Sediment Remediation of the Xiawangang River, Zhuzhou City, China

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Introduction

The Xiawangang River is an artificial discharge channel constructed in the 1970s, approximately 4 km in length starting from an area of metal smelting and manufacturing and discharging into the Xiangjiang River (Figure 1). The width of the Xiawangang River ranges from 4 to 10 meters, water depth ranges from 0.1 to 1.5 meters, and average yearly flow is 4.3 m^3/s. Sediment of the Xiawangang is contaminated with several metals including cadmium (Cd), lead (Pb), mercury (Hg), and arsenic (As) due to point and non-point discharges from this industrialized section of the watershed.


Figure 1.

The overall objective of this project was to outline a sediment remediation and environmental rehabilitation approach for the Xiawangang River in order to decrease human health and environmental risks associated with metals-contaminated sediment. Sediment remediation at this site potentially included mechanical and/or hydraulic dredging depending on river access and hydrodynamics of the watershed. In addition, sediment dewatering and management was proposed, including the use of lined (i.e., 40-mil polyethylene liner and/or geogrid) dewatering pads, debris management, other particle size screening techniques, and subsequent disposal of contaminated sediments. In addition, *ex situ* stabilization and solidification (S/S) of contaminated fines was recommended prior to transportation and disposal of excavated material in an appropriate disposal facility. This design also incorporated source control, best management practices (BMPs) and downstream passive technologies (e.g., sediment traps, turbidity curtains, and limestone culverts) to minimize recontamination of the River channel due to unidentified sources and other contaminated areas (sediments and soils) of the river not accessible during remediation. Subsequently, restoration of the system included flood control, revetments, debris removal, bank stabilization, stormwater management, habitat rehabilitation, source control, and in-stream flow control structures (e.g., weirs, dikes, dams, and levees).

Due to limited access to the River, the footprint was divided into ten operational sections for sediment excavation and remediation (Figure 2). From initial surveys, the estimated volume of *in situ* contaminated sediment to be removed from the Xiawangang was 36,800 m3 (Table 1).


Figure 2.

Table 1. Proposed Xiawangang River Remediation Sections Described by Surface Area, Sediment Volume Characterized for Removal, and Associated Particle Size Distribution.

WESTON Proposed Section	Surface Area (meters^2)	Total Volume Sediment (meters^3)	Total Volume By Particle Size (meters^3)			
			Gravel	Sand	Silt	Clay
1	4,796	5,584	1,464	3,923	713	248
2	1,707	2,049	537	1,439	261	91
3	2,744	3,293	858	2,286	443	147
4	2,697	2,130	441	856	797	106
5	1,001	2,002	414	805	749	100
6	5,489	6,077	1,251	2,439	2,283	308
7	5,209	8,200	1,096	2,944	3,912	760
8	4,014	6,229	832	2,236	2,971	577
9	1,096	1,193	223	305	721	80
10	134	134	25	34	81	9
TOTAL	**28,887**	**36,891**	**7,141**	**17,267**	**12,930**	**2,427**

Additionally, the sediment volume identified for removal was characterized by particle size distribution. Primary contaminants of concern include Cd (10.26 metric tons), Pb (84.04 metric tons), As (10.73 metric tons), and Hg (0.27 metric tons) (2007 and 2009 monitoring data) (Table 2).

Table 2. Mass (Metric Tons) of *In Situ* Metal Targeted for Removal within Each Section of the Xiawangang River.

Weston River Section	Mass of Metal within Each Section (metric tons)							
	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Lead (Pb)	Mercury (Hg)	Nickel (Ni)	Arsenic (As)	Zinc (Zn)
1	1.552	0.991	10.598	12.720	0.041	0.554	1.624	86.173
2	0.570	0.363	3.889	4.667	0.015	0.203	0.596	31.616
3	0.916	0.584	6.251	7.502	0.024	0.327	0.958	50.822
4	0.592	0.378	4.043	4.852	0.016	0.211	0.619	32.870
5	0.557	0.355	3.800	4.561	0.015	0.199	0.582	30.895
6	1.689	1.078	11.535	13.844	0.044	0.603	1.767	93.784
7	2.280	1.455	15.564	18.680	0.060	0.813	2.385	126.547
8	1.732	1.105	11.823	14.190	0.045	0.618	1.811	96.130
9	0.332	0.212	2.264	2.717	0.009	0.118	0.347	18.408
10	0.037	0.024	0.254	0.305	0.001	0.013	0.039	2.065
TOTAL	**10.26**	**6.55**	**70.02**	**84.04**	**0.27**	**3.66**	**10.73**	**569.31**

Note: Results represent the volume of sediment from each River section multiplied by the 2011 average sediment concentration (n=29) for the 20-cm depth horizon and the 100-cm depth horizon.

CHALLENGES

This was a very challenging sediment remediation site for several environmental, occupational, and implementation reasons (Figure 3). Risks to successful implementation of this remediation project included but were not limited to:

- Occupational health and safety concerns due to extremely high contaminant concentrations, multiple exposure pathways, and incomplete performance expectations for bank stabilization and source control.
- The overall objectives and beneficial uses of the Xiawangang River had not been defined.
- The remediation and rehabilitation performance goals had not been defined and thus the scope of work had several unrefined assumptions for overall success and subsequent contractor(s) compensation.
- There was limited in-channel footprint for sediment management, therefore processing (e.g. stabilization and solidification) of contaminated materials would primarily occur off-site.
- The work zone had several areas of restricted access due to active industrial facilities, power lines, pipelines, steep and unstable channel banks, railways and roads.

Additional challenges to performing a sediment remediation and subsequent rehabilitation at this site included several data gaps such as:

- Previously conducted remedial investigations and feasibility studies were incomplete, but were subsequently used to develop remediation and treatment recommendations and project goals. Additionally, these investigations and recommendations were performed by third party researchers with no prior experience in sediment remediation and without clearly defined objectives.
- "Ground-truthing" of project objectives and performing data gap investigations was not performed, which led to increased risk(s) of executing this remediation project.
- There was no regional guidance on development of a Stormwater Management Plan.
- There was no regional guidance on point and nonpoint source control other than relocation of point source dischargers out of the watershed.
- Design and execution of the current remediation plan had no operation and monitoring component as part of a sustainable remediation plan except a Wastewater Discharge Standard (Class I-B) permit monitored at the outfall to the Xiangjiang River.

F
Figure 3.

- There was no risk-based effects guidance for this type of watershed and thus the assumptions for deriving clean-up performance goals were analytically derived versus environmental effects-based.

Defining the Performance Objectives

In order to define success of this sediment remediation, we proposed to use mass removal of targeted contaminants (e.g., Cd, Pb, As, and Hg). Typically, analytical guidelines are used to derive effects-based goals and thresholds (e.g., ecological toxicity bioassays) of water and sediment at designated monitoring stations (e.g., discharge of creek into River). Our assumption for this project was that by removing a targeted mass of these metals from the Xiawangang Watershed, environmental risks within the watershed and at the discharge will be reduced below these effects-based goals. Overall, a sediment removal performance assessment program was detailed to monitor and measure the mass of sediment, trash, debris, and associated metals contamination removed from each section of the Xiawangang River during this remediation effort.

Technical Approach

An implementation plan, timeline to completion, and river section construction sequence were outlined including engineering details of channel access, water control structures, TSS management, sediment excavation and management techniques, challenges, assumptions, and other operational guidance (Table 3 and Figure 4).

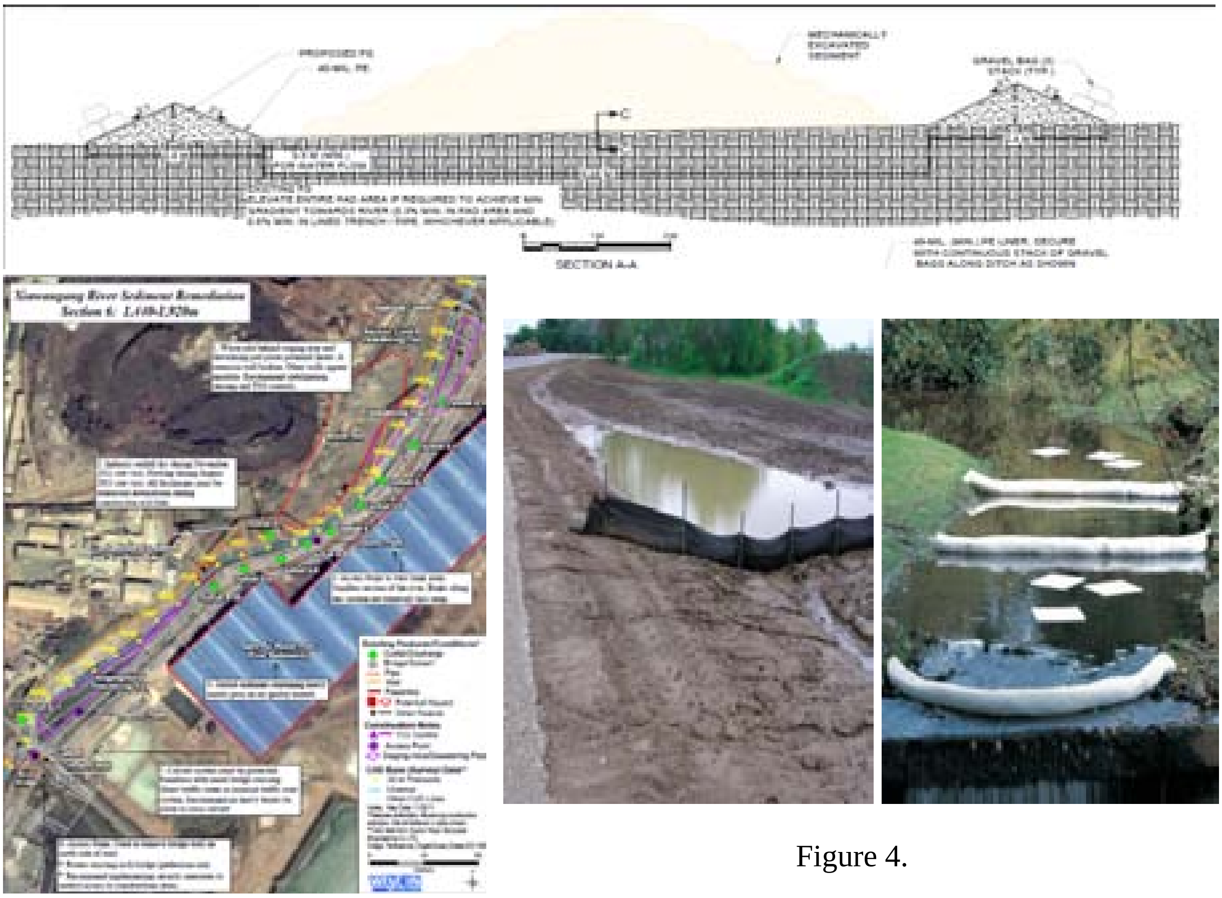

Figure 4.

Table 3. Implementation Plan Summary, Timeline to Completion, and River Section Construction Sequence

Section	Transect (m)	*In situ* Sediment Volume (m3)	Total Mass* (dry metric tons)	S/S Volume** (m3)	Timeline to Completion+ (days)	Construction Sequence
1	3070 - 4060	5,584	12,696	4,120	28	2
2	2840 - 3070	1,790	4,068	1,321	9	3
3	2260 – 2840	5,436	11,948	4,120	54	4
4	2020 – 2260	246	508	195	6	3
5	1920 – 2020	2,002	4,136	1,588	15	4
6	1440 – 1920	6,077	12,562	4,826	30	3
7	780 – 1440	8,200	17,424	7,104	41	2
8	230 – 780	6,229	13,232	5,397	31	3
9	40 – 230	1,193	2,658	970	12	4
10	0 - 40	134	298	109	12++	1***
TOTALs		36,891	79,530	29,750 (59,500 mt)	95+++	

*average specific gravity = 2.0
**Assumes no gravel, cobble, or rock
***Excavate discharge area and install turbidity curtains
+30 days mobilization (e.g., access ramps and dewatering pads)/6 days performance verification and demobilization per River Section
++Excavation of a sediment retention basin at the discharge and turbidity curtain installation
+++100 m3 excavated and hauled to temporary staging or processing area per day per River Section (weather permitting)

River Section 6 - Site Specific Example

Assumptions - Primary access is limited to the west bank at the highway. A secondary bridge and privacy/security wall are located on the upstream side of the bridge (west bank) and will need to be protected against heavy loads and/or removed for construction of an access ramp to this operational section. Turbidity curtains will be used at the 1400 m bridge and downstream of excavation activities as necessary. A sediment retention basin will be constructed at 1280 m.

Challenges - Access to section 1660 to 1920 m is limited by overhead pipes (Figure 5). Bank stabilization and outfall management are critical in this section (particularly the west bank) due to degrading retaining walls, bank instability, and lack of source control.

Mechanical Sediment Excavation

- Construct access ramps and sediment staging areas on the east bank of the Xiawangang River at 1440 and 1720 m, upstream and downstream of overhead pipes. Access on the east bank is possible with removal of several brick security walls

Figure 5.

and widening/stabilization of the access road. An access ramp would need to be constructed at both locations to navigate around overhead pipes.

- Water control at the industrial plant outfall will have to be installed to manage water volume and sediment excavation would take place in the wet. Alternatively, discharges from these plants will have to be diverted downstream around the channel during excavation.
- Construct a sediment management/dewatering area along the east bank, upstream of the 1460 m access ramp. Another sediment staging area may be constructed on the west bank at 1800 m and the east bank at 1900 m.
- Use excavators, front-end loaders, skid steers, and/or laborers to excavate the sediments from 1440 to 1920 m.
- An overhead pipe is located at 1660 m and will allow for small equipment and skid steer excavation only. The channel is shallow, wide, and stable. However, several waste pile retaining walls are crumbling, unstable and at risk for further degradation. Revetments and shoreline protection will be required to minimize additional runoff.
- Additional TSS management (e.g., turbidity curtains and sediment retention basin) will be controlled at the 1400-m bridge.
- Use front-end loaders and skid steers to transport sediment, trash, and debris from dewatering pad to trucks.

Summary - There is a difference in opinion about the use of novel and/or sparsely available equipment and technologies in order to accomplish remediation and restoration goals in China. Although the regulatory authority and other government agencies welcome the use of global approaches, equipment, and technologies and are working diligently to establish regulatory guidance and protocols, Chinese contractors and engineering firms are reluctant to risk failure and execute sediment remediation projects with anything other than maximum labor and minimum technology. For example, the sediment remediation project proposed for the Xiawangang River required less than 10 workers with proper excavation equipment and technical guidance to safely remediate the Xiawangang River in 90 operational days. However, local contractors were not incentivized and chose to use 100s' of laborers, shovels, and wheelbarrows to remove contaminated sediments with minimum regard for human health (due to potential contaminant exposure) and/or safety (due to unsafe working conditions).

The upside to using manual labor for sediment excavation in China is there is a willing and able work force available everyday to work hard in extreme conditions. The downside of this work force is their overall inexperience working in difficult environmental and occupational conditions while supervised by inexperienced managers and no one with the ability to recognize risk(s) as they occur. The upside to using modern technology and equipment is the increased safety, increased performance efficiency, and reduced number of laborers in the exclusion zone. The downside is the lack of equipment, experienced operators, and experienced contractors in China, potential delays due to equipment break-downs and/or lack of spare parts, and the populace's slow acceptance of these approaches *in lieu* of labor-only execution. Overall, China is quickly recognizing the need for balance, simultaneously incentivizing local contractors to use more modern means to perform sediment remediation while maintaining a work force that is adequately trained to work safely in these difficult environments where equipment is not able to access.

Contaminated Sediment Remediation and Restoration: Comprehensive Approach

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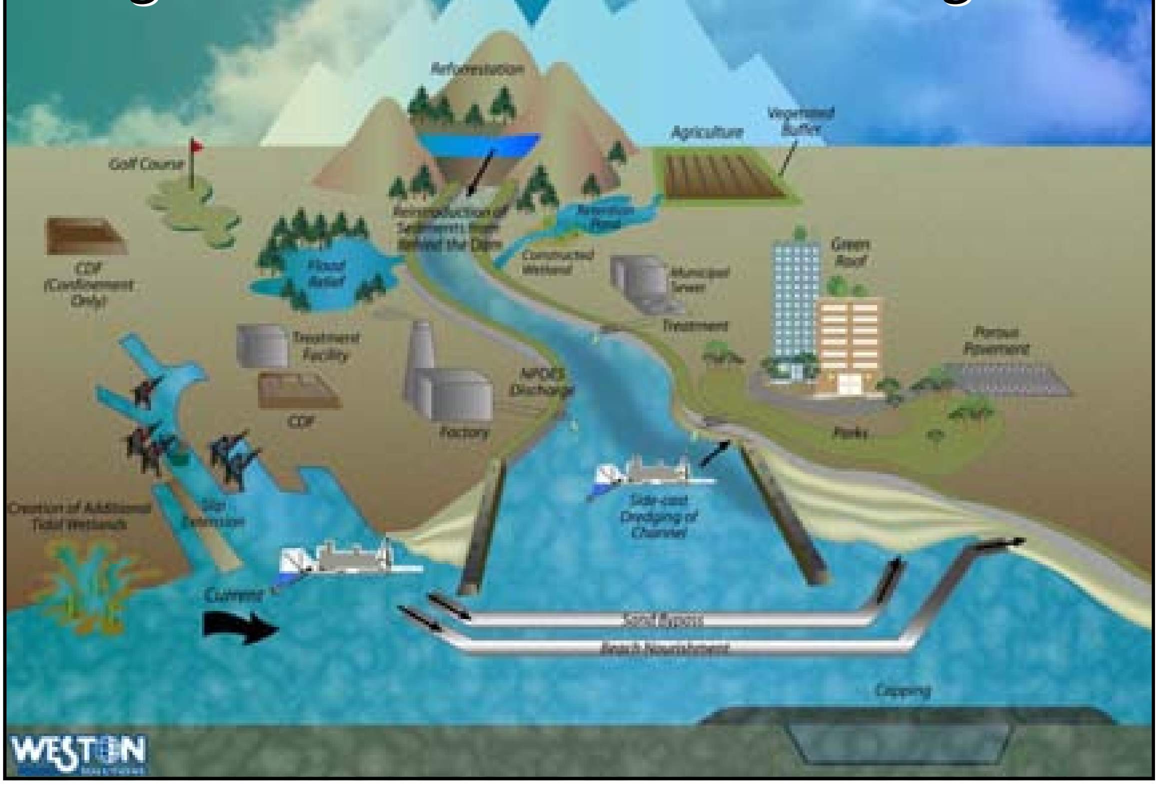
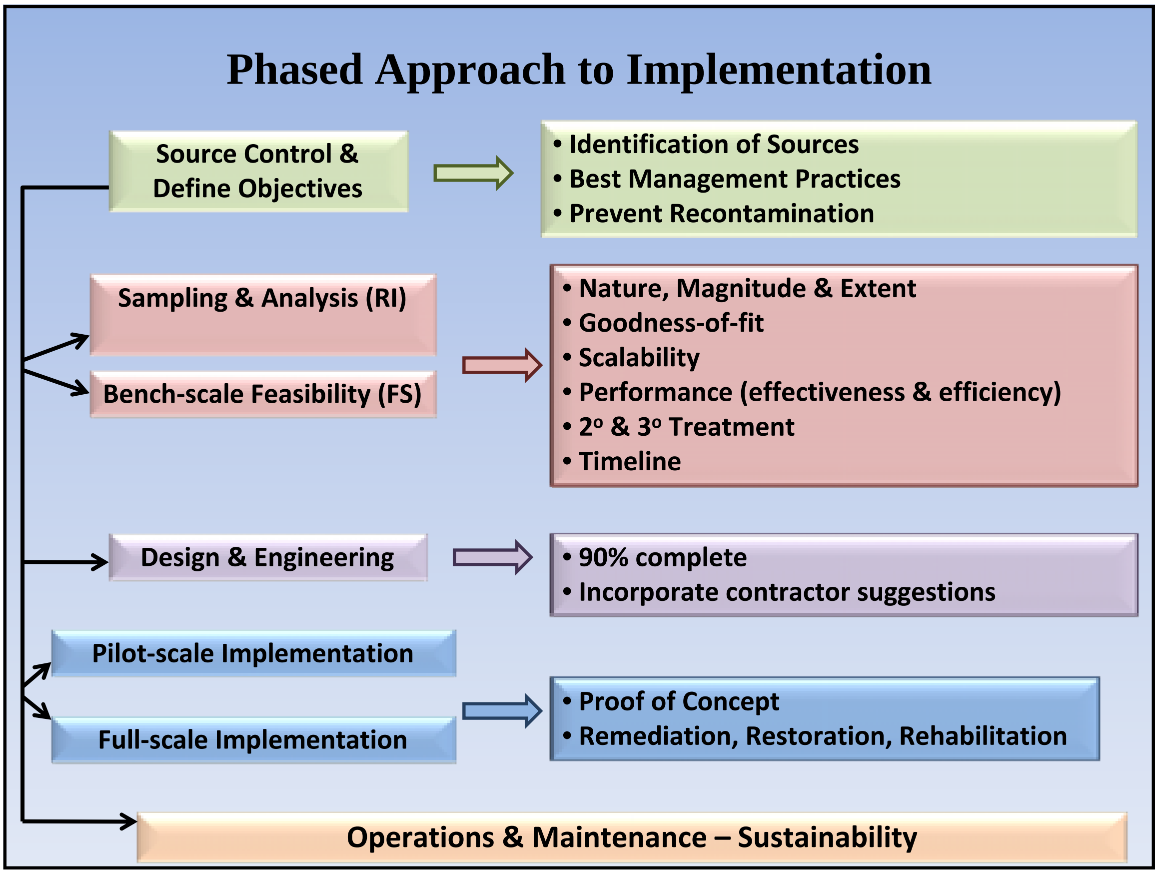
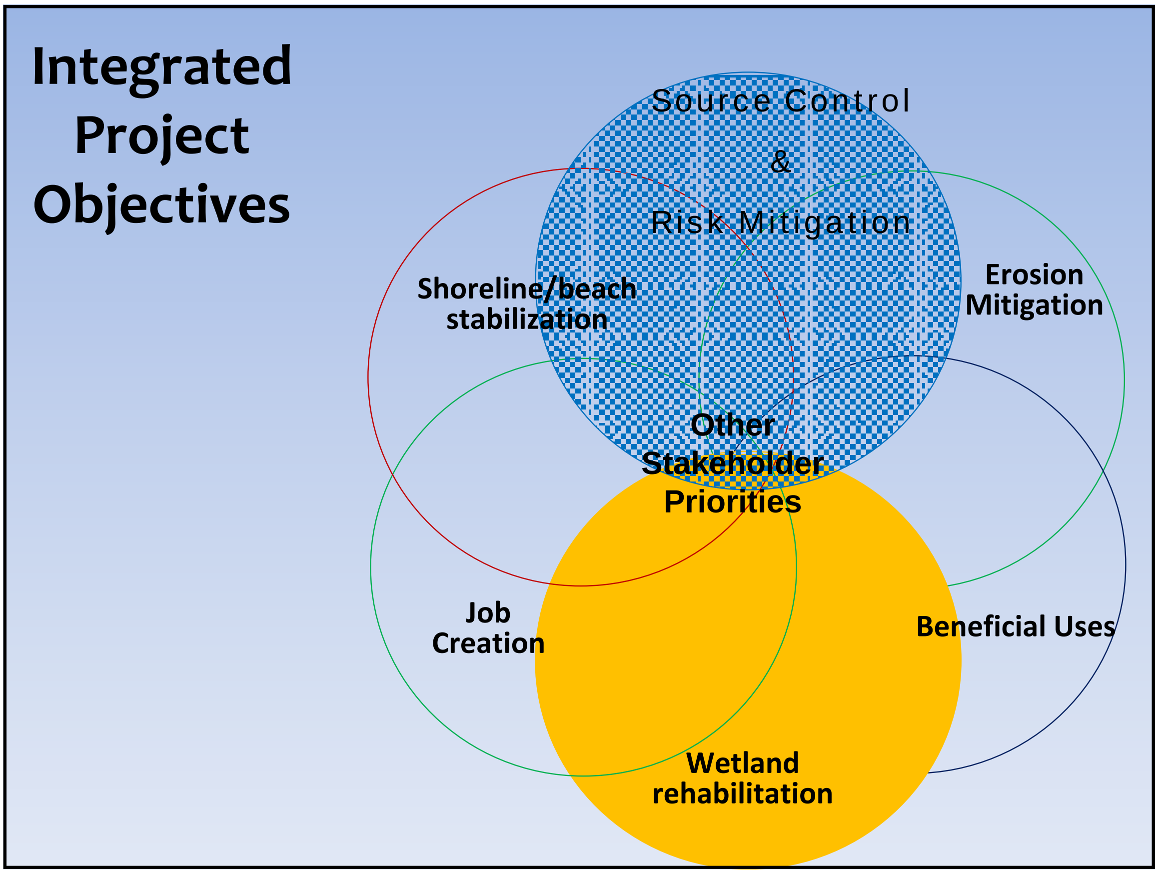



Phased Approach to Implementation
Source Control & Define Objectives
• Identification of Sources
• Best Management Practices
• Prevent Recontamination
Sampling & Analysis (RI)
Bench-scale Feasibility (FS)
• Nature, Magnitude & Extent
• Goodness-of-fit
• Scalability
• Performance (effectiveness & efficiency)
• 2º & 3º Treatment
• Timeline
Design & Engineering
• 90% complete
• Incorporate contractor suggestions
Pilot-scale Implementation
Full-scale Implementation
• Proof of Concept
• Remediation, Restoration, Rehabilitation
Operations & Maintenance – Sustainability


Integrated Project Objectives
Source Control & Risk Mitigation
Shoreline/beach stabilization
Erosion Mitigation
Other Stakeholder Priorities
Job Creation
Beneficial Uses
Wetland rehabilitation

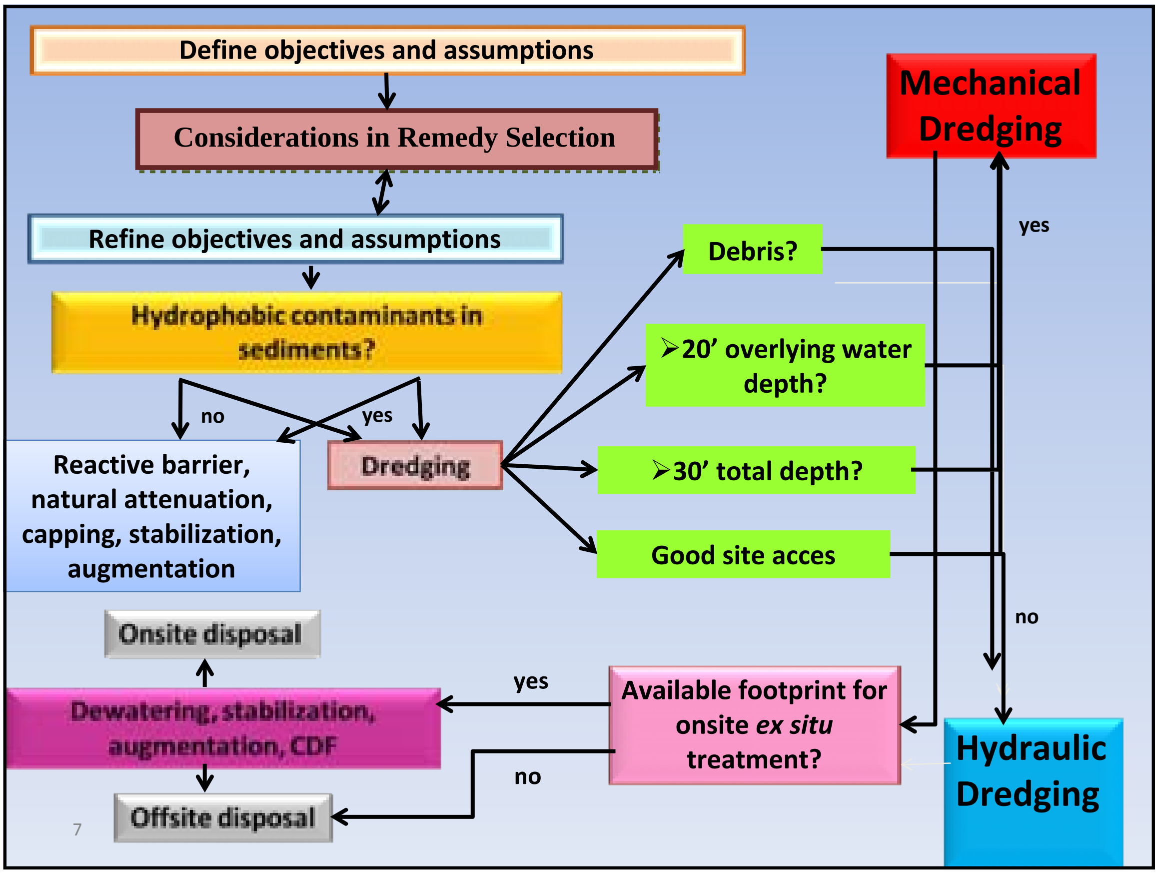
Risk Management Goals and Objectives for Successful Remediation

Typically use several sediment quality metrics to determine the contaminants of concern and biological risks for each Site based on established benchmarks & multiple lines of evidence (weight of evidence approach).

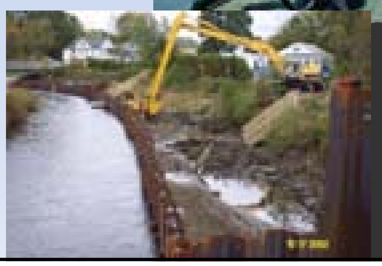
1. **Analytical endpoints and thresholds**
2. **Toxicity to sentinel test species**
3. **Benthic community assessment (simultaneously evaluated with habitat conditions)**
4. **Biological tissue concentrations (i.e., bioaccumulation in benthic macroinvertebrates and/or fish species)**

Considerations in Remedy Selection

- Extent & Magnitude of contamination
- Identification/isolation of source
- Stability of the Site
- Proximity of sensitive receptors
- Engineering Feasibility
- Cost
- Societal/ Cultural concerns
- Risk/Uncertainty
- Permanence
- Fate chemistry
- Weather
- Hydrology, tides, water temperature
- Geomorphology
- Equipment availability & mobilization
- Residuals
- Post-treatment of water and air
- Available onsite footprint
- Disposal options and availability
- Monitoring requirements
- Contaminated media
- Neighbors/work restrictions



Current Strategies & Technologies for Metals-contaminated Sediments



Removal

- Dredging
  - Mechanical (e.g., environmental bucket)
    - ➢ Pros: manage material directly, < water
    - ➢ Cons : > residuals, limited precision, < production
  - Hydraulic (e.g., hydraulic pump, dredge)
    - ➢ Pros: > precision, < residuals, less re-handling, > production
    - ➢ Cons: >> water
- Excavation in the Dry
  - ➢ Pros: >> precision, << water, < residuals
  - ➢ Cons: >> costs, <production

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Current Strategies & Technologies for Metals-contaminated Sediments

Ex-Situ **Treatment**

- **Dewatering (geotextile tubes, mechanical technologies, retention basin)**
- **Physical separation (hydrocyclones)**
- **Addition of ammendments (cement, fly-ash) for dewatering & stabilization**
- **Land farming, biopiles, phytoremediation, mycoremediation etc.**
- **More aggressive treatment process (soil washing, chemical oxidation, thermal treatment, etc.**

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Soil Washing Technologies

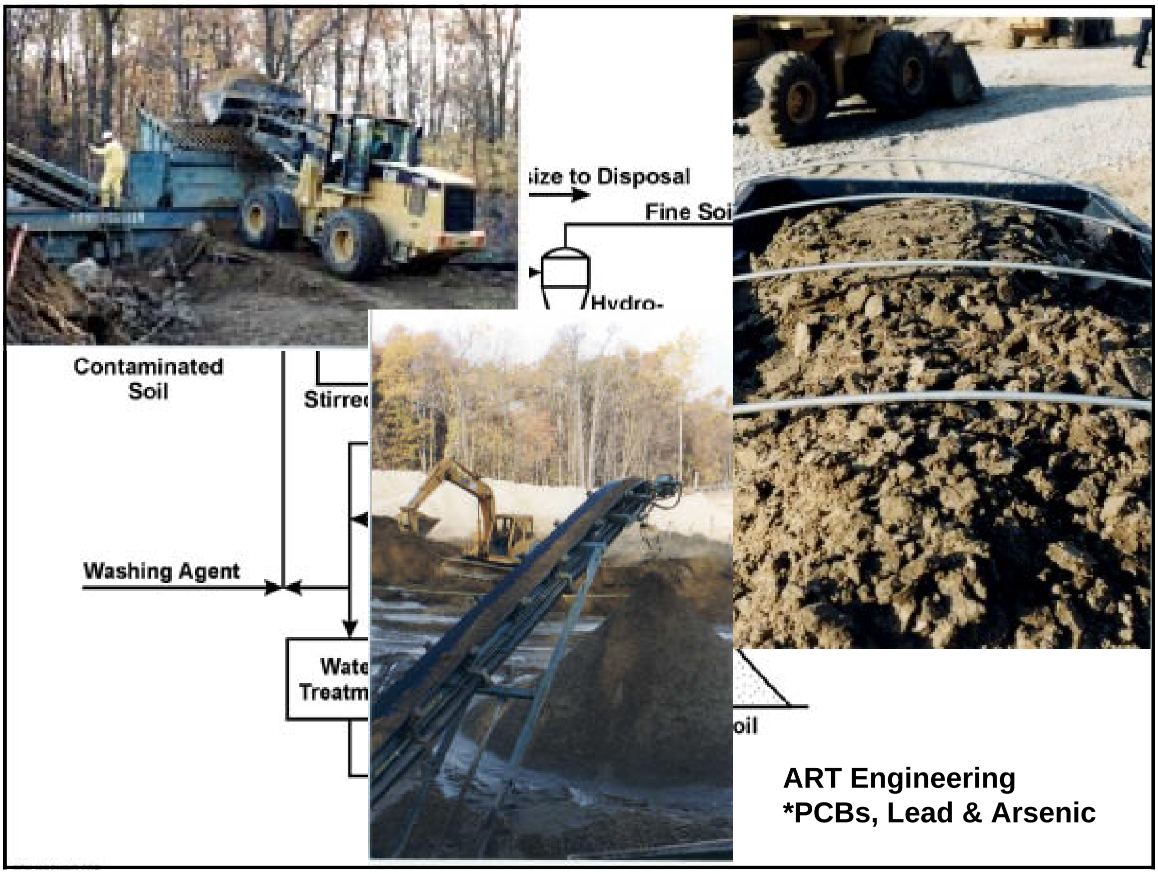
1) Dissolving or suspending contaminated soils in a wash solution (e.g., chemical manipulation of pH for a period of time); or

2) Concentrating contaminated soils into a smaller volume of soil through particle size separation, gravity separation, and attrition scrubbing.

*The contaminated water generated from soil washing is treated with the technology(s) suitable for the contaminants.

Factors that may limit applicability and effectiveness include:

- Complex waste mixtures (e.g., metals with organics).
- High humic content in soil may require pretreatment.
- The aqueous stream will require treatment.
- Additional treatment steps may be required to address hazardous levels of washing solvent remaining in the treated residuals.
- It may be difficult to remove organics adsorbed onto clay-size particles



ART Engineering
*PCBs, Lead & Arsenic

ART Engineering
King of Prussia Superfund Site
*Chromium, Copper & Nickel

Selected Case Studies

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12 Mile Creek – Lake Hartwell, SC

- 300,000 cubic meters of PCB and metals contaminated sediment from two stretches of the creek .
- Goal is removal of two dams to facilitate natural attenuation of impacted sediments in the downstream lake, and restoration of the creek for recreational use.
- Water treatment system for dewatering of excavated sediments, designed to polish up to 380 L/s prior to discharge back to creek under state permit.

Atlas Tack

- Former manufacturing facility dumped metals, cyanide, SVOCs, PCBs, pesticides, VOCs and other solid wastes in and adjacent to the estuarine marsh.
- Treated:
  - 4,500 tons of lead and cadmium-contaminated material using stabilization techniques.
- Characterized, transported and disposed:
  - 108,000 tons of soil, sediment, debris, and crushed brick and concrete.
- Restored:
  - 32 acres of low and high saltwater marsh.
  - 760 meters of tidal creek and tributaries.
  - 28 acres of freshwater emergent wetland.
  - 73 acres (approx.) of upland areas.

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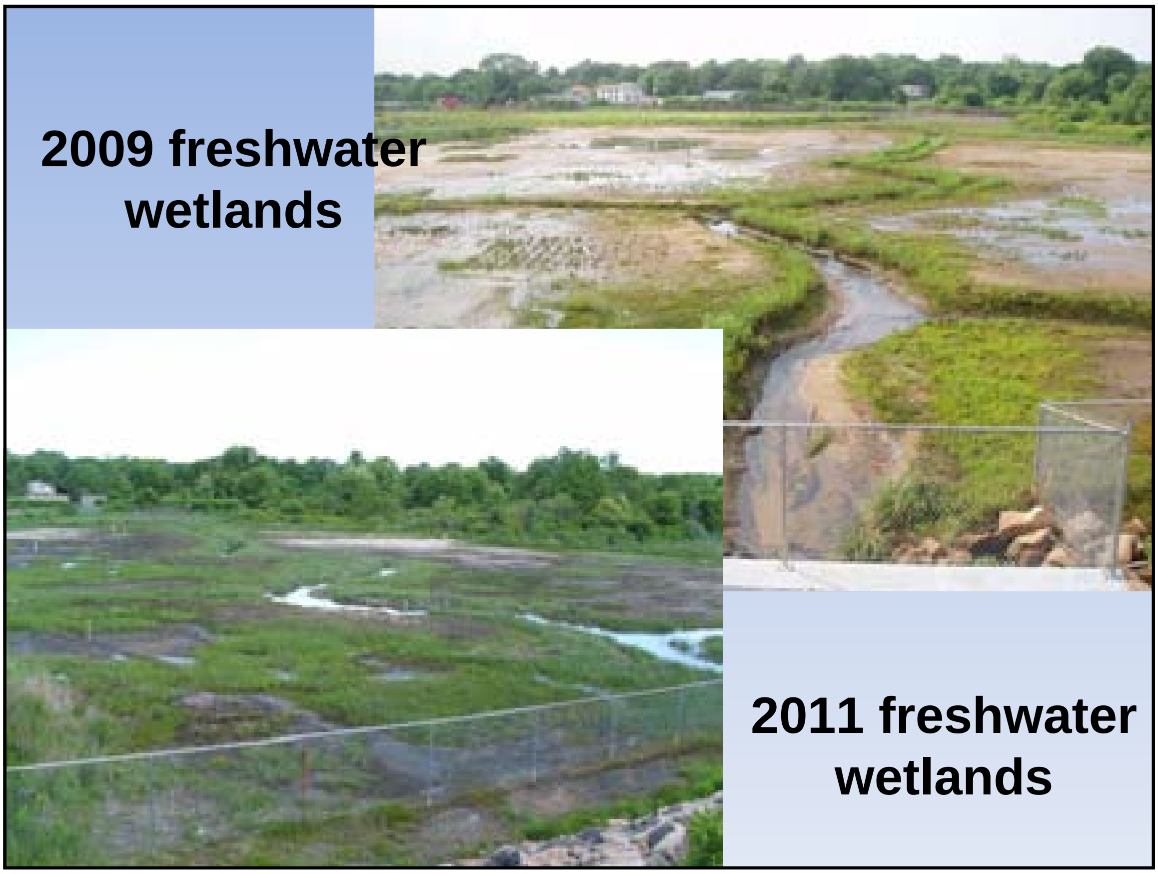

2009 freshwater wetlands
2011 freshwater wetlands


BUCK MINE, Michigan
– Metal polluted site
• Permits
• Site preparation, construction of dewatering facilities and haul routes
• Mechanical dredging in the wet
• Adding pH-neutralizing limestone
• Construction of flow control structures
• Construction and installation of an emergency spillway
• Restoration of wetland areas

Miami River, FL

Fully integrated dredging and sediment processing approach to remove 550,000 cubic meters of sediment

Sediment processing method:

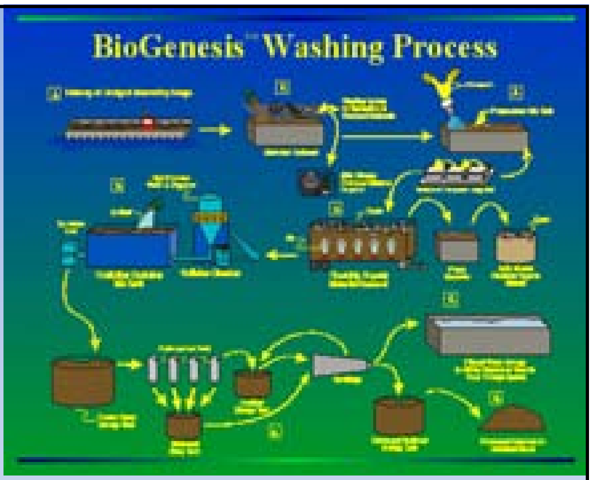
- Sand separation/mechanical dewatering
- Direct loading into trucks from barges at the dockside processing site
- Gravity draining in a staging area

Debris, tires, and rock are removed at the dockside processing site

Metals are separated to the greatest extent possible for reclamation

Dredge return water is utilized for separated material washing in a closed loop system. Excess water is treated before being discharged back into the river.

Both the dredging and land-side operations are monitored to limit and minimize noise, odors, and air pollution, including dust.

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Historical Trends of Dioxin-like Compounds and Brominated Flame Retardants in Sediments Buried in Different Reservoir Systems in Taiwan

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Abstract

Dated sediment cores provide the reference record to investigate the historical input of persistent organic pollutants into the environment and identify possible sources in the vicinity area. In this study, two sediment cores, one at Feitsui Reservoir and the other at Sun Moon Lake (SML) were taken in 2008 and 2009 in north and central of Taiwan, respectively. Samples were Soxhlet-extracted and cleaned up by the CAPE Technologies coupled carbon-acid silica column, and the concentrations of seventeen 2,3,7,8-polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), twelve dioxin-like polychlorinated biphenyls (DLPCBs), and twenty-four polybrominated diphenyl ethers (PBDEs) were measured by HRGC/HRMS in SIM mode. The concentrations of PCDD/Fs and DLPCBs in different depth of sediment cores ranged from 0.036 to 2.63 ng WHO-TEQ/kg and 0.021 to 0.251 ng WHO-TEQ/kg, respectively, at Feitsui Reservoir. The high values were detected from 1998 to 2000. The results indicated that the increase in the PCDD/Fs and DLPCBs concentration of the sediment core was related to the operation of municipal solid waste incineration (MSWI) in the vicinity area of the Feitsui reservoir. Additionally, the concentrations of PCDD/Fs and DLPCBs measured in sediment core collected at Sun Moon Lake ranged from 1.14 to 4.42 ng WHO-TEQ/kg and 0.005 to 0.305 ng WHO-TEQ/kg, respectively. The high values were detected from 1971 to 1978. The results indicated that the variation of PCDD/Fs and DLPCBs contents in different depth of sediment core is similar to that of the pesticides (DDT, PCP and CNP) usage in Taiwan. OCDD contributed more than 95% to the total PCDD/Fs concentration in all samples, while PCB-118 was the most dominant congener of DLPCBs, followed by PCB-105 and PCB-77. In addition, the concentrations of 24 tri- through Deca-BDE congeners in the sediment core collected at Feitsui Reservoir range from 0.129 to 6.75 ng/g, followed by BDE-209, BDE-47 and BDE-99. The sediment core collected at SML range from 0.041 to 2.16 ng/g, followed by BDE-209, BDE-207 and BDE-183.

Key words: PCDD/Fs, PCBs, PBDE, core, pesticide.

Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (DLPCBs) are persistent organic pollutants (POPs), which are formed and released unintentionally from anthropogenic sources. These compounds have accumulated for many years in environmental sinks such as soils and sediments due to their persistence in environmental matrices. Moreover, it has been shown that PCDD/Fs are impurities found in commercial pentachlorophenol (PCP) products[1]. Therefore, the impure compounds found in soils and sediments are another source of PCDD/F contamination in addition to those resulting from combustion and industrial processes. Brominated flame retardants, including polybrominated diphenyl ethers (PBDEs) have been incorporated in numerous products to reduce flammability. PBDEs are relatively persistent in the environment and have the potential to bio-accumulate through the food chain. As sediment is the ultimate sink for persistent pollutants, including PCDD/Fs and heavy metals, vertical profiles of residues in dated sediment cores have been used as historical records of pollution[2]. Several studies have investigated the vertical profiles of dioxin-like compounds in sediment cores and have found the depositional histories of these persistent compounds in the sediment bed [3,4]. In this study, the vertical profiles of a wide variety of PCDD/Fs, PCBs and PBDEs in two sediment cores, collected from Feitsui Reservoir and Sun Moon Lake (SML) in northern and central Taiwan, respectively were evaluated. Feitsui Reservoir is the source of domestic water supply for the Taipei Metropolitan Area (Figure 1), which with a storage capacity of 406 million m^3 is approximately 170 m above sea level. The catchment area is 30 times greater than the reservoir surface area. Reservoir construction began in mid-1979 and was completed for water storage in mid-1987. The SML is located (23°52′N, 120°55′E) near the geographical center of the island (Figure 2). Prior to 1919, the lake surface was 727 m above sea level, with an original surface area of 5.4 km^2 and mean water depth of 4.6 m. Following the construction of a dam which was completed in 1939, the water table rose by as much as 23 m and the surface area of the reservoir expanded to 8.4 km^2. SML is a high-mountain lake which is far away from the municipal or industrial areas, a unique place to study the atmospheric deposition of anthropogenic pollutants. Hence, we consider that the lake is a relative natural setting for monitoring the atmospheric fallout of dioxin-like compounds and PBDEs.

Materials and methods

In June 2008, a 64 cm sediment core was collected at a location downstream near the Feitsui Reservoir (Figure 1) in northern Taiwan. The site was at the former site of a tea farm along riverbanks that were flooded after the reservoir's completion. In 2009, a sediment cores (34 cm) was sampled at south bay of the SML (Figure 2) in 2009. The core was delivered to the laboratory within 2 hours and was sectioned immediately to slices with thickness of 1 cm. In this study, sediment samples were freeze-dried and then ground to 100-200 mesh-sized powder using an agate mortar and pestle. The water content of the sediment was calculated based on the variation of the mass weight of sediment before and after freeze-dried process. The sediment cores were analyzed for PCDD/Fs as well as age determination (^{210}Pb and ^{137}Cs), total organic carbon (TOC) and water content. For PCDD/Fs, DLPCBs and PBDEs analysis, the sediment core samples were then spiked with known amounts of US EPA Method 1613, M1668B and Wellington WP-CVS, as internal quantification standards. The samples were analyzed with high-resolution gas chromatography (HRGC)/high-resolution mass spectrometer (HRMS) (Jeol JMS-700). In this study, ^{210}Pb was measured via its daughter isotope ^{210}Po (half life:138 days) by alpha spectrometry. In general, the sedimentation rate estimated by ^{210}Pb was based on stationary deposition. In contrast, ^{137}Cs gives more accurate dates, and is particularly useful for recent sedimentation studies. Based on the TOC measurements, the mean sedimentation rate of Feitsui Reservoir was determined to be 3.1 cm/year. In SML ^{210}Pb was measured by alpha spectrometry via its daughter isotope ^{210}Po (half life: 138 days). The profiles of excess ^{210}Pb in sediment core collected at south bay of SML are shown in Figure 3. Similar depth profiles of excess ^{210}Pb were also obtained by gamma counting of ^{210}Pb (Figure 3). As seen in Figure 3, the mean sedimentation rates of the sediment core collected at SML were determined as 0.47±0.13 cm/year. This agrees with the results obtained using the alpha counting method (0.48±0.13 cm/year). Figure 3 also shows the down core distribution of ^{137}Cs activity with peaks occurring at depths of 15.5 cm at the center, outflow and south bay of SML. The peak corresponded to measurement of the historical fallout maximum in 1963. From the ^{137}Cs profile (Figure 3), we estimated the mean sedimentation rate at south bay of SML from 1963 to be 0.34 cm/year, which is in agreement with those derived from ^{210}Pb dating. Hence, sedimentation rate at the south bay of SML were determined to be 0.47±0.13 cm/year, based on the depth profile established through gamma counting of ^{210}Pb.

Results and discussion

The measurement results (Figure 4) indicated that the concentrations of PCDD/Fs and DLPCBs in different depth of sediment cores ranged from 0.036 to 2.63 ng WHO-TEQ/kg and 0.021 to 0.251 ng WHO-TEQ/kg, respectively, at Feitsui Reservoir. The high values were detected from 1998 to 2000. Prior to 1991, no significant PCDD/F and DLPCB emission sources existed in the area of the reservoir of interest. However, the rapid increase in municipal solid waste (MSW) in Taiwan motivated the government to enact a policy of building large-scale municipal solid waste incinerators (MWIs) island-wide during the 1990s. From 1991 to 1996, four large-scale MWIs in the vicinity of the reservoir of interest were built and started to operate successively. Analysis results demonstrate that the PCDD/F concentration of the sediment core measured in the reservoir reached their peak when the MWIs in the area started to operate. In August 1997, the Taiwanese government set 1.0 ng TEQ/Nm^3 as the PCDD/F emission limit for existing large-scale MWIs, tightening it to 0.1 ng TEQ/Nm^3 from August 2001. In Figure 4, the PCDD/F and DLPCB concentrations of the sediment core decreased from 2.63 and 0.251 WHO-TEQ/kg in 1998 (depth: 22 cm) and 1999 (depth: 24 cm), respectively, to 1.28 and 0.134 WHO-TEQ/kg in 2001 (depth: 29 cm). Hence, the significant decrease in the PCDD/F concentration in sediment core observed in 2001 may be related to the new PCDD/F emission limits (0.1 ng TEQ/Nm^3) promulgated in August 2001. The technologies retrofitted to reduce PCDD/F emissions from existing MWIs were evaluated at that time. In the core sampled at the south bay of SML, the water content at each depth of the sediment core increased with increasing TOC content. The reservoir was completed for water storage use in 1939. In those early years, submerged soil and plants released nutrients back into the water body, enhancing primary productivity. The representative year of the sediment core collected at the south bay of SML estimated from the ^{210}Pb profiles also indicate that the year of depth 34-36 cm would be around 1939. This estimated year was comparable to the depth which showing significant increases in TOC and water content. Figure 5 shows that the PCDD/F (1.14 to 4.42 ng WHO-TEQ/kg) and PCB (0.005 to 0.305 ng WHO-TEQ/kg) concentrations in sediment cores measured at south bay of SML were higher than those measured at Feitsui Reservoir in northern Taiwan. The high values were detected from 1971 to 1978. Based on the $^{210}Pb_{ex}$ and ^{137}Cs activity analyzed (Figure 3) in the three sediment cores at SML, Figure 5 shows the temporal trends of PCDD/F and DLPCB concentrations measured in sediment core at SML.Our measurements indicated that the PCDD/F and DLPCB concentrations increased in the 1970s. A previous report indicated that around 1,000 tons of pentachlorophenol (PCP) were generated in Taiwan during the 1960s and 1980s. The previous study[1] indicated that the significant higher PCDD/F concentration (130 to 26,000 ng I-TEQ/g) was measured in the active ingredient of PCP. The most abundant congeners were OCDD and H_pCDD. That was similar with our measurement conducted in the sediment samples. The higher chlorinated PCDD/Fs in sediments may be owing to that the major mass fluxes of OCDD originate from the impurities in PCP directly into the sediment[1]**.** In this study, the PCDD/F and PCB concentrations within the sediment core began to increase in 1960 and reached a peak (4.42 and 0.305 ng WHO-TEQ/kg) in 1971 and 1974, respectively. In 1985, the Taiwan government proposed the regulation of PCP manufacture and use; hence, the variation in PCDD/F content within the sediment cores correlates with the rate of pesticide production in Taiwan. As a replacement for PCP, CNP came into extensive use a field herbicide in Taiwan during the 1980s. Over 6,000 tons of Chlornitrofen (CNP) were generated in Taiwan during the 1970s and 1990s. In 1995, the Taiwanese EPA proposed regulations concerning the manufacture and use of CNP. Hence, a decreasing trend in the PCDD/F content of sediment cores collected in SML was observed in this study. In addition, the concentrations of 24 tri- through Deca-BDE congeners in the sediment core collected at Feitsui Reservoir range from 0.129 to 6.75 ng/g, followed by BDE-209, BDE-47 and BDE-99. The sediment core collected at SML range from 0.041 to 2.16 ng/g, followed by BDE-209, BDE-207 and BDE-183.

Acknowledgements
The authors acknowledge the financial supports provided by Taiwan EPA (EPA-97-E3S4-02-04, EPA-98-E3S4-02-05 and EPA-99-E3S4-02-03) and National Science Council (NSC 101-2111-M-010-001-) of the Republic of China.

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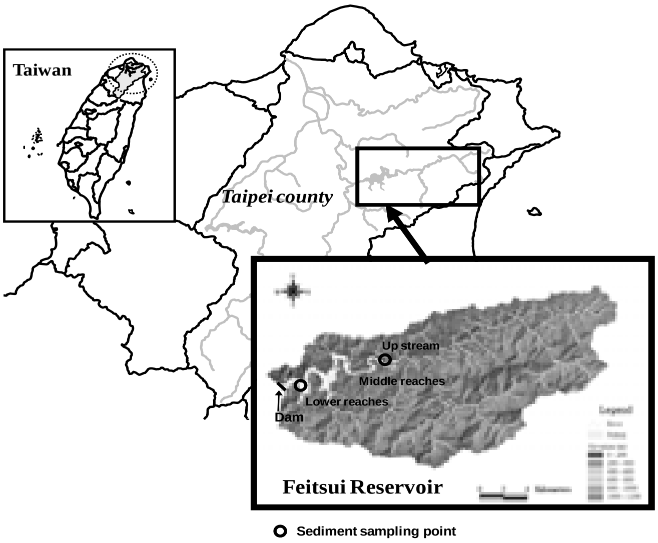

Figure 1 Relative location of sampling site in Feitsui Reservoir in northern Taiwan.

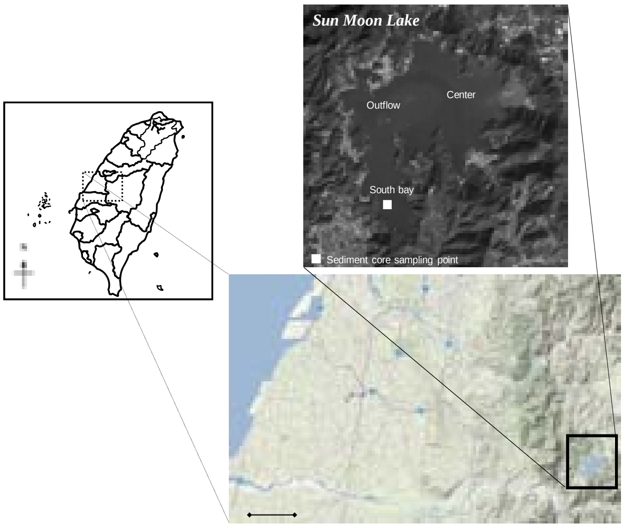

Figure 2 Relative locations of sampling sites in Sun Moon Lake in central Taiwan.

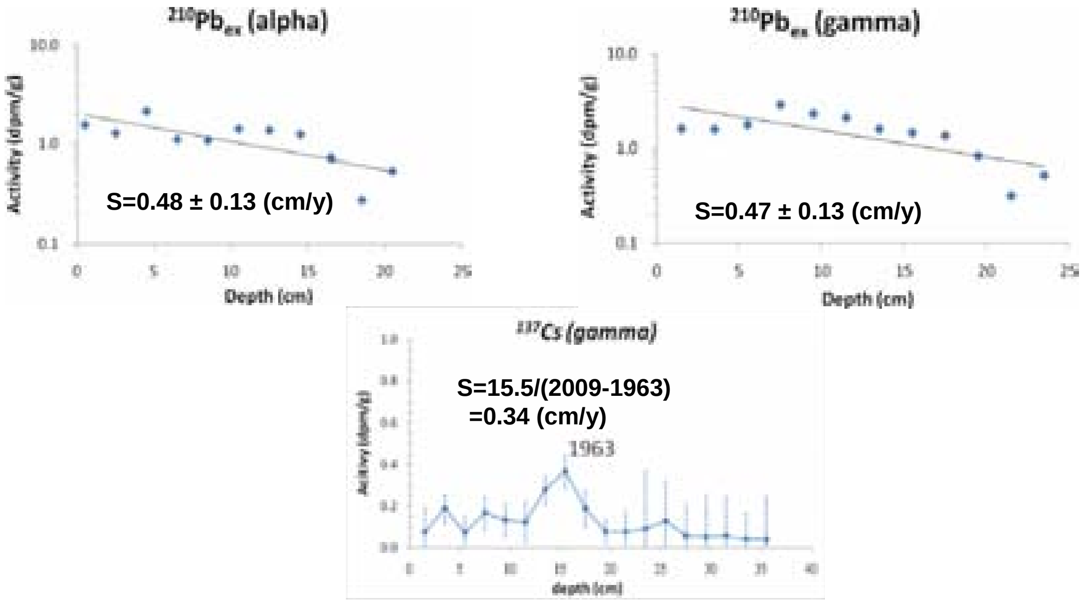

Figure 3 The depth profile of $^{210}Pb_{ex}$ and ^{137}Cs activity in sediment core at south bay of SML.

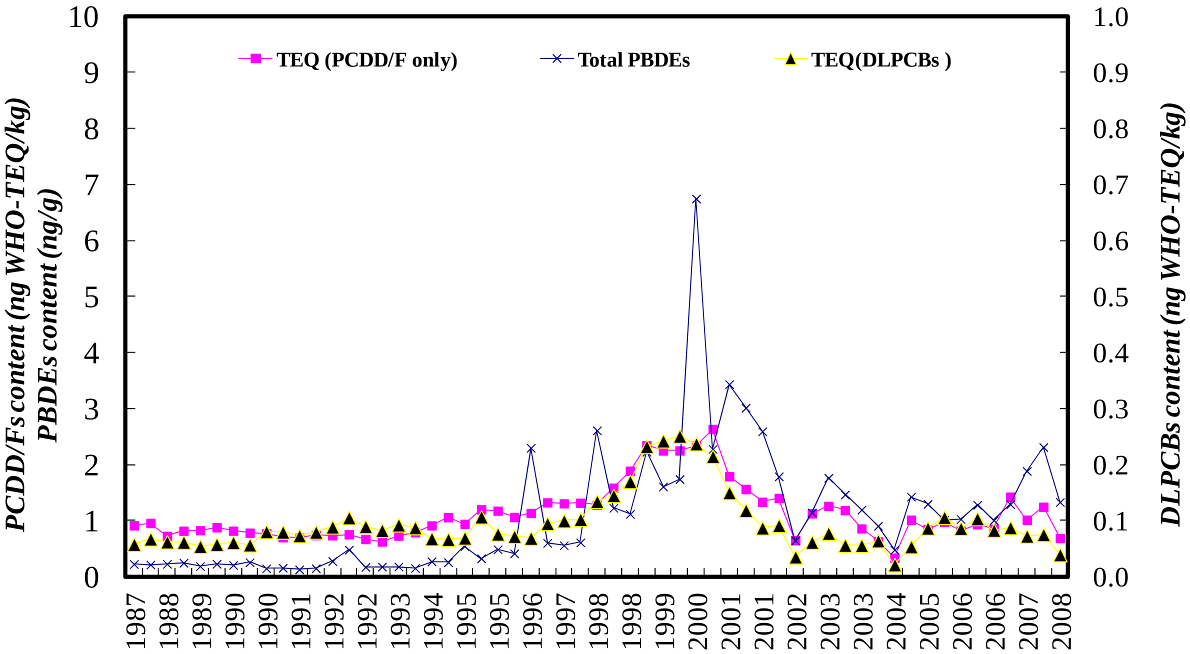

Figure 4 Temporal trends of PCDD/F, DLPCB and PBDE concentrations of the Feitsui Reservoir in northern Taiwan.

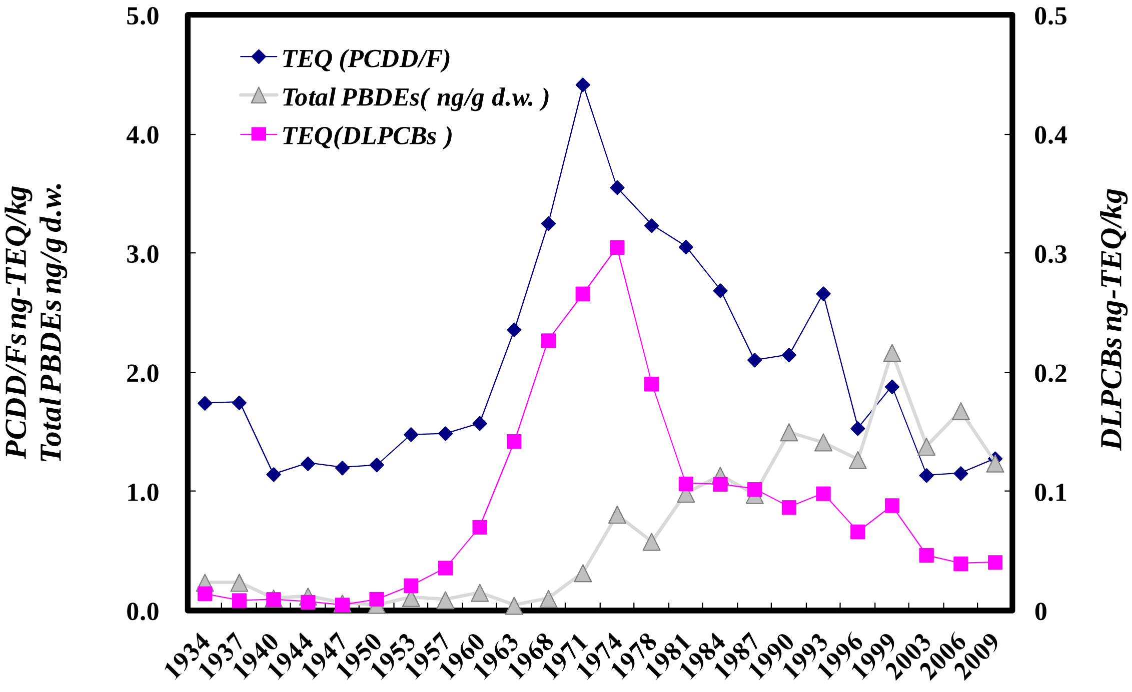

Figure 5 Temporal trends of PCDD/F, DLPCB and PBDE concentrations of the SML in central Taiwan.

Historical Trends of Dioxin-like Compounds and Brominated Flame Retardants in Sediments Buried in Different Reservoir Systems in Taiwan

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Moo Been Chang [c] and Kai Hsien Chi [d]

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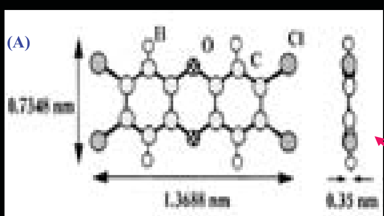
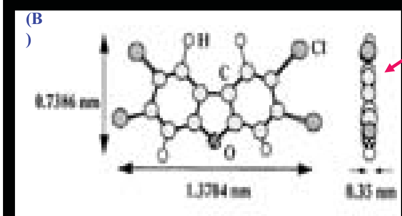
[b] *Institute of Environmental and Occupational Health Sciences, National Yang Ming University, Taipei, Taiwan.*
[c] *Graduate Institute of Environmental Engineering, National Central University, Chungli, Taiwan.*
[d] *Institute of Environmental and Occupational Health Sciences, National Yang Ming University, Taipei, Taiwan.*

Dioxin-like compounds

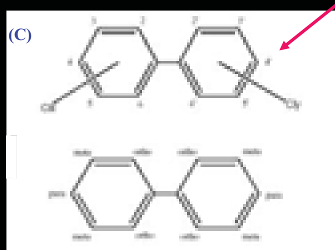
- ✓ Combustion processes emit a variety of pollutants including acid gases, particulate matter, heavy metal, polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxin and dibenzofurans (PCDD/Fs).





210 species

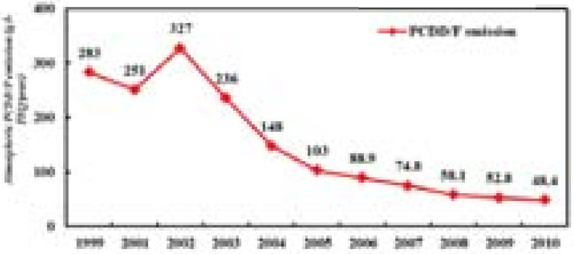
209 species

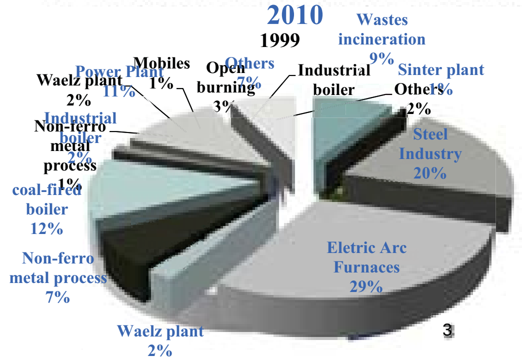


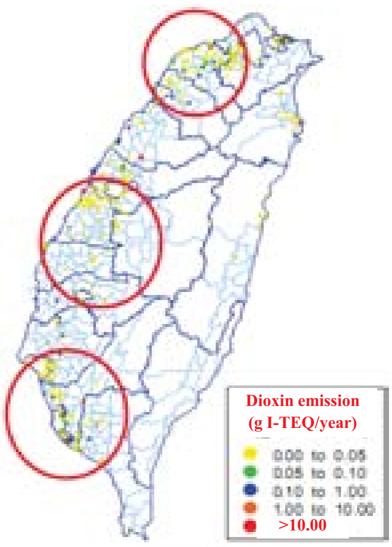
Structure of (A) PCDDs (B) PCDFs (C) PCBs

(Nagano et al., 2000)

Inventory of PCDD/F emission in Taiwan





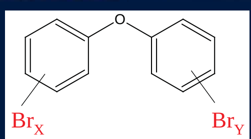


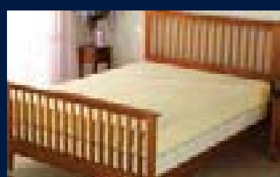
3

(Taiwan EPA，2011

Polybrominated dipenylethers (PBDEs)

- Flame retardants save lives
- Brominated flame retardants are most cost effective
- 3 major classes of brominated Flame Retardants

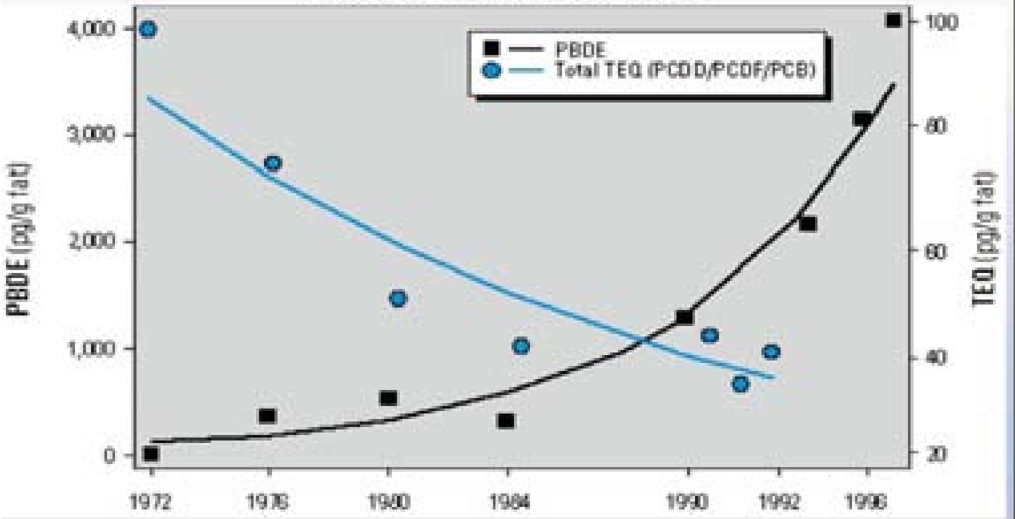




- Global, transboundary problem
- Persistence in environment
- Bioaccumulation
- Toxicity in animals
- Data gaps in humans

The figure that started it all for us in California . . .

Organohalogen Compounds in Human Milk in Sweden
(Norén and Meironyté, 1998)



Sediment Core Studies of Temporal Trends

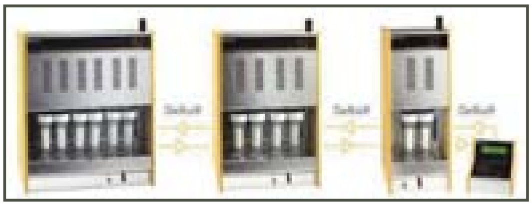
- Questions regarding the contribution made by natural sources to the overall environmental burden of PCDD/Fs can be partially addressed using the results from analyses of the temporal distribution of PCDD/Fs in sediment core samples.
- Sediment cores provide a historical record of contaminant inputs into the environment and have been used by several researchers to study temporal trends in PCDD/F and PCB deposition.

The Feitsui reservoir serving as the source of domestic water supply for the Taipei Metropolitan Area, started to operate in 1987 with the storage of 406 million m^3. The reservoir has a surface area of 10.24 km^2 and a mean depth of 40 m with the maximum depth of 114m near the dam. The catchment area is 30 times the reservoir surface area.

The SML is located near the geographical center of Taiwan. Prior to 1919, the lake surface was 727 m above sea level, with an original surface area of 5.4 km^2 and mean water depth of 4.6 m. Following the construction of a dam which was completed in 1939, the water table rose by as much as 23 m and the surface area of the reservoir expanded to 8.4 km^2. SML is far away from the municipal or industrial areas.

Sediment core sampling process

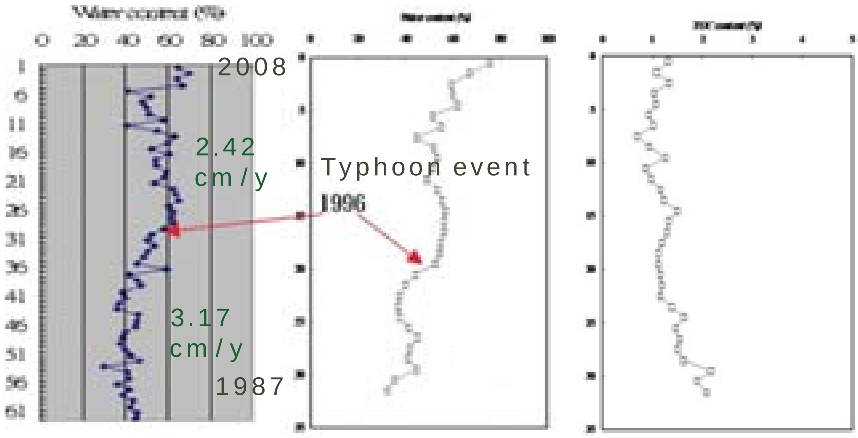
The core collection was performed directly by cautiously inserting plastic tubes into the bottom sediment by hand. In June 2008, a 64 cm sediment core was collected at a location downstream near the Feitsui Reservoir in northern Taiwan. The site was at the former site of a tea farm along riverbanks that were flooded after the reservoir's completion. In 2009, a sediment cores (34 cm) was sampled at south bay of the SML.



Soxtherm extraction

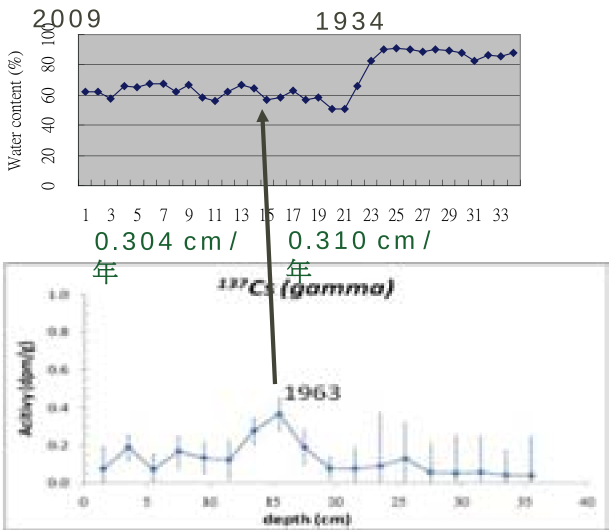
Column clean-up

Sediment core dating
(Feitsui reservoir in Northern Taiwan)

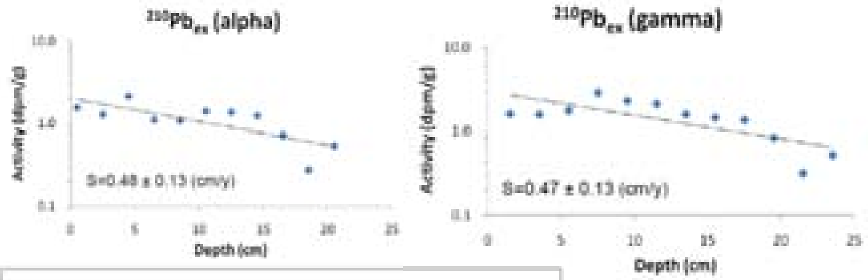


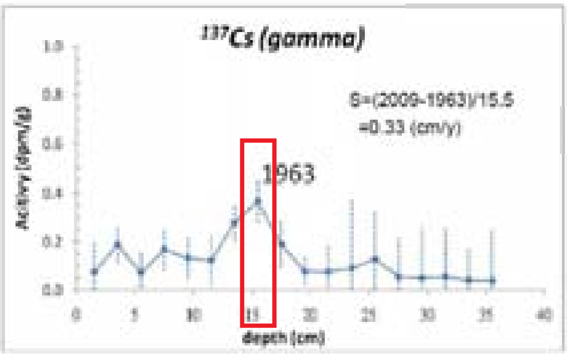
Chi et al., Chemosphere, 2011.

Sediment core dating
(Sun Moon Lake in Central Taiwan)



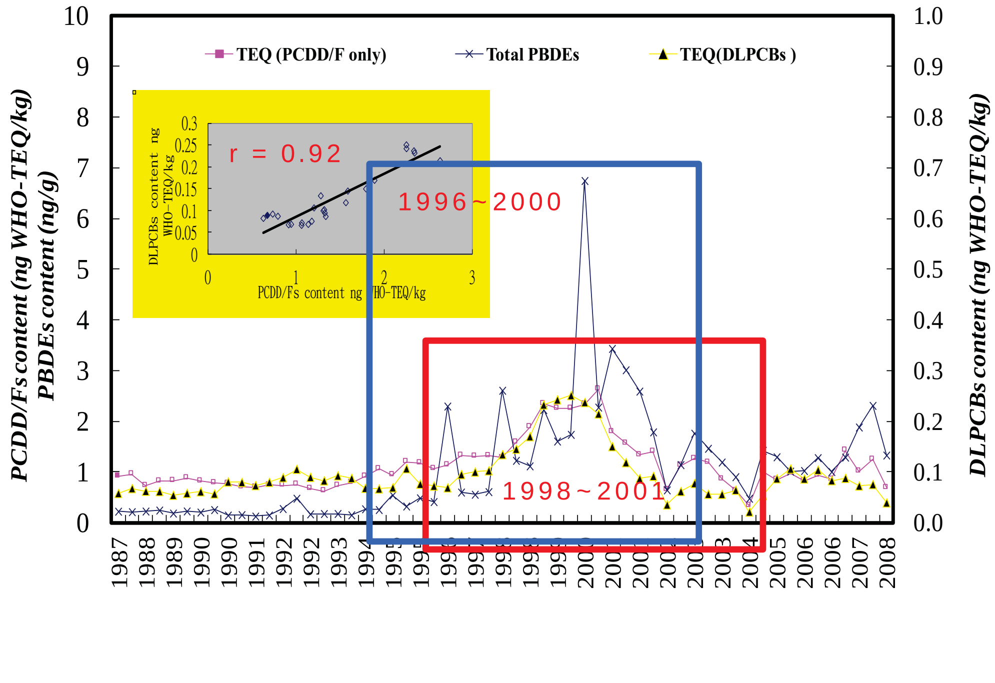
Sediment core dating
(Sun Moon Lake in Central Taiwan)





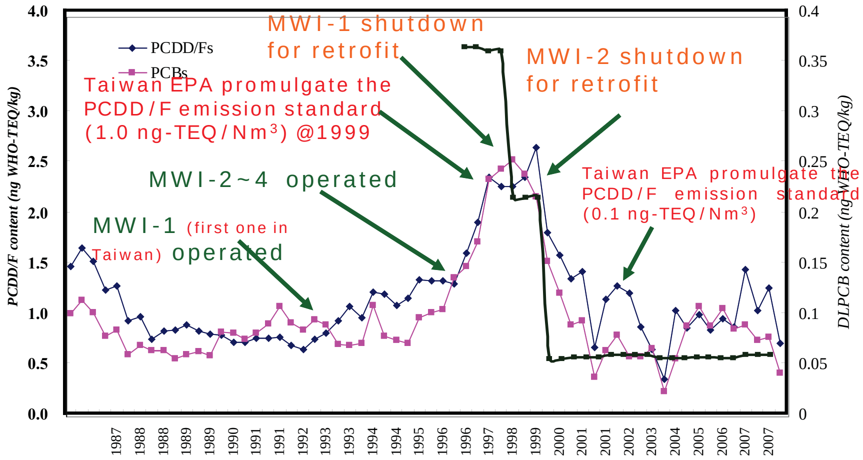
In SML, the mean sedimentation rates of the sediment core collected at SML were determined as 0.47±0.13 cm/year. The down core distribution of ^{137}Cs activity with peaks occurring at depths of 15.5 cm. From the ^{137}Cs profile, we estimated the mean sedimentation rate at south bay of SML from 1963 to be 0.34 cm/year.

Temporal trends of PCDD/F, DLPCB and PBDE concentrations of the Feitsui Reservoir in northern Taiwan

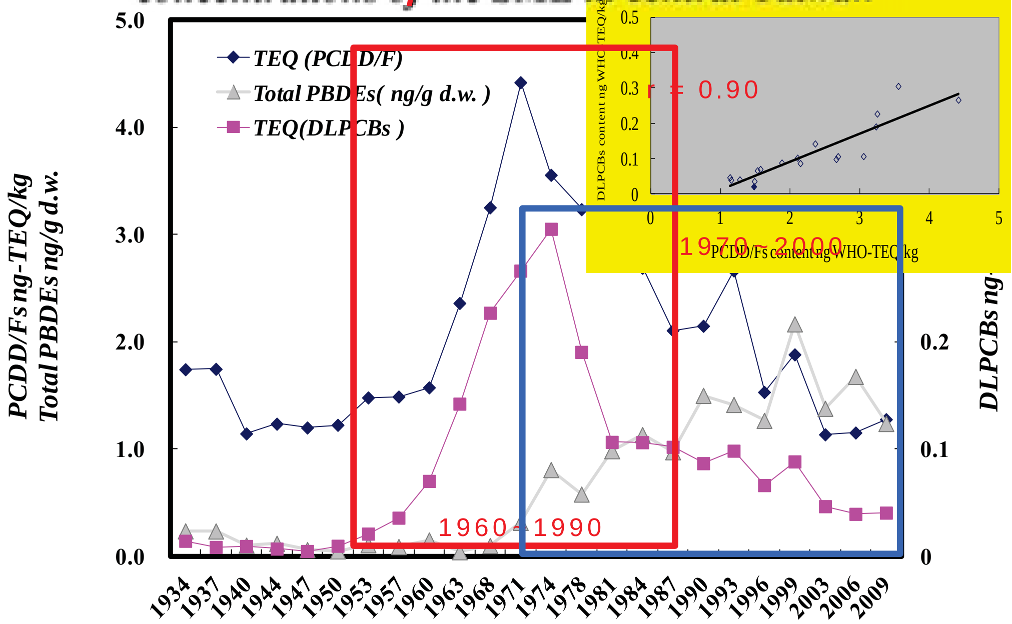


Possible sources in Feitsui Reservoir in northern Taiwan

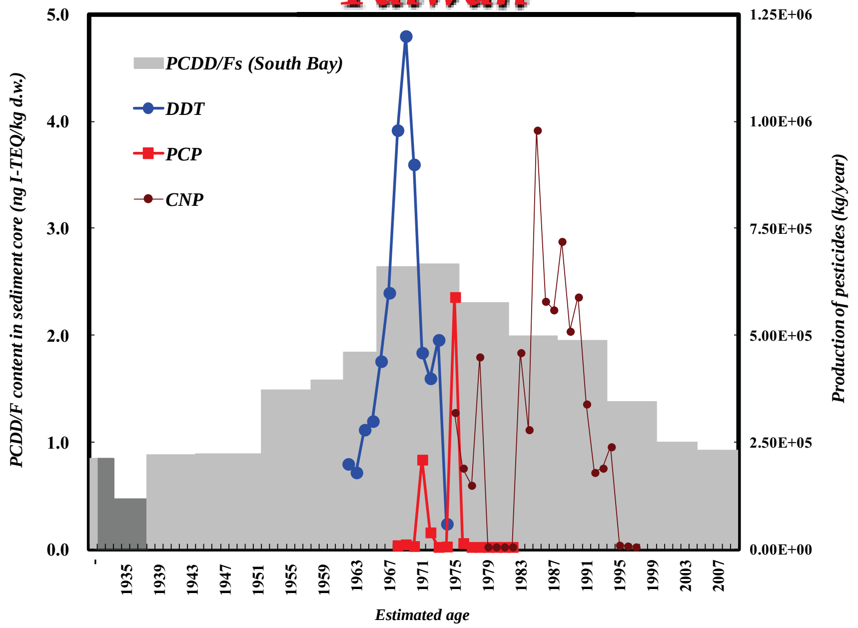
Year	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
DIOXIN EMISSION ng/年	54.8	54.0	28.4	0.212	0.468	0.885	0.848	0.311	0.380	0.254	0.881



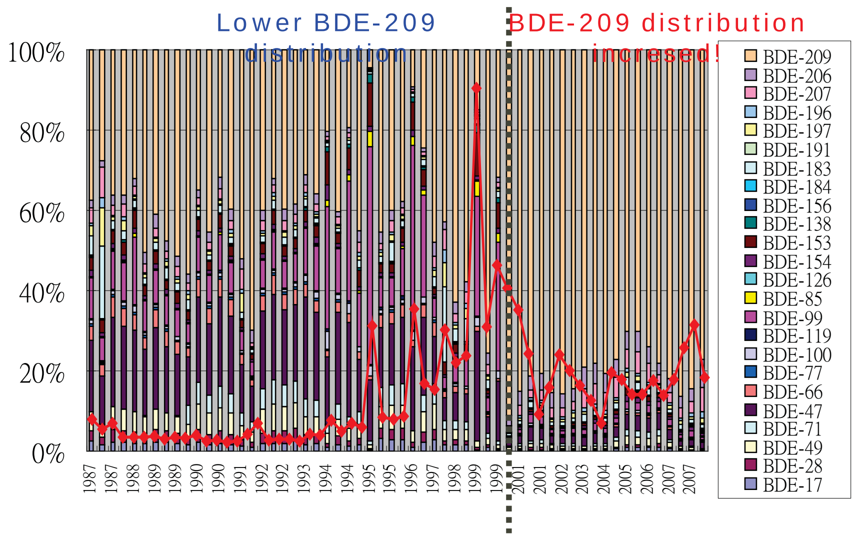
Temporal trends of PCDD/F, DLPCB and PBDE concentrations of the SML in central Taiwan



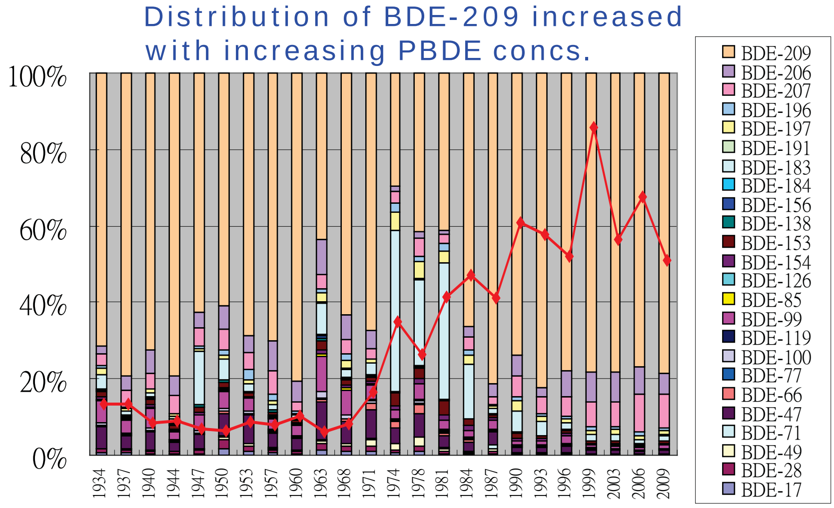
Possible sources in SML in central Taiwan



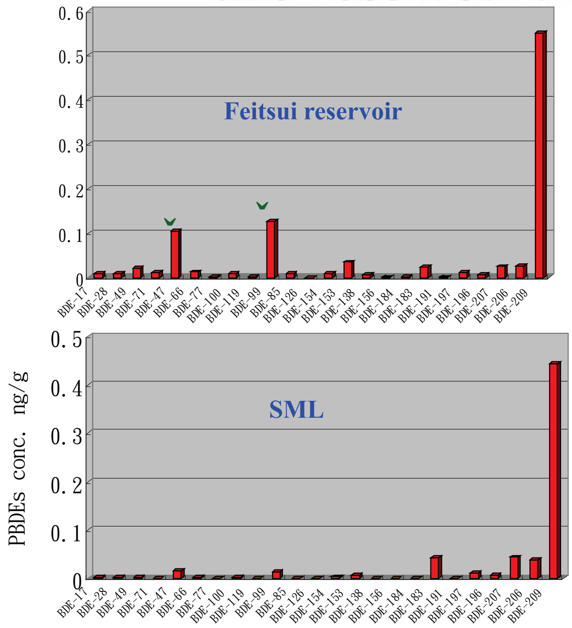
Temporal trends of PBDE compounds of the Feitsui Reservoir in northern Taiwan



Temporal trends of PBDE compounds of the SML in central Taiwan



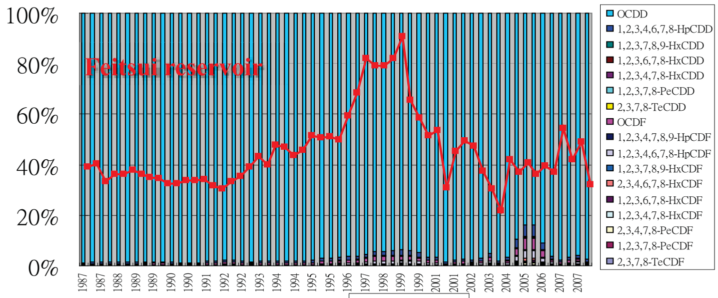
Distribution of PBDE congener in two reservoir in Taiwan

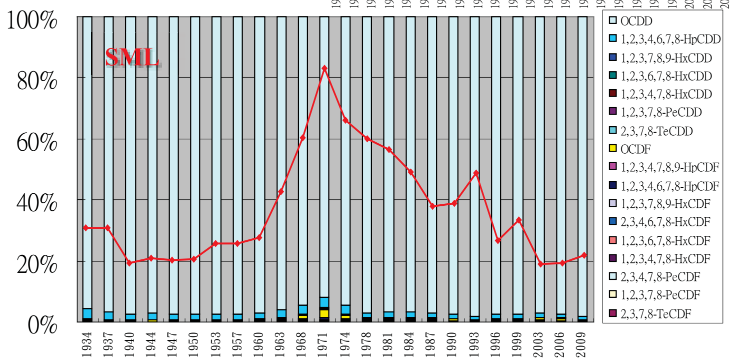


Distribution of PCDD/F congener in two reservoir in Taiwan

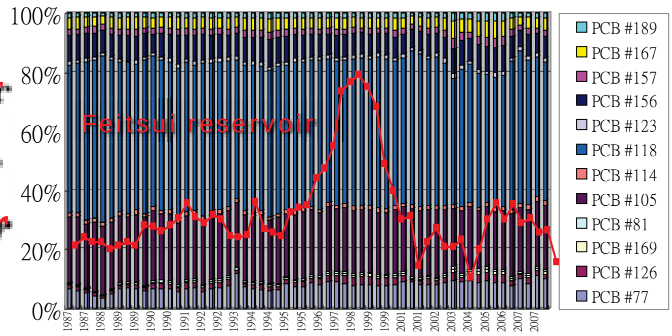
OCDD:97%

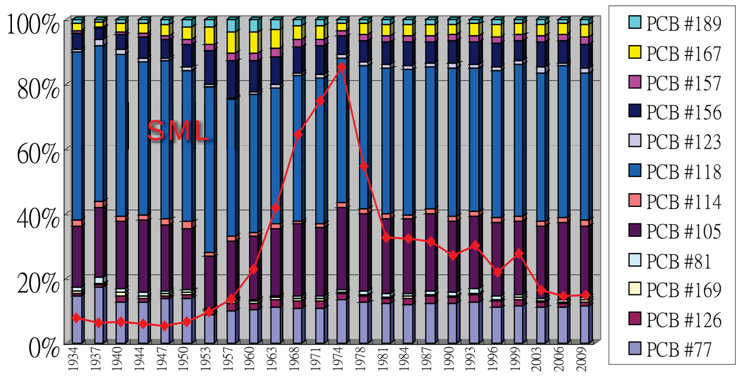
OCDD
1,2,3,4,6,7,8-HpCDD
OCDF
1,2,3,4,6,7,8-HpCDF





Distribution of PCB congener in two reservoir in Taiwan





PCB#118:50%
PCB#105
PCB#77

Summary

1. *In northern Taiwan, the significant decrease in the PCDD/F and PCB concentration in sediment core observed may be related to the new PCDD/F emission limits (0.1 ng TEQ/Nm^3) promulgated in 2001.*
2. *In central Taiwan, the PCDD/F concentrations in sediment core increased in the 1970s. That may be owing to that the major mass fluxes of OCDD originate from the impurities in PCP directly into the sediment.*
3. *The decreasing trend of PCDD/F and PCB concentrations can be observed in sediment core in northern and central Taiwan, however, the significantly increases of PBDEs especially of BDE-209 were observed in our study in Taiwan .*

- Thank You for Your Attention !!

Acknowledgements:

The authors acknowledge the financial supports provided by Taiwan EPA (EPA-97-E3S4-02-04, EPA-98-E3S4-02-05 and EPA-99-E3S4-02-03) and National Science Council (NSC 101-2111-M-010-001-) of the Republic of China.

Presentation Abstract - Innovative approaches to dealing with contaminated sediments

Author: Jonathan D Atkinson _ Environment Agency UK

Historic contamination from industrial use and ship/boat building and maintenance has led to contaminated sediments in rivers and harbours of all sizes and shapes all over the world. . It's estimated that 20 percent of the top six inches of all sediment in U.S. rivers, lakes, streams and estuaries is contaminated**.** Europe-wide, the volume of dredged material is very roughly estimated at 200 million cubic metres per year. There are three types of dredging: capital, maintenance and remediation dredging. Contamination mainly leads to problems in maintenance dredging because given standards or regulations do not allow the free disposal in the aquatic system

At the last conference in Taiwan two years ago we heard several papers on how complex and costly it was to remove contaminated sediments from places as diverse as Sydney harbour in Australia and stretches of the Mississippi river in the US. We heard of historic problems in places like Minimata, Japan

Some of the problems are not so significant, the contaminated materials having been buried by clean sediment deposition in low flow systems and the contamination has little current impact on river bed fauna or the water quality and aquatic life that it supports.

Others in more dynamic systems regularly release contaminants into the water column as particles or via diffusion into the water phase. This can impact river and marine flora and fauna and human use of water resources for consumption or recreation. We heard how in Sydney fishermen have been advised not to eat the fish they catch, similar advisories are issued by the Environment Protection Agencies and Public Health bodies in the US, Europe and worldwide.

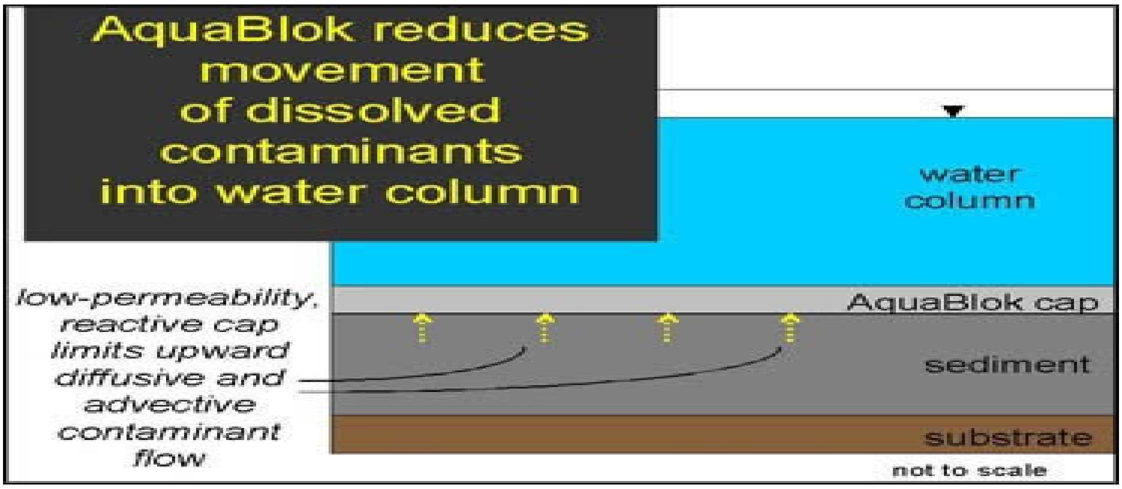
Traditionally dredging has been used to clear sediments from rivers for navigational purposes or to manage flood risks. This originally took little account of contamination and sediment disturbance has led to significant effects from released contamination, especially where there are sensitive aquatic habitats. Biological impacts can be enhanced up the food chain by bioaccumulation.

As we heard at the last conference past practice had begun to address issues of contamination by removal and disposal to landfill of some kind. This is expensive and can lead to significant impacts during the actual dredging operations. Improvement of dredging tools and control of sediment locally through temporary physical containment can ameliorate some of these effects, but again operations become expensive and difficult. Moving contaminated sediments from waterways to landfill also just moves the problems elsewhere and landfill is increasingly difficult, with pre-treatment actions sought prior to deposit of these dredge materials.

Innovative approaches to recovering dredge materials for some form of re-use, as engineering fill, in block making or other types of engineered materials are being considered through the use of solidification and stabilisation technologies, which is a huge step forward. Innovative treatments using cement technology for stabilising materials has been researched in Europe over the last 10 years. New forms of accelerated stabilisation using carbon dioxide additions have now shown commercial scale promise. Carbon8, a spin out company from the University of Greenwich in the UK has recently been involved using waste ash for block making using carbon capture. The technology has been applied to contaminated sediment materials and drill cutting waste as well. http://www.c8s.co.uk/

In some cases channel clearance has considered jet dredging , clearing navigation reaches by mobilising the river bed sediments into flux so they can be washed downstream and deposited in deeper waters or on lower reaches of the river where a wider navigable channel is available. In some instances where low levels of contamination are the issue and the receiving environment can provide natural attenuation this may be cost-effective. But for heavily contaminated sediments this can lead to disastrous impacts on sensitive aquatic ecosystems downstream. Regulatory authorities may therefore reject this otherwise cost effective dredging system. The EU funded Sednet Programme offers a good commentary on the above problems and solutions in the European context.
http://www.sednet.org/download/Sednet_booklet_final.pdf

In-situ capping of sediments with clean mineral based materials has been tried and is successful in some applications, but many fluvial/tidal systems are highly dynamic and capping can be disturbed by seasonal sediment mobilisation or by mechanical disturbance caused by river boat use. In addition the placement of thick layers of mineral capping materials such as sand or clay can have significant impacts on the benthic flora and fauna, often destroying it in the short term.



http://www.aquablokinfo.com/index.php?option=com_content&task=view&id=11&Itemid=119

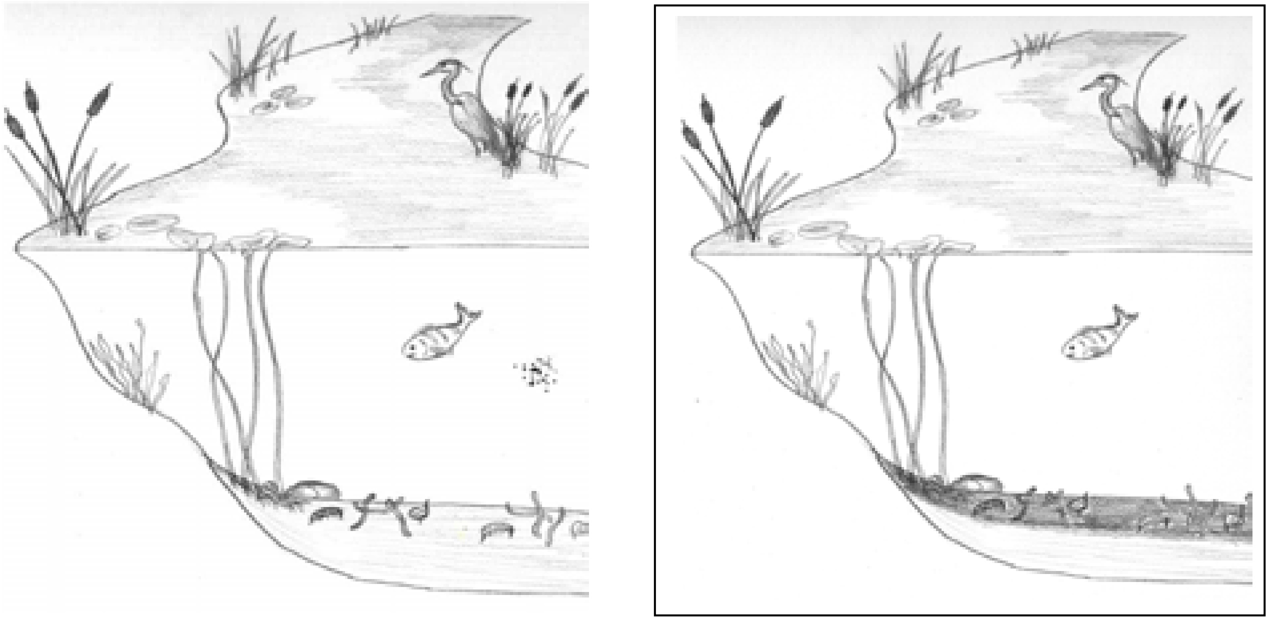
Thinner mineral caps can have fewer impacts on the aquatic flora and fauna but may be less use in locking down heavily contaminated sediments and preventing flux into the water phase over longer time periods, requiring regular re-applications.

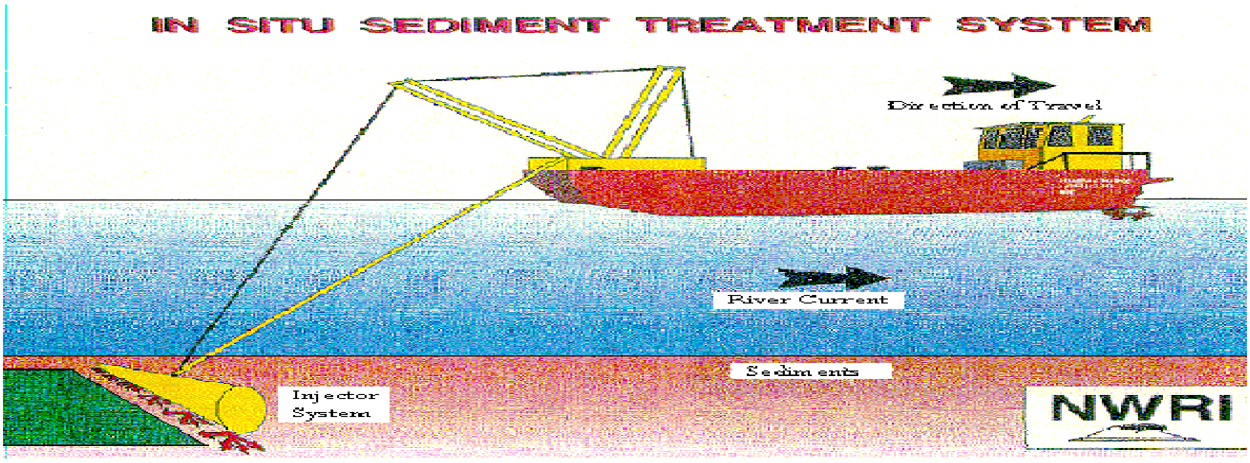
Various research efforts have led to innovative capping applications using materials borrowed from land and water remediation such as the use of activated carbon and more complex capping layers have been developed, for instance clay and AC mixes.

There are some significant examples of success on trials of this type of approach see links for further info.

http://pubs.acs.org/doi/abs/10.1021/es2011397
http://www.niehs.nih.gov/research/supported/assets/docs/d_i/in_situ_sorbent_amendments_its_not_just_pixie_dust.pdf

CONCEPTUAL MODEL: BEFORE and after TREATMENT





Providing the complex capping layers at the required locations can be difficult and expensive, but the research shows some significant improvements in reducing contaminant impacts. In addition the materials can be relatively stable and long lasting in settings that are characteristic of limited sediment disturbances.

However in highly dynamic systems loose placed materials are still subject to fluvial/marine fluxes and long term sediment movements may result in exposure of contaminated sediments again and renewed impacts on flora and fauna.

The costs of using materials like AC can be significant, but waste sourced char materials such as biochar may be able to off-set some of these costs and use what would otherwise be a waste material for beneficial use. The use of biochar materials in treating land contamination and preventing fluxes of agricultural inputs and chemicals is being realised more and more by worldwide research, but its use in aquatic systems could also be beneficial as part of cost-effective sediment capping systems.

C-Cure research, a spin out company from a partnership between the UK Forestry Commission and the University of Surrey at Guildford has been developing char products for some time and has had significant success in treating various containments in solid and aqueous settings.

C-Cure's products are particularly effective as a media to remove heavy metal and metalloid ions from various industrial process and produced water discharges as well as a medium for hydrocarbon treatment and removal. Problems that the C-Cure technology is considered appropriate for development of a solution include:

http://www.forestry.gov.uk/fr/INFD-67AE69

Taking these types of products and further developing them can perhaps offer alternatives to those types of sediment capping used to date, where installation of materials that are effective as treatment mechanisms can be difficult, especially at depth and expensive.

The latest approach to sediment capping and contaminant flux control is looking at using combined materials in geotextile mats to achieve a stable cap that can be tailored with various thin layers of treatment materials such as clay and biochar to achieve significant reductions in contaminant release from sediments. The mats or blankets can be laid on stream/river beds and anchored, creating a thin, stable, active treatment capping that has less impacts on bed flora and fauna.

Work on this is in its early days but the ideas have been conceived and are being developed in the UK and the US independently and show some promise.

UNH associate professor Kevin Gardner and research assistant professor Jeffrey Melton have developed a system they believe will work. They've created a patch -- black geotextile mats designed to cap and stabilize pollution in place. The mats are six feet square and one inch thick. They consist of a mixture of reactive materials sandwiched between two layers of geotextile fabric, creating a sort of quilt that traps pollutants but allows water to flow through. The reactive "filling" of this quilt contains three different substances that bind and stabilize different pollutants. One such substance -- a UNH-patented technology based on a natural form of phosphorus -- treats toxic heavy metals associated with industrial pollution such as lead, copper, zinc and cadmium.
"But you don't just find one pollutant at a site," says Melton. "Everything is all mixed up in the sediment." So he and his colleagues added organoclay and activated charcoal, which adhere to and treat toxic chemicals such as polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons, (PAHs), and petroleum products that routinely enter waterways through stormwater runoff.

"Polluted sediment is a nationwide problem," says Richard Langan, CICEET's UNH co-director. "We need better tools to identify and treat areas where this pollution has the potential to threaten human and ecosystem health. Technology demonstrations like these, that take advantage of cutting-edge science, are key to making that happen."

The project is funded by the Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET), a partnership of UNH and the National Oceanic and Atmospheric Administration, and NH Sea Grant.

The approach of a suspended curtain with a similar sandwich of treatment materials could also be used alongside traditional dredge applications where deeper, more complex contamination needs to be addressed, allowing removal of contaminated sediments while protecting the wider environment by controlling fugitive fluxes from the dredging operations.

The appropriate approach will always be site specific and understanding of the dynamics of the fluvial/tidal systems, the bed sediments and sources of new sediment, deposition rates and disturbance mechanisms, as well as aquatic flora and fauna will be required. Alongside these surveys an understanding of channel use and dredging requirements for navigation and flood risk management will all impact on the particular approach required for sediment control and ensuring contaminated sediments do not create environmental impacts, but the tools available are increasingly innovative in this complex environment.

Environment Agency

England and Wales, United Kingdom

Environment Agency

Innovative approaches to sediment contamination

Name: Jonathan Atkinson

Job title: Technical Specialist; Groundwater, Hydrology & Contaminated Land

Date : October/November 2012

Environment Agency

Historic contamination from industrial use and ship/boat building and maintenance has led to contaminated sediments in rivers and harbours of all sizes and shapes all over the world

Environment Agency

Bankside Clean-ups can successful remove historic sources, but historic contamination continues to impact in sediments

Contaminated sediments

- In low flow systems not a significant problem, the contaminated materials are buried by clean sediment deposition so there is little current impact on aquatic fauna or the water quality
- More dynamic systems regularly release contaminants into the water column as particles or via diffusion
- Impacts river and marine flora and fauna and human use of water resources for consumption or recreation

Environment Agency

Traditionally dredging has been used to clear sediments from rivers for navigational purposes or to manage flood risks

- Mechanical means were used
- This took little account of contamination
- Sediment disturbance led to further mobilisation/spread of contamination
- Effects on sensitive aquatic habitats
- Biological impacts can be enhanced up the food chain by bioaccumulation

Environment Agency UNCLASSIFIED 6

Mechanical Dredging

<u>Mechanical dredging issues:</u>

•Log jams keep clam or bucket open through water column.

•Contaminants leak out into water current and carry them downstream

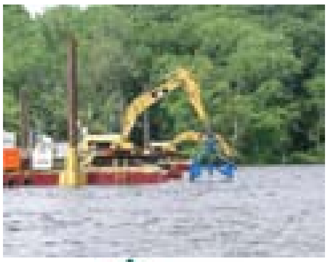
Environment Agency

Mechanical Dredging Problems

Hudson River PCB Clean-Up:

- "Hudson River dredging released almost 25 times more PCBs into the water than expected", General Electric
- "GE, in its report, said 3 percent of PCBs dredged were re-suspended in the water — far higher than the estimated 0.13 percent rate. The company said there was a fivefold increase in the concentrations of PCBs in upper-river fish last year."
- "GE concluded that it was not practical to attempt to meet both the existing productivity standards and the standards to make sure dredging doesn't re-contaminate the river. The company called for changing either the recontamination or productivity standards."

- <u>25 times more PCB's in Hudson river (USA), phase 2 dredging plan reviewed</u> http://www.dredgingtoday.com/2010/01/22/25-times-more-pcbs-in-hudson-river-usa-phase-2-dredging-plan-reviewed/



IMS

Environment Agency

Versi-Dredge

Better practice had begun to address issues of contamination by removal and disposal to landfill of some kind.

- Using different extraction techniques
- Still expensive disposal to landfill
- Often needs some form of additional treatment for stabilisation and transport needs
- Additional controls needed to control sediment mobilisation into water column
- Added expense of these containment measures

Environment Agency UNCLASSIFIED 9

Hydraulic vs. Mechanical

a.) Hydraulic dredging produces the lowest levels of resuspension.

b.) Hydraulic dredging can be engineered to minimize volatization.

c.) Hydraulic dredging works faster than mechanical dredging.“

IMS *Versi-Dredge*

Versi-Dredge: Patented Self-Propulsion

- STARWHEEL DRIVE
- Most effective dredge propulsion system available on the market today.
- Patent is held exclusively by IMS.
- Will not cause massive turbidity like prop drive propulsion
- No cables, no anchors, no hassle!
- Will not interrupt boat traffic.
- Increases efficiency by up to 40%.
- Paddle Wheel Mode paddles dredge into position and also works well in sludgy applications.
- Bottom Traction Mode walks dredge forward on bottom surface with positive traction and stability.
- Won't clog up like propellers.

IMS

Versi-Dredge

Versi-Dredge: River Dredging

- **United Kingdom**
  - An IMS Model 5012 HP Versi-Dredge deepens a portion of the River Thames in the United Kingdom.
  - The 5012 HP was ideal for the project since it could use its Starwheel Drive self-propulsion system to propel itself without disrupting boat traffic.
  - This is one of the first U.S. built dredgers to ever work on the River Thames which is a major achievement for IMS.

IMS

Versi-Dredge

Overview of common contaminated sediment dredging/treatment options

- • No Action
- • Monitored Natural recovery
- • Removal (Dredging)
- Methods
  - Mechanical
  - Hydraulic
  - Dewatering

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Dredgings Disposal Issues

- Dredging Disposal Issues:
  - Open Ocean Disposal:
    - No or Low Contaminants
  - Upland Disposal Options:
- • Untreated (Usually Landfill)
- • Beneficial Reuse
- • Landfill (Cap / Fill)
- • Excitu Treatment and Disposal or Reuse

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Dredging needs to be cost-effective

- Avoiding disposal costs – jet dredging option
- Mobilising the river bed sediments into flux so they can be washed downstream and diluted
- But for heavily contaminated sediments this can lead to disastrous impacts on sensitive aquatic ecosystems downstream
- Regulatory authorities may therefore reject this otherwise cost effective dredging system

Environment Agency UNCLASSIFIED 15

Key Considerations for selection of techniques for Remedial dredging

- Volume
- Response of Contaminant(s) to Remedial Technologies
- Contaminant Dispersion: (Parse into water?)
- Site Logistics
- Dewatering Requirements
- Transport Logistics
- Disposal Requirements/ Constraints

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Possible alternative approaches to addressing contamination in sediments

- In-situ capping of sediments with clean mineral based materials, clays, sands or limestone –some success
- but many fluvial/tidal systems are highly dynamic
- capping can be disturbed by seasonal sediment mobilisation or by mechanical disturbance caused by boat use.
- significant impacts on the benthic flora and fauna

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Research efforts have led to innovative capping applications using materials borrowed from land and water remediation

- C-Cure – UK Forestry Commission and Surrey University at Guildford.
- Products effective as a media to remove heavy metals and hydrocarbons from various industrial process and produced water discharges.
- http://www.forestry.gov.uk/fr/INFD-67AE69

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Research cont/

- There has also been some work done in the USA and Norway on using activated carbon applications into stream beds to assist in reducing impacts on fauna and emissions back into the water column.
- Further details:

http://www.niehs.nih.gov/research/supported/assets/docs/d_i/in_situ_sorbent_amendments_its_not_just_pixie_dust.pdf

Environment Agency UNCLASSIFIED 19

Complex design and installation

- The research shows some significant improvements in reducing contaminant impacts in some settings, especially with AC additions
- The materials can be relatively stable and long lasting.

BUT

- Providing the complex capping layers at the required locations can be expensive
- Installation difficulties in getting consistent layer

Environment Agency UNCLASSIFIED 20

KEY LEARNINGS FROM UMBC PILOT-SCALE STUDIES, GRASSE RIVER, NY

- AC can be applied to sediment in a large scale
- AC remains in place 3 years after placement
- Reductions in porewater PCB levels
- Reductions in tissue PCB levels
- Over time, the AC-amended sediment is covered with new sediment deposit in this setting

Contact : ughosh@umbc.edu

Environment Agency UNCLASSIFIED 21

DELIVERY DEVICES USED AT GRASSE RIVER, NY

Injection and mixing in an enclosed rototiller

Tine injection system
Designed and built by Brennan with inputs from collaborators

PILOT DEMONSTRATION IN GRASSE RIVER (Participants: Alcoa, EPA, UMBC, Stanford University, Anchor Env., Brennan, Tetra Tech, ArcadisBB&L, QEA)

Contact : ughosh@umbc.edu

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Some settings are highly dynamic

- Loose placed materials are still subject to fluvial/marine fluxes and mechanical disturbance leading to patchy cover
- Long term sediment movements may result in exposure of contaminated sediments again
- Some biological activity can bring buried contamination back to sediment surface
- Causes future renewed impacts on flora and fauna and human use

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Making capping systems more cost effective and robust

- Using alternatives to activated carbon, such as waste sourced biochar
- The use of biochar materials in treating land contamination and preventing fluxes of agricultural inputs and chemicals is being realised more and more by worldwide research
- Its use in aquatic systems could also be beneficial

Environment Agency UNCLASSIFIED 24

What about Installation issues and long term stability

- Independent research in the UK and USA has led to trials of capping materials in mats or blankets
- Work on this is in its early days but the ideas have been conceived and are being developed in the UK and the US independently and show some promise

Environment Agency UNCLASSIFIED 25

Capping Mats for treating contamination

- Combining materials in geotextile mats to achieve a stable cap, suitably anchored
- Thin layers of treatment materials such as clay and biochar in a sandwich to achieve designed treatment of CoC
- Active treatment capping that has less impacts on re-establishment of bed flora and fauna or design to encourage re-colonisation.

Environment Agency UNCLASSIFIED 26

Researchers test sediment-scrubbing technology at the Cocheco River in New Hampshire, USA

"We need to know how these mats behave when they're buried under mud for a few years, compared to how they performed in the lab. What will happen to them in this intertidal zone with boats, waves, birds, and weather? How will they impact bugs and other aquatic life in the sediment"

University of New Hampshire's associate professor Kevin Gardner and research assistant professor Jeffrey Melton

http://geosyntheticsmagazine.com/articles/1008_f1_scrubbing.html

But if contaminants still need to be removed due significant effects

- If heavily contaminated sediments still need to be removed for navigation, flood risk or remediation objectives, how is contaminant flux to be addressed from dredging operations cost-effectively
- Treatment blankets or curtains with a similar sandwich of materials could perhaps offer some control of fugitive released sediment and contamination

Environment Agency UNCLASSIFIED 28

Silt curtains are specifically designed to contain and control the dispersion of suspended solids in the water column during pile driving, site work, dredging and bank reprofiling,

- Silt Curtain

- Clear Effect

AquaticEngineering

Tel: +44 (0) 560 3117936
caroline@aquaticengineering.co.uk

EA working with Aquatic Engineering in UK to develop treatment blankets and curtains to meet Water Framework Directive Requirments

- For use in treating contaminated sediments
- For controlling contaminants released into the water column during necessary dredging works
- To prevent bankside diffuse releases

30

Conclusions

- The appropriate approach will always be site specific – there is no silver bullet
- Requires understanding of the dynamics of the fluvial/tidal systems, the bed sediments and sources of new sediment, deposition rates and disturbance mechanisms,
- Aquatic flora and fauna interactions need to be understood
- Channel use and dredging requirements for navigation and flood risk management must be catered for

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The Way forward

- More research to ensure contaminated sediments do not create environmental impacts and harm sensitive or valued habitats and man's use of rivers and estuaries is maintained for navigation, employment and food resources
- Innovative tools are developed and available to deal with this complex and dynamic environment which has been significantly impacted by historic contaminating activities

Environment Agency UNCLASSIFIED 32

Useful Links

- http://www.sednet.org/download/Sednet_booklet_final.pdf
- http://www.c8s.co.uk/
- http://www.niehs.nih.gov/research/supported/assets/docs/d_i/in_situ_sorbent_amendments_its_not_just_pixie_dust.pdf
- http://www.forestry.gov.uk/fr/INFD-67AE69
- http://www.epa.gov/superfund/health/conmedia/sediment/guidance.htm
- http://www.cefas.defra.gov.uk/our-science/assessing-human-impacts/dredged-marine-sediments/managing-contaminated-sediments.aspx

Environment Agency UNCLASSIFIED 33

Innovative approaches to sediment contamination

- Thank you for your attention
- Jonathan Atkinson
- We are the Environment Agency, (England and Wales, UK). It is our job to look after your environment and make it a better place – for you, and for future generations.
- The Environment Agency.
  Out there, making your environment a better place.

Environment Agency UNCLASSIFIED 34

Use of phytoremediation for both managing selenium and producing biofortified plant products and biofuel under adverse soil conditions

G.S. BAÑUELOS

USDA-ARS, Water Management Research Unit, 9611 S. Riverbend Ave., Parlier, CA 93648, USA

ABSTRACT

Interest in selenium (Se) remediation technology has escalated during the past two decades. Although not known to be essential for plants, selenium is essential but can be toxic for humans and animals at excessive concentrations. A major Se controversy in the 1980's emerged in central California when the general public and scientific community became aware of selenium's potential as an environmental contaminant. Consequently, a plant-based remediation technology, defined as 'phytoremediation,' received increasing recognition as a low-cost and environmentally friendly approach for managing soluble selenium in the soil and water environment. Sustainable long-term field phytoremediation of Se is, however, dependent upon acceptance and widespread use by growers. Producing products with economic value from plants used in the cleanup of selenium-contaminated soil would certainly be an additional benefit to the phytoremediation process, which could help sustain and expand its long-term use in selenium-laden soils in the Western USA, China and India. This paper discusses the production of selenium-biofortified plant products and biofuel from plants grown for the remediation of selenium under field conditions in the San Joaquin Valley, California.

INTRODUCTION

Irrigation of seleniferous soils has produced subsurface drainage that contaminated wetlands and led to deformities in fish and migratory birds in the western United States (Lemly 1997). The U.S. Geological Survey identified about 267,000 square kilometers of lands susceptible to irrigation-induced selenium contamination (Seiler et al. 1999). A plant management remediation strategy for selenium-contaminated drainage was developed based upon early research conducted by Bañuelos and Meek (1990). In this regard, California researchers demonstrated phytoremediation of selenium under various field conditions (Bañuelos et al. 2002; Zayed et al. 2000; Wu et al. 2000; Frankenberger and Karlson 1995; Lin et al. 2002; Bañuelos 2000). Bañuelos (2002) reported that potential crops used for the phytoextraction of selenium in Central California, e.g., broccoli (*Brassica oleracea*), canola (*B. napus*), and mustard (*Synapis alba*), would not only remove soluble Se from soil, but harvesting the selenium-enriched crops may produce products of potential economic importance for the grower (Bañuelos 2009; Stapleton and Bañuelos 2011). Similarly, other commodity products may be producible from crops used for phytoremediation, such as using extracted mustard/canola oil mixed with diesel fuel for the production of both biofuel for diesel engines and further using the seed by-products after oil extraction as animal feed meal (Bañuelos et al. 2009). The objective of this paper is to report on the derivation and novel utilization of potential phyto-products that were produced from Brassica plants grown for the remediation of Se in poor quality soils in Central California.

MATERIALS AND METHODS

Multi-year field studies were conducted with *B. napus* var. Hyola (canola), *Synapis alba* var. Ida Gold (mustard), and *B. oleracea* var. Marathon (broccoli) on different 20-ha field sites at Red Rock Ranch in the westside of central California. Brassica crops were selected because their ability to accumulate selenium under moderately high salinity and boron (B) levels (Bañuelos et al. 1996). The soil in the study area was classified as an Oxalis silty clay loam (fine montmorillonitic, thermic Pachic haploxeral with a well-developed salinity profile).

Two water sources were available for irrigation- canal water from the California aqueduct and selenium-laden drainage water produced from other growing sites on Red Rock Ranch. The canal water had concentrations of Se < 0.01 mg L^{-1}, B < 1 mg L^{-1}, and a salinity (electrical conductivity) [EC] < 1 dS m^{-1}, while the drainage water had a range of selenium concentration from 0.100 to 0.150 mg L^{-1}, boron from 4 to 7 mg L^{-1}, and a sodium sulfate-dominated salinity (EC) of 5-8 dS m^{-1}. Seeded fields initially received "canal water" until plants were deemed established (between true 2nd or 3rd leaves). Thereafter, irrigation scheduling was based upon weather data reported from California Irrigation Management Information System (CIMIS) located at the University of California Westside Research Station (less than 5 km from the field site at Red Rock Ranch).

Broccoli was harvested 95-100 d after transplanting, and separated into floret, stalk, and leaves. Samples were collected, processed, and acid-digested as described by Bañuelos and Akohoue (1994). Concentrations of selenium in acid digests were measured by inductively coupled plasma-mass spectrometer (ICP-MS). External quality control standards for soils, soil extract, and plant tissue samples were obtained from the National Institute of Standards and Technology (NIST), including wheat flour (SRM 1567; Se content of 1.1 ± 0.2 μg g^{-1} DM, 94% recovery) and internal soil standards (sediments collected from Kesterson Reservoir, CA, with a total Se content of 7.5 and 25 mg kg^{-1}, 94% recovery, respectively). Canola and mustard plants were swathed 150 d after seeding when the pods first began to turn yellow and allowed to cure and ripen from 10-14 d in the swath before combining. Canola/mustard seeds were then processed for its oil with a "horizontal press" and "extruder" (Insta-Pro, Int., Des Moines, IA) at a conservative rate of 2.7-4.5 metric tons of seeds per day at Red Rock Ranch, and processed further (transesterified). The residual selenium-enriched seed meal was collected, and analyzed for total Se content.

RESULTS/DISCUSSION

The success of a selenium phytomanagement strategy using crops like canola, mustard, and broccoli is dependent on their ability to accumulate Se under increasing salinity and boron contents in the soil (Bañuelos 2010). Vegetative and seed yields for canola in this study were comparable to yields reported with good quality water (Bañuelos et al. 2002a), while fresh weight floret yields for broccoli in this study were approximately 35% lower than typical yields of broccoli grown in Central California. Since sulfate and selenate are biogeochemical analogs, the high sulfate concentration in the drainage water likely inhibited plant uptake of selenate and kept the plant selenium concentrations under 7 mg kg^{-1} DM (Table 1). The phytoextraction of selenium by canola, mustard, and broccoli apparently not only removed selenium that has accumulated in the soils after irrigation with selenium-laden drainage water, but harvesting the selenium-enriched crops, e.g., broccoli florets, produces selenium-biofortified crops for the grower. Generally, the Se concentrations were <5 mg kg^{-1} DM in the broccoli florets. In this regard, total plant Se content should not be used as the sole indication of the nutritional value of the selenium-enriched plant material. The specific form of selenium contained in the plant or plant product will determine its potential benefit for human and animal nutrition (Whanger 2004). Preliminary work by Bañuelos et al. (unpublished 2012) shows that the main chemical form of selenium contained in a plant's tissue may vary depending on the crop and crop organ. The predominant organic selenium forms varied as selenomethionine (SeMet), selenocystathionine (SeCyst), and methylselenocysteine (MeSeCys), along with inorganic forms of selenite and selenite. For example, MeSeCys is monomethylated, not misincorporated into human proteins, and thus is the least toxic form of Se and yet be a potentially anti-carcinogenic form of selenium (Ip and Ganther 1992).

As an essential nutrient for humans, the daily selenium intake was recommended by the US National Academy of Sciences to be approximately 55-100 µg Se. Selenium is known as an antioxidant, and reportedly capable of depressing anticancer activity (Clark et al., 1996; Whanger 2004). Hence, using broccoli as a recipient crop for selenium-laden drainage effluent may produce a selenium-biofortified high nutritional value crop that has the potential to be a source of supplemental dietary selenium for humans. The production of selenium-enriched products may be a new approach for improving human nutrition status in Se-deficient regions of the world (Bañuelos 2009), such as China, UK, Europe, Australia, and New Zealand (Zhu et al. 2009). Tan et al. (2002) reported that approximately 15% of the world population experienced Se deficiency.

In animal nutrition, selenium deficiencies are generally a far greater problem than selenium toxicities in livestock in the United States. In this regard, Bañuelos and Mayland (2000) substantially improved the selenium status of lambs (*Ovis aries*), cattle (*Bos taurus*), and rabbits (Bañuelos et al. 2002c) by mixing selenium-enriched vegetative material (plant tissue from canola plants previously used as recipients of selenium-laden drainage water) with animal feed rations or canola seed meal (Bañuelos et al. 2010). Although selenium-enriched broccoli leaves produced in this study were not used in any animal feed study (Table 1), Wiedenhoeft and Barton (1994) have previously shown that broccoli leaves were more comparable to a traditional forage because of their low fiber and high protein content. Hence, selenium-enriched broccoli leaves could also be considered for blended use in animal forage.

Canola and mustard seed yields in this study were approximately 2 Mg ha^{-1} (Table 1). Under ideal field conditions, canola and mustard seeds contain about 35-40% oil. Using a ‘horizontal press/extruder,’ we managed to extract 50% of the available oil with a possibility of increasing the oil extraction efficiency by some improvement of the oil press/extruder. Table 2 shows yields of seeds, cake meal, and canola and mustard oil that is available for blending with diesel fuel for the production of biofuel at different oil to diesel fuel ratios typically used in the biofuel industry. The use of blended biofuels may not only reduce fossil diesel consumption but also result in a reduction in certain atmospheric pollutant emissions (e.g., particulate matter, carbon monoxide, and volatile organic compounds). Clearly a partial switch from conventional diesel fuels to blended biodiesels within the agro-industry in Central California gives growers using canola and mustard as a selenium phytoremediation crops, the first-hand ability to improve air quality in sensitive air quality regions. Importantly, because of mild climate and warm temperatures occurring in Central California, we can expect less “cold-temperature behavior” (e.g., gelling and hardening) of the blended biodiesel.

In addition to utilizing the vegetative parts of the plant for animal forage, selenium-enriched seed meal, the major by–products resulted from the oil extraction processes of seed crushing, pressing, and extruding, is of high nutritional quality for use as part of a feed ration. Canola meal is one of the most widely traded protein ingredients around the world. Dairy cows readily consumed the Se-enriched cake-like seed meal as part of their daily feed ration in a preliminary feed trial in Central California (Bañuelos et al. 2010). More importantly, the Se concentration in canola meal was less than 2 mg kg^{-1} DM. Dietary requirements for selenium generally range from 0.1 to 0.3 mg kg DM (NRC 1985). Canola seed meal in animal feed rations or mustard seed as a potential biofumigant (Stapleton and Bañuelos 2009) makes economical sense after extracting the seed oil from canola and mustard for biofuel production.

CONCLUSIONS

Developing successful phytoremediation strategies for selenium or potentially other trace elements is dependent on selecting plants or crop rotations that are most effective for removing the potential contaminant, e.g. selenium, from the soil or waters over a long period of time. When possible, potential plant candidates should also be evaluated for the ability to realistically produce products that may have economical value as a selenium-biofortified food and feed supplement, or become useful from biofuel production. Chances for widespread acceptance and usage of phytoremediation technology could exacerbate if there are marketable products from the harvested plant. Using Brassica plants like canola, mustard, and broccoli for the phytoremediation of Se under field conditions could result in phyto-products enriched with the essential trace element in broccoli, feed meal, organic fertilizer, and also oil that can be used as a biofuel additive.

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Table 1 Fresh and dry weights and tissue Se concentrations for canola, mustard and broccoli irrigated with drainage water during two growing seasons†.

Crop/Organ	Fresh weight yield ($Mg\ ha^{-1}$)		Dry weight yield ($Mg\ ha^{-1}$)		Se concentration ($mg\ kg^{-1}$ DM)	
	1st Year	2nd Year	1st Year	2nd Year	1st Year	2nd Year
Canola/Mustard						
Stems	44.7(1.6)a‡	52.2(1.8)b	5.1(.32)a	5.1(.29)a	4.3(.13)a	3.8(.11)a
Leaves	70.1(2.7)a	78.2(2.9)b	7.6(.39)a	8.2(.31)a	5.8(.18)a	6.2(.15)a
Roots	8.5(.71)a	10.1(.83)a	2.3(.36)a	1.9(.35)a	2.9(.10)a	3.1(.13)a
Seeds	NA§	NA	1.9(.12)a	2.1(.11)a	1.8(.08)a	2.1(.06)a
Broccoli						
Stalks	34.7(1.2)a	36.5(1.6)a	3.4(.36)a	3.7(.34)a	2.9(.09)a	2.5(.12)a
Leaves	62.7(2.4)a	68.3(1.1)b	6.0(.29)a	6.5(.29)a	3.7(.15)a	3.2(.14)a
Florets	10.2(.42)a	12.5(.51)a	1.3(.21)a	2.0(.26)b	4.5(.12)a	4.0(.13)a
Roots	10.1(.89)a	11.8(.78)b	2.1(.33)a	2.6(.30)a	2.6(.11)a	2.9(.12)a

† Values were computed based on population density and plant yields described in materials and methods.
‡ Within each row for each respective fresh weight yield, dry weight yield, and Se concentration, means followed by the same letter are not significantly different at the $P< 0.05$ level by Duncan's multiple range test.
§ Not applicable

Table 2 Projected production of biofuel (without transesterification) from blending mustard oil with fossil diesel fuel based upon average seed yield and extracted mustard oil.

Seed yield	Yields after oil extraction:		Projected production of biofuel		
	Seed Meal	Mustard Oil	B100†	B20‡	B10§
$Kg\ ha^{-1}$	---------- $Kg\ ha^{-1}$ -----------		------------------------ $L\ ha^{-1}$ ----------------------------		
4000	2600	1400	1538	7690	15380

† B100 is 100% mustard oil. Mustard seed contains 35% oil with a density of 0.91 g/mL.
‡ B20 is 20% mustard oil blended with 80% diesel.
§ B10 is 10% mustard oil blended with 90% diesel.

Risk Assessment of As in Soil and Groundwater for Safety of Road Construction to Resident Health

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Background

In southeastern part of Korea, there are large heavy industrial districts (Pohang and Ulsan City) where most of automobiles, steel manufacturing and ship building industries are located. In order to reduce the traffic burdens in surrounding of the industrial districts the Korea Express Co., Korean Government subsidiary, has started to construct the highway between the two cities.

However, in the middle section of the road construction sites (Nokdong) (Fig. 1), high concentrations of arsenic (As) were detected in portable groundwater and rocks with exceeding the national safety guidelines of As, listed in Soil Environment Conservation Act (SECA). Rocks are from the underground tunnel excavation. Rock analysis on As was made after crushing the rocks into particle size less than 2mm in diameter.

Therefore residents submitted the civil petition to the provincial government to halt the construction. Residents raised concerns on contamination of land and their health risk. Accordingly, the construction has been halted for several months causing huge amounts of economic losses to consultants etc.

There were As-Zn Deposit and thus As mines in Nokdong region long time ago. These closed mines located far from the road construction site. Geology of this region include diatreme. Biotite granite, welded tuff intrusion, granodiorite, volcanic formation, etc. (Fig. 1). Typical minerals such as arsenopyrite (FeAsS) and pyrite (FeS_2) are commonly found in the rocks. When these minerals are oxidized the environment becomes acidic and thus solubility of minerals increases releasing As and Fe.

There have been serious disputes among residents, consultants and Korea Express Co. Stakeholders have different views on the origin of As. One group wishes to continue road construction but the other group keeps filing petitions to governments to secure their requests.

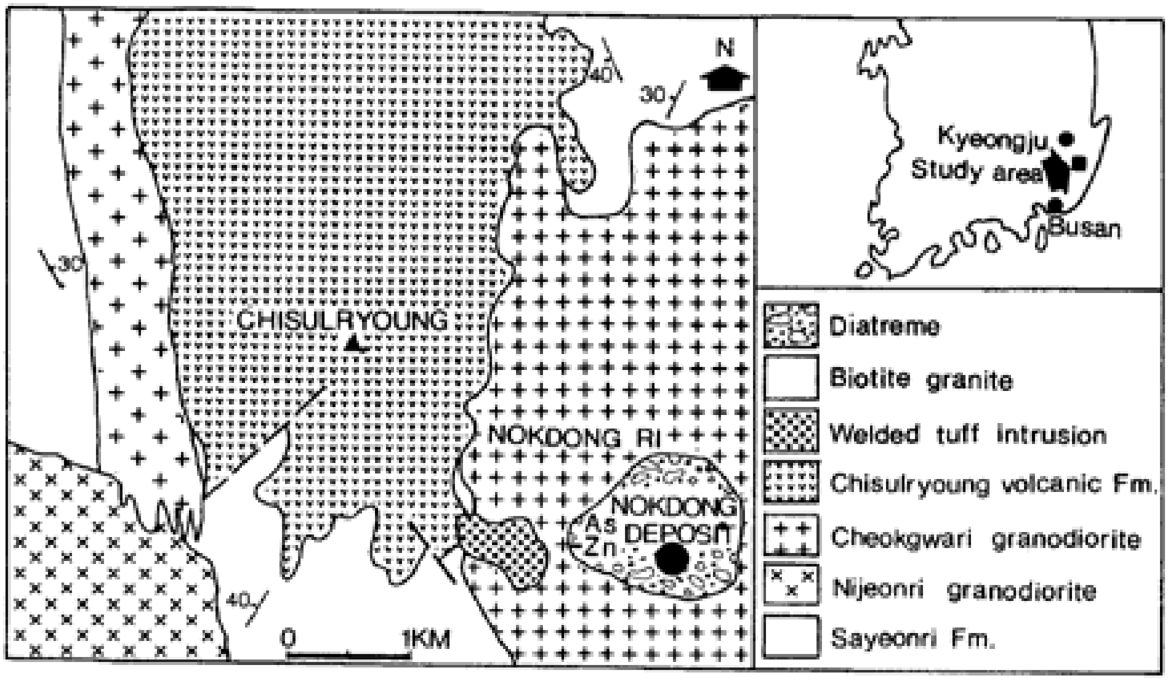

Fig. 1. Locations of risk assessment sites and geological characteristics of the region.

Points of Contention

The most interested parties in this case are residents who own a large lands and construction companies. Major points in dispute were as follows.

(1) Why is groundwater contaminated with As and where As in groundwater is derived from? Residents insisted that road construction caused high levels of As in groundwater. On the other hand, companies responded that As in portable groundwater was detected prior to road construction and is of natural origin due to geological characteristics of this region.

(2) Road construction contaminated soil, surface water, sediment, and crops in lands with As. In case the properties were contaminated the value of land will be degraded and high amounts of taxes should be invested to remediate the contaminated media.

(3) What kind of analytical method for As in rock samples should be taken. In Korea, rocks from road construction are classified as wastes. Rocks can be reused for various purposes if rock analysis for contaminants meet the standard criteria designated in the law. Thus construction companies insisted that rock sample should be analyzed for As based on TCLP (EPA 1311 method) using weak acid leaching solution because rocks are not soil. On the other hand, residents insisted that since rocks are disposed to land as basal materials for road construction As analysis should

be based on total extraction using aqua regia after rocks are crushed into particles less than 2mm in diameter. Results from the two approaches can be different a lot in terms of regulations and interests.

Numerous meetings have been held but the counterparts' opinions went parallel. A breakthrough to resolve this situation was seriously needed. Major points of interest among stakeholders are conflicted each other so that a series of integrated investigation such as are conducted.

Environmental Impact Assessment (EIA)

To find out whether road construction caused concerns mentioned above, firstly the EIA was conducted by analyzing several thousand samples of soil, groundwater, surface water, sediment, and crops. Results showed that As levels in most of these samples were below the standard criteria. There was no direct evidence that road construction could contaminate the surrounding environments and biomass including crops by releasing As from rocks. This is because major sources of As are from mineral and the solubility is quite low. In construction sites, rocks from the excavated tunnels were contained in the landfill areas with HDPE liners. Results from the TCLP, SPLP, SBET, and fractionation showed that trace amounts of As might be only derived from rock samples.

Column leaching study with filling column with the crushed rocks was conducted to check a possible downward movement of As to groundwater when being disposed to lands. In the leachate, few As has been detected. Also bioassay was conducted to grow crops on media that is composed of arable soil and crushed rocks with different ratios. No arsenic transfer from media to crops were observed.

In many groundwater samples, As level exceeded the criteria which is higher than 10 ug/L for portable water. Survey results indicated that most of As were derived from oxidation of minerals such as arsenopyrite (FeAsS) and pyrite (FeS_2) commonly found in this site. There was As-Zn deposit in Nokdong area. [$FeAsS + 7/2O_2 + 4H_2O \rightarrow Fe(OH)_3 + AsO_4^{3-} + SO_4^{2-} + 5H^+$; $(FeS\text{-}As) + 7/2O_2 + H_2O \rightarrow Fe^{3+} + SO_4^{2-} + AsO_4^{3-} + 2H^+$]. Arsenic was released into portable groundwater through natural geochemical processes. Significant levels of As have been found in these groundwater even before the road construction.

EIA results indicated that there is no direct evidence that As released from rocks can play as a secondary contaminant to diffuse to other environmental media.

Risk Assessment

Scientific data from the EIA were provided but residents were still in against the construction since As is still detected in groundwater. As a final decision tool, risk assessment of As in soil and groundwater was conducted based on the Moe guideline to evaluate a potent impact on residents' health.

Exposure pathways of As were intake of crops, soil ingestion, groundwater as drinking water. Conceptual model for risk assessment was based on guideline. Results indicated that only drinking groundwater posed a health threat and exposures from crop intake and soil ingestion were negligible.

Based on risk assessment, the portable groundwater having As concentration higher than criteria has been closed and prohibited to drink. After risk assessment, risk management and communication were very important to make residents understand the natural processes occurring in the construction site. Finally road construction could resume with risk assessment, communication and management.

Risk Assessment of Arsenic in Soil and Groundwater: Is Highway Construction Safe to Resident Health?

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[1]Kangwon National University, [2]Chungnam National University and [3]Ministry of Environment
Korea

Oct. 31, 2012

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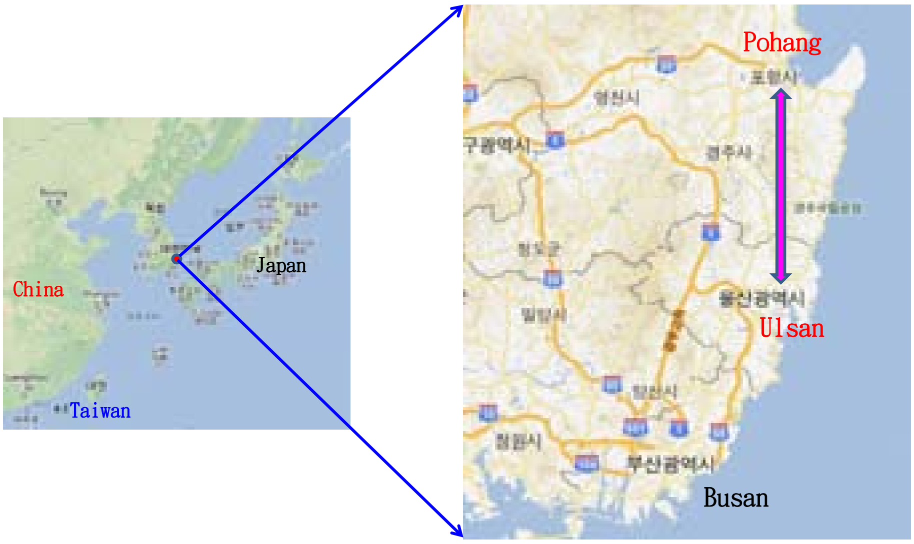
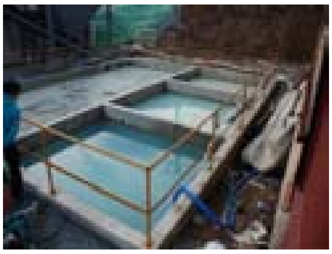
Highway Construction: Ulsan-Pohang





Press Releases (Summary)

1. Rocks from tunnels; High levels of As; Use for fill materials for raising road levels
2. [As] $_{Rocks}$ >>>> Standard Criteria of [As]$_{Soil}$
3. [As] detection in Groundwater; Will increase with construction???
4. Dispose rocks in arable lands; As leaching into Groundwater???

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Current Regulations

Rocks — Rocks from construction sites are classified into Wastes; Waste Management Act (WMA)

Metals — No standard criteria for metals in rocks; Soil Environmental Conservation Act (SECA)

Test — Analyses for As are different from Acts; Aqua Regia (SECA) vs Leaching (WMA)

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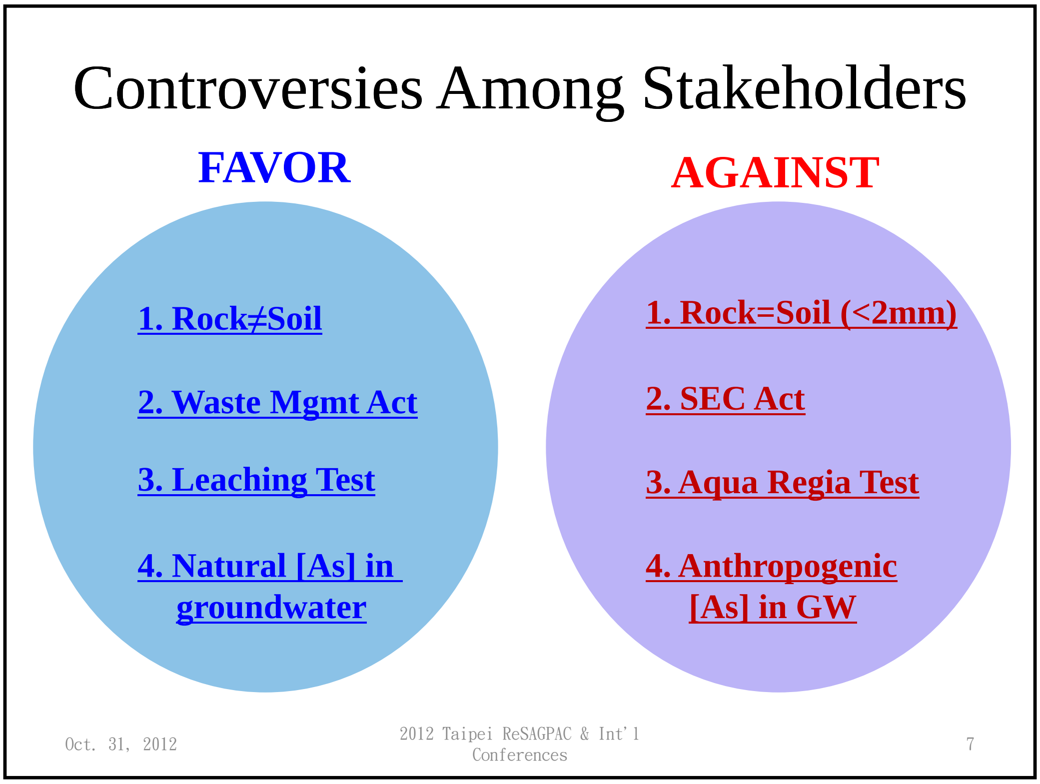
Controversies Among Stakeholders
FAVOR
AGAINST
1. Rock≠Soil
2. Waste Mgmt Act
3. Leaching Test
4. Natural [As] in groundwater
1. Rock=Soil (<2mm)
2. SEC Act
3. Aqua Regia Test
4. Anthropogenic [As] in GW
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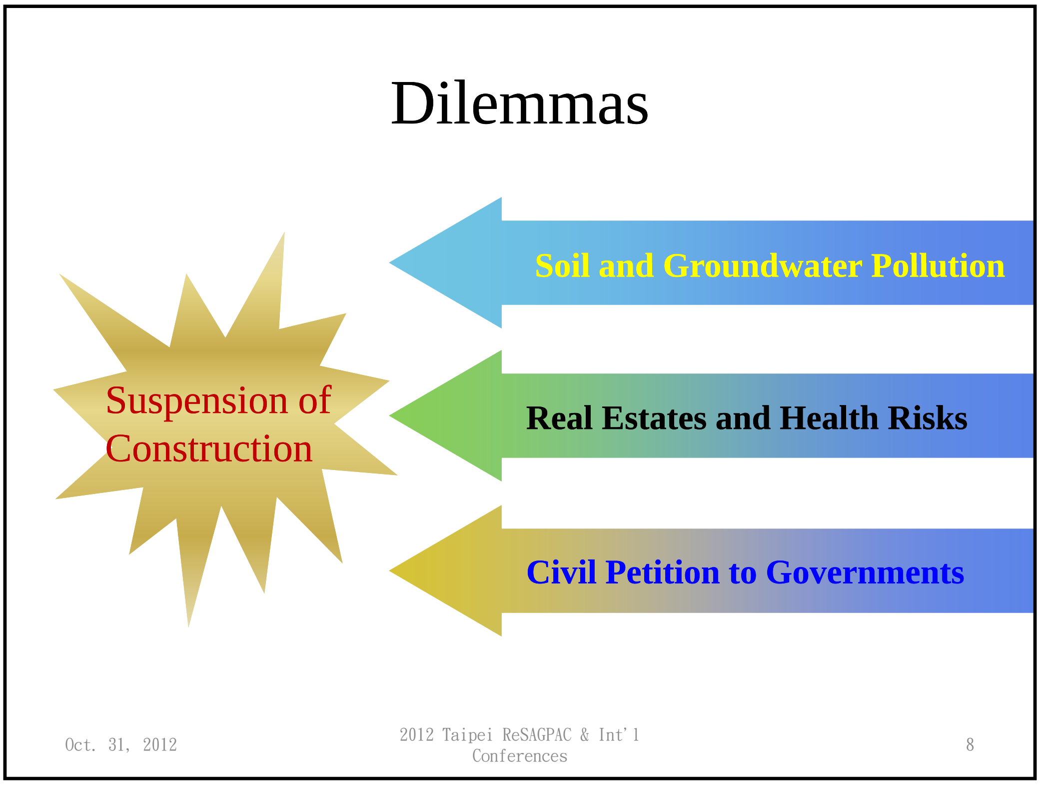
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Suspension of Construction
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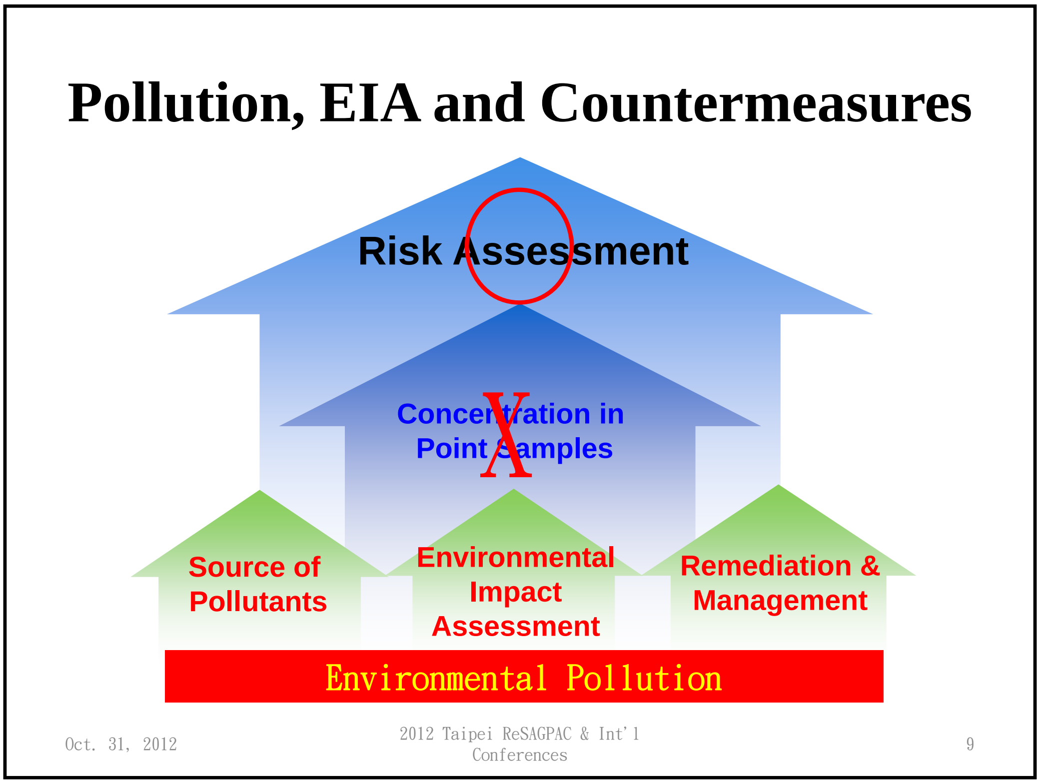
Pollution, EIA and Countermeasures
Risk Assessment
Concentration in Point Samples
X
Source of Pollutants
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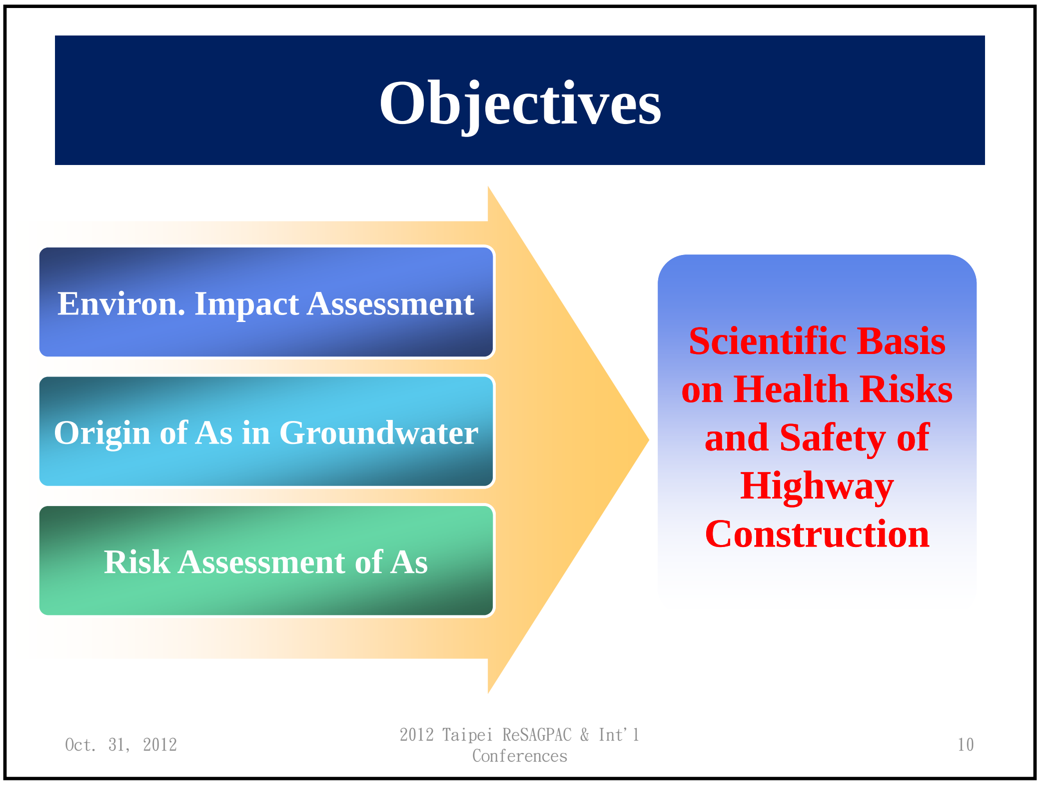
Objectives
Environ. Impact Assessment
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1. EIA: soil, rock, crops, surface and groundwater, crops, and leachate etc
2. As Transport : Column leaching test
3. As Transfer to Crops
4. Risk Assessment

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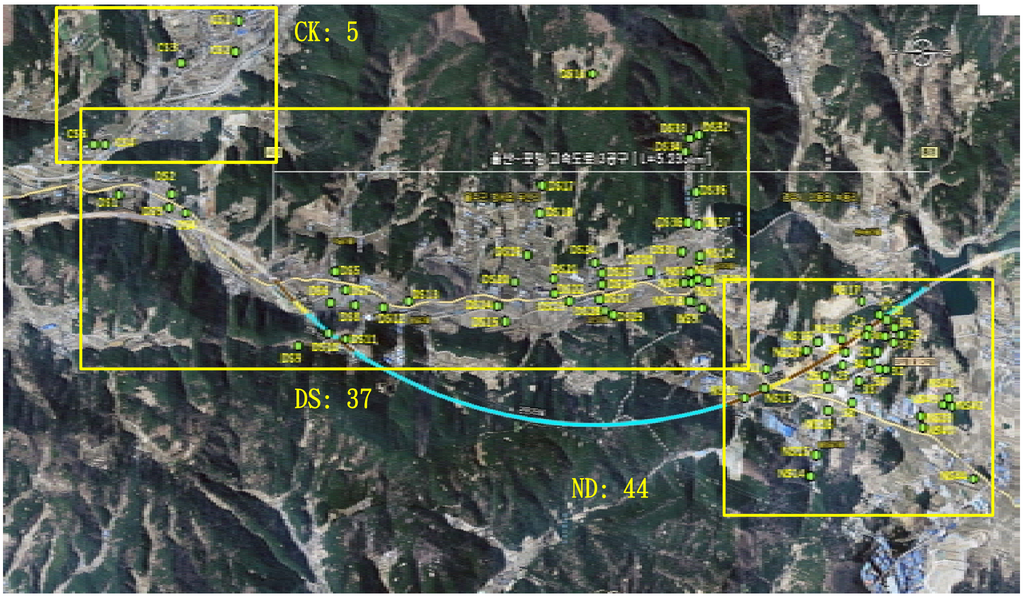
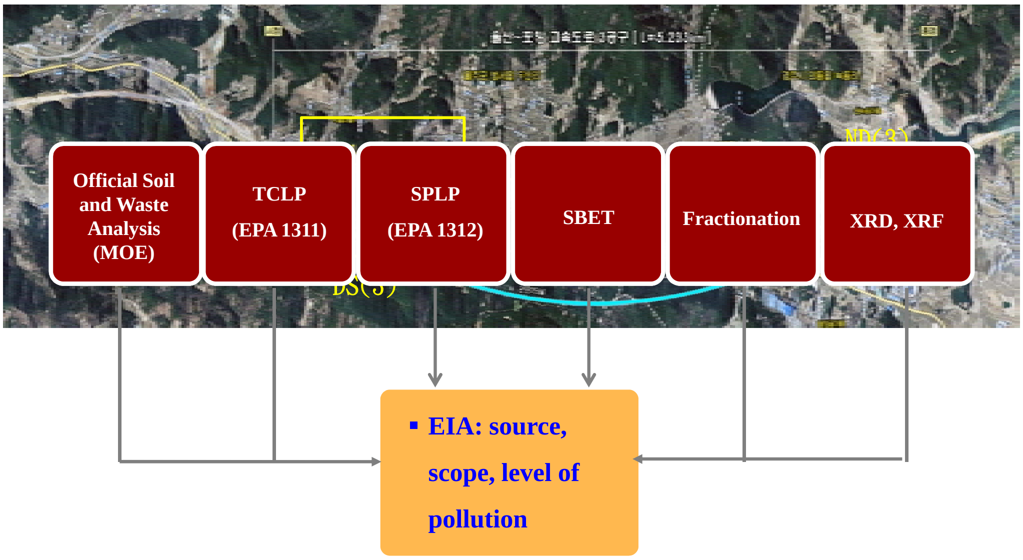
Part I. Environmental Impact Assessment (EIA)

1. Soil and Rock

Soil Samples (86)



Rock Samples (6)



Arsenic in Soil and Rock Samples

Samples	Acts	Analytical Methods	As Criteria	Ranges	Means
Soil (86)	SECA	Aqua Regia	Threshold 25 mg/kg	0.56-251.3	16.1
Rocks (6)	WMA	d-HCl (pH 5.8-6.3)	1.5 mg/L	ND	ND
	SECA	**Aqua Regia**	**25 mg/kg**	**0.0-268.6**	**39.9**
	-	TCLP(EPA1311) pH 2.88, 4.93	5 mg/L	ND-0.693	0.231
	-	SPLP(EPA1312) pH 4.2	5 mg/L	ND	ND
	-	SBET Glycine(pH 1.5)	5 mg/L	ND-0.21	0.74

SECA: Soil Environmental Conservation Act
WMA: Waste Management Act
ND: Not Detected

Discussion

[AS] in Soils & Rocks

1. [As] in soil (5/86 samples) exceeded criteria
2. [As] in rocks not extractable with dilute acids

[As] in rocks by aqua regia exceeded criteria!

1. Rock=soil?
2. STD Method?
3. Regulation?
4. Violation?

- As in rocks: not contaminate the soils
- As in rock: natural origins
- Rocks need to proper treatment

Part I. Environmental Impact Assessment (EIA)

2. Water and Crops

As in Water and Crops

Water and Crop Samples

- Surface Water: 11
- Groundwater: 12
- Leachate: 7
- 11 Crops (35 samples) (Rice, pepper, potato etc.)
- Official Anal. Method for As

Samples	As Standard	Ranges	Mean
Surface water	50 ug/L	5-16	9.0
Groundwater	**10 ug/L**	**0-35**	**11.2**
Crops	na	-	0.04 mg/kg
na: not available			

As

- **No impacts on surface water and crops**
- **[As] in groundwater exceeded drinking water criteria**
- **As from rocks samples from construction?**
- **As from natural minerals such as arsenopyrite?**

Part II. Assessment of As Transport to Groundwater

Leaching Tests from Soil Mixtures and Cement Moldings

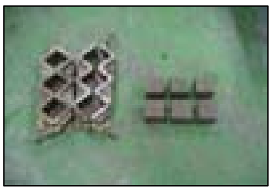
Column Leaching Test

sample	Total [As]	Mixing ratios (w/w, %)										
Soil	0.0	100	90	80	70	60	50	40	30	20	10	0
Rock (<2mm)	96.3 mg/kg	0	10	20	30	40	50	30	70	80	90	100

Rock Mixing (%)	60		90	
As Loading (mg)	46.98		70.47	
	Cumulative As Leached(mg)	Leaching Ratio (%)	Cumulative As Leached (mg)	Leaching Ratio (%)
PV 1	0.000	0.000	0.000	0.000
PV 2	0.000	0.000	0.002	0.002
:	:	:	:	:
PV 10	0.013	0.027	0.063	0.090
PV 11	0.019	0.039	0.063	0.090
:	:	:	:	:
PV 15	0.035	0.074	0.091	0.129
PV 16			0.091	0.129

As Leaching from Cement Molds


Rock+sand+cement+solidifying agent+water

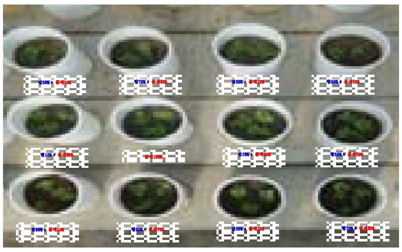
Method	• Korea Leaching Test • EPA TCLP • EPA SPLP • 4 weeks batch
Results	• No arsenic leached from cement mold • Recyclable as filler and cement molds

Part III. As Uptake by Crops:

Transfer Factor (TF)

Transfer Factor of As to Crops

Pot Mixing Ratio	Soil	0-100%
	Rock (<2mm)	100-0%
Crops grown	Lettuce and Chinese Cabbage	
Survey	Growth parameters and yield	
Transfer Factor (TF)	TF = [As in crops]/[As in soil]	



Rock/soil ratios (wt/wt)	As Fractions						Transferable As fractions	Results
	F1	F2	F3	F4	F5	Sum		
	---------------------- mg kg^{-1} ----------------------						%	
0:100	ND	ND	ND	ND	ND	0.00	-	
10:90	0.11	0.16	3.16	0.77	4.06	8.26	3.27	No As
90:10	0.15	0.19	10.95	8.64	59.2	79.09	0.43	taken up!
100:0	0.22	0.18	13.65	13.57	65.5	93.07	0.43	

Part IV. Origin of As in Groundwater

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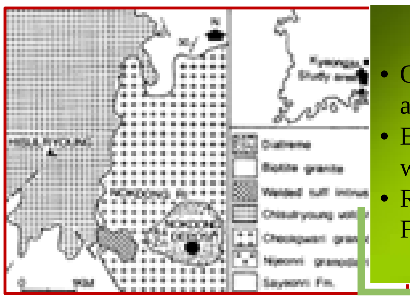
Origin of As in Groudwater



[As] in Water

- Oxidation of arsenopyrite
- Exchange of Arsenate with phosphate
- Release of As from $Fe(OH)_3$ by reduction

- **Major minerals: Pyrite, arsenopyrite, magnetite, sphalerite etc. (Park et al. 1991)**
- **Nogdong (ND) Mines for As ; High As in rocks**
- **Weathering of arsenopyrite: As oxidation to GW**

Arsenopyrite : $FeAsS + 7/2O_2 + 4H_2O \rightarrow Fe(OH)_3 + AsO_4^{3-} + SO_4^{2-} + 5H^+$
As-containing Pyrite : $(FeS\text{-}As) + 7/2O_2 + H_2O \rightarrow Fe^{3+} + SO_4^{2-} + AsO_4^{3-} + 2H^+$

As in GW

As in groundwater is originated from natural oxidation of arsenopyrite

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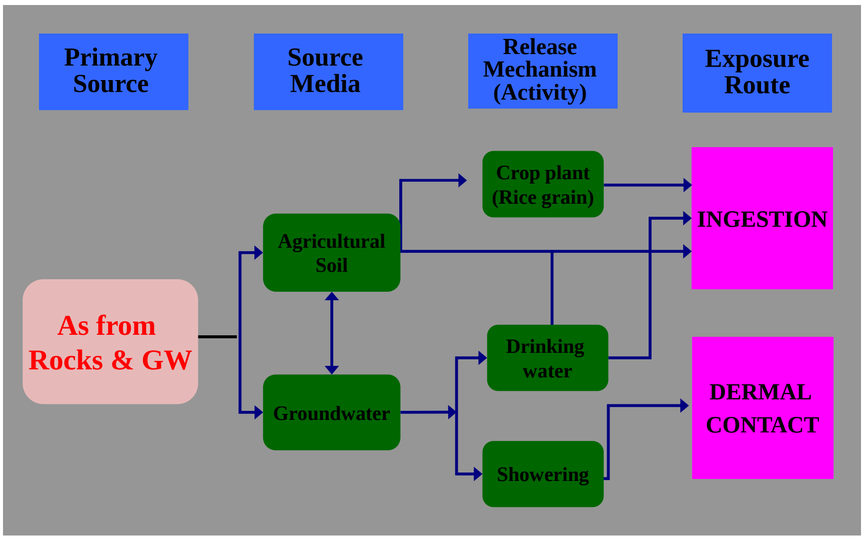
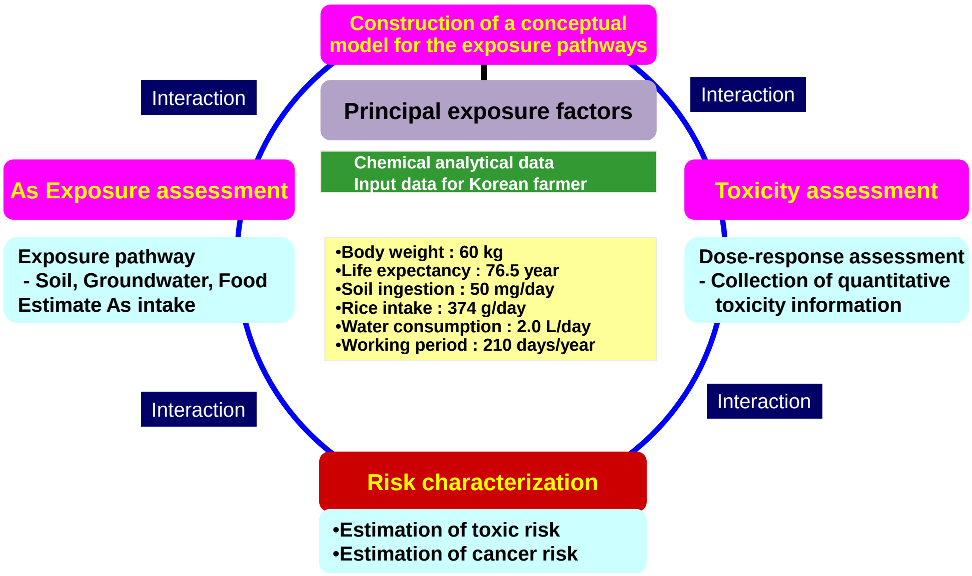
Part V. Health Risk Assessment

Conceptual Site Model (CSM)



Risk Assessment Modeling



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Risk Characterization

- ADD: mg/kg day)= $\dfrac{C * IR(s, p, w) * ED * EF}{BW * AT * 365}$
- Cancer Risk = SFo * ADD
- Non-cancer Risk = $\dfrac{ADD}{RfDo}$
- **Hazard Index (HI)** $= ADD_1/RfD_1 + ADD_2/RfD_2 + \cdots + ADD_i/RfD_i$

  $= \sum HQs$

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Health Risk Assessment of As to Residents

- **Cancer Risks of As (TCR: 10^{-4}~10^{-6})**

Sites \ Exposure Pathway		Soil Ingestion	Water Intake	Rice Intake
Overall		3.9×10^{-6}	5.5×10^{-5}	2.9×10^{-5}
Sites	CK	3.2×10^{-6}	-	-
	DS	5.7×10^{-6}	1.3×10^{-4}	3.1×10^{-5}
	ND	2.6×10^{-6}	3.0×10^{-5}	3.2×10^{-5}

- **Toxic Risk of As (permissible HI: <1)**

		Soil	Water	Crop	ΣHQ	HI
Overall		0.009	0.122	0.064	0.195	0.214
Sites	*CK*	0.007	–	–	0.007	0.008
	DS	0.013	0.290	0.069	0.371	0.412
	ND	0.006	0.066	0.072	0.144	0.145

Summary and Conclusion

Summary

Items	Contents	Major Results
Pollution	Soils	▪ 5/86 samples exceeded criteria
	Rocks	▪ ND by leaching tests; High conc. by aqua regia
	Surface Water	▪ No impacts
	Groundwater	▪ Few samples exceeding criteria; natural origin
	Crops	▪ No criteria for As; low As in rice
Transport	Leaching	▪ Few As leached in column; no release from cement molds
	Transfer Factor	▪ No As uptake by lettuce and cabbage
Health Risks	MOE and EPA Models	▪ Low cancer risk ▪ Low toxic risk ▪ no major impact from highway construction

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Conclusion

- As in groundwater was derived from minerals and their oxidations contributed to relatively high levels of As in groundwater
- Rocks from tunnel are recyclable as road fill materials with liners and cement aggregates
- Risk assessment is efficient tool for judging safety of highway construction to resident health
- **With low environmental impacts on environment and health risks, it is recommended to resume the highway construction**

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Thank you!

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感 謝!

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