Environmental Science

- X-ray Fluorescence (XRF): chemical composition (quantification, mapping)
- X-ray Absorption Fine Structure (XAFS) Spectroscopy: chemical speciation (oxidation state, coordination, nearest neighbors)
- Surface Scattering and Diffraction: surface structure, sorption processes
- Microtomography: 3D imaging of internal microstructure (porosity, fluid flow, composition)



Arsenic in Cattail Root Plaque





Copper Speciation in Fluid Inclusions





# Anatomy of a µXAS Experiment



# Soil and Environmental Science Research Thrusts and Frontiers

- Metal(loid) Speciation and Reactivity in Heterogeneous Systems
- Nutrient Cycling/Sequestration
- Particulate Transport and Reactivity
- Microbe/Metal/Carbon Interactions at Critical Zone Interfaces
- Plant/Soil Interfacial Processes
- Climate Change and Carbon Cycling



# Speciation of Heterogeneous Systems


# A site contaminated by heavy metals (Pb, Cd, Cu, Zn)

the next say and then the fig. ---

Superior States

# Arsenic, a public health crisis

2010 ASA-CSSA-SSSA nternational Annual Meetings Oct. 31-Nov. 3 • Long Beach, CA



#### **Maatheide Area, Belgium**





1990

2002

• 135 Ha of bare land due to elevated Zn, Pb, and Cd concentrations from the Zn smelting facility in Maatheide, Belgium. • Cleanup strategy: *In situ* immobilization of contaminants, by addition of beringite and compost combined with metal tolerant plants.



#### **μ- focused SXRF and EXAFS (non-treated soil)**



## Candidate Phases for Ni Precipitates: Hydroxides



Ni (OH)<sub>2-x</sub> $A_x$ 

 $\alpha$ - Ni hydroxide

 $Ni_{1-x}Al_x(OH)_2A_x$ 

LDH (hydrotalcite)



# Percentage Zn desorbed from the non-treated and treated zinc smelter soils





## **BIOMET data**

	pH 6		pH 7.5	
	Bioavailable Ni (mg/kg)	% of Total	Bioavailable Ni (mg/kg)	% of Total
Matapeake	1640	90	2447	27
Berryland	2606	70	3492	27
Fort Ellis	3027	74	3020	25



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Cumulative Zn desorption (in %) by DTPA-TEA-Ca from (a) the alkaline soil (Alk) and (b) the acidified soil (Acid), after 1 and 30 days (d) of flooding, and draining to saturation (Sat) or field capacity (FC).







Linear least-squares fitting results for bulk-XAFS spectra of the (a) alkaline soil (Alk) and (b) the acidified (Acid) soil, air-dried or flooded for different periods (d = days), and drained to saturation (Sat) or field capacity (FC). Solid lines represent the k3-weighted  $\chi$ -spectra and the dotted line represents the best fits obtained using linear least-squares fitting.



Real-time Kinetics at the Molecular Scale



## Experimental Setup Used to Collect Quick-scanning X-ray Absorption Spectroscopic (Q-XAS) Data





#### Real-time, *in-situ* Kinetics Batch Experiments





#### As(III) Oxidation by Hydrous Manganese Oxide (HMO)

#### **Q-XAS Batch Reactor**

- Continuous data collection (2,000 points s<sup>-1</sup>)
- Collection of XANES spectrum in 980 ms
- 5 mM As(III), 1 g L<sup>-1</sup> HMO, pH 7.0 , 5 mM NaCl



#### **Experimental Goal**

- Characterize initial (<30 s) reaction rates



# Data (solid) and Linear Combination Fits (dots) of Individual As K-edge XANES Spectra Used to Determine As(III) and As(V) Concentrations





## As(V) and As(III) Concentrations Determined from Traditional Batch and Q-XAS Methods







First-order As (III) Depletion Rate Plots Determined from As(III) Concentrations Using Batch (A and C) and Q-XAS (B and D) Methods.

> UVERTING DELAWARE



First-order As (III) Depletion Rate Plots Determined from As(III) Concentrations Using Batch (A and C) and Q-XAS (B and D) Methods.

> UVERTING DELAWARE

## Cr(III) Oxidation Kinetics using a Q-XAS Technique



Landrot et al. 2010. Environ. Sci. Technol. 44: 143–149.



#### **Initial Conditions and Rate Parameters**

[Cr(III)]	[HMO]	k (sec-1)		
(mM)	(g/L)	рН=2.5	pH=3	pH=3.5
100	20	0.204/0.228	0.277/0.202	0.295/0.364
80	20	0.202/0.220	0.270/0.198	0.353/0.308
60	20	0.197/0.215	0.303/0.208	0.302/0.357
40	20	0.208/0.235	0.266/0.199	0.296/0.363
100	20	0.204/0.228	0.277/0.202	0.295/0.364
100	15	0.206/0.207	0.293/0.219	0.291/0.328
100	10	0.169/0.171	0.287/0.244	0.280/0.311
100	5	0.157/0.203	0.257/0.316	0.283/0.346
		k (averaged) in sec-1		
		pH=2.5	рН=3	рН=3.5
		0.192/0.211	0.279/0.227	0.300/0.340

Landrot et al. 2010. Environ. Sci. Technol. 44: 143–149.

0.201

0.242

0.322











Chemistry of Low Atomic Number Elements

# AI, B, C, CI, Mg, N, Na, P and S



#### Nutrient Management: Human and Ecosystem Health

#### Nuisance seaweed blooms in Delaware's Inland Bays





## The problems when marshland is gone

L: Brackish and saltwater tidal marshes along the Delaware Estuary absorb excess water during floodings, reducing upland damage. Wetlands fiilter out pollutants before they reach the Delaware River and Bay.

**2:** When marshes recede, soils, sediment and pollutants aren't filtered and end up in Delaware's waterways. Nutrients from farm runoff and motor oil, road salt, and antifreeze from suburban development pass into clean water.

#### A functioning marsh

Beyond filtering out pollutants, wetlands are important for other reasons. At high tide in tidal marshes, water covers low-lying areas, drawing ospreys and other birds that feed on fish in the shallow water. High ground remains dry, attracting wildlife such as foxes, turtles and frogs.

High, dry

ground

Snapping turtle

**High tide** 

Marsh Open water

Development/farm

runoff and pollutants

darshv

Low tide

Osprev

10.03555

oetation

Silver

bass

Green tree frog

**Development/farm** 

rsh

Poliutants

reach open

watar

Sanderling

runoff and pollutants

#### **Nature thrives**

In a thriving marsh, plants and animals make their home. Commercial and game fish breed and raise their young in coastal marshes and estuaries. Inland wetlands are the only places many animals and plants can live. More than 143 species of birds have been documented living in marshy areas, making Delaware a prime bird-watching site. Here are some types of wildlife that are common to Delaware's wetlands.

The News Journal/DAN GARROW



#### Water Pollution in China



#### **Eutrophication of lakes**





#### Eutrophication of city rivers



# **Fertilizer Overuse and Misuse**

#### Sources of N and P Pollution



In the latest pollution resource survey of China, it is reported that agricultural pollution accounts for 50-60% of N and P pollution to water bodies.

### Milestones in the study of P sorption mechanisms







## P XANES and EXAFS analysis





## NMR and DFT





Chapter 1, Figure 16 Three-dimensional SOM(HA + carbohydrates + proteins + water) model structure. Element colors are: carbon (light blue); hydrogen (white), oxygen (red); nitrogen (deep blue); and sulfur (dark yellow) [from Schulten and Schnitzer (1997) with permission of the publisher].


There is not a regularly repeating structural unit or set of units that is characteristic of HS. Consequently, no two molecules of HS are alike.





#### **Organo-Mineral Interactions**

One of the major mechanisms for
C stabilization

 Controlled by the chemistry of organic matter and mineralogy (Fe&Al oxides, aluminosilicates)

Impacted by the coupled geomorphological, hydrological and microbial processes



Trumbore et al., 2008, Science

#### Christina River Basin Critical Zone Observatory

**Overall Hypothesis:** Organo-mineral complexation, a key process for stabilizing carbon, is limited by the supply of the mineral surfaces and the mixing of minerals with organic matter in natural ecosystems



Vation





## **Advanced Characterization Techniques**

#### Near-edge X-ray Absorption Fine Structure (NEXAFS)





#### SGM beamline, CLS

- Characterize C and N functional groups of soil organic matter without any pretreatment.
- Spot Size: 1000\*100 MICRONS



### **Advanced Characterization Techniques**

#### Scanning Transmission X-ray Microscopy (STXM) – NEXAFS





SM beamline, CLS



Acquire sequence of images over NEXAFS spectral region at 30-40nm resolution

- Map distribution of C and C forms and the major elements (K, Ca, Fe, Al, Si) in soils at nanometer scale.
- Assess the interactive mechanisms of C with specific soil minerals.

## **Soil Carbon Speciation by NEXAFS**



Footslope soil: enriched in aromatic C=C depleted in aliphatic C-H



# Color-coded Composite Maps of C, Ca, Fe, Al and Si from Pasture Soil Clay Fractions













Fe is intimately associated with Al and Si.

Discrete quartz particles.

C is closely associated with clay particles, as particulate organic matter has been excluded from the clay fractions. The discrete SiO<sub>2</sub> particles contain little or no C



#### **Distribution of C Functional Groups**



The majority of OM forms associated with soil organo-mineral assemblage are aromatic C=C, carboxylic-C and polysaccharides



## **C** Distribution on Ferrihydrite via Adsorption





#### **Desorption of Adsorbed and Coprecipitated C on Ferrihydrite**



Desorption efficiency: 0.1M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> > 0.1M NaOH > 0.1M NaH<sub>2</sub>PO<sub>4</sub>

The proportion of C being desorbed is larger for adsorbed C than coprecipitated C, indicating coprecipitation leads to greater C stability than adsorption.

The proportion of C being desorbed increases with C loading and reaches a maximum at 1 mg C m<sup>-2</sup> SA.



# Particulate Transport and Reactivity



# Soil and Land Use/Degradation

Soil erosion via water and wind on cropland in USA - >1.7 billion tons/yr (2007) Salinization Human Impacts (Anthropocene) Land Degradation – urbanization, sealing, compaction 33-50% of ice-free earth's surface transformed by human action "The reaction of land to occupancy determines the nature and duration of civilization." (Aldo Leopold, 1933)



Source: NASA http://www.nasa.gov/multimedia/imagegallery/image\_feature\_989.html







Source: http://www.sciencemediacentre.co.nz/2009/09/23/risk-of-respiratory-illness-as-blanket-of-dust-de

#### Beijing Takes Steps to Fight Pollution as Problem Worsens



A flag-raising ceremony in Tiananmen Square obscured by thick smog.



# Burning of e-wastes



# **Poultry Dust**



# What's the problem?

- Extensive research shows that particulate matter has had consequences on both respiratory and cardiovascular systems
  - Asthma
  - Chronic Bronchitis
  - Cardiovascular Disease
- Fine and ultrafine PM
  - Lung deposition
- Toxicity
  - Arsenic



# Schematic of Methodology





# Micro X-ray Fluorescence (XRF) Map of Poultry Particulate Matter



Figure 3: 2.5mm x 2.5mm X-ray fluorescence (XRF) map of filtered PM10 sample (10um-2.5um particles). Colored circles indicate the location of high intensity areas or "hotspots" corresponding to either As (red), Fe (green), or Mn (blue).





# Scanning Electron Microscopy

S4700 15.0kV 12.3mm x2.00k SE(M) 3/7/12

Fig's 1 and 2 show SEM images from a single indoor  $PM_{10}$  sample. Particles are primarily found to be spherical and platy in shape. Fig 2 (right) shows a closer look at particles aggregated together.





#### Confocal Microscopy Image of Indoor PM<sub>2.5</sub>

**BLANK FILTER** 



# Interfaces Between Disciplines is "Where the Action Is" in Research



Team members interface skills and contributions









# **External Collaborators**

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James Dynes, Canadian Light Source Jian Wang, Canadian Light Source Chithra Karunakaran, Canadian Light Source Tom Regier, Canadian Light Source

Ken Livi, The Johns Hopkins University Ana Rule, The Johns Hopkins University

Jim Kubicki, The Pennsylvania State University Rufus Chaney, USDA, Beltsville Anthony Aufdenkampe, Stroud Water Research Center Peter Leinweber, Rostock University





Canadian Centre canadien Light de rayonnement Source synchrotron

JOHNS HOPKINS











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