

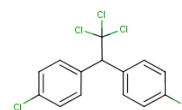
Monitoring of Persistent Organic Pollutants under Stockholm Convention and Human Health

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Hong Kong Baptist University

Inaugural Lecture, Oct 9, 2015, HKBU

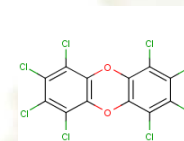
Persistent Organic Pollutants

Persistent Organic Pollutants (POPs) are groups of pollutants (including **dioxins**) that cannot be easily degraded, are strongly lipophilic, can easily be enriched in food chains, and can be transported for long distance.



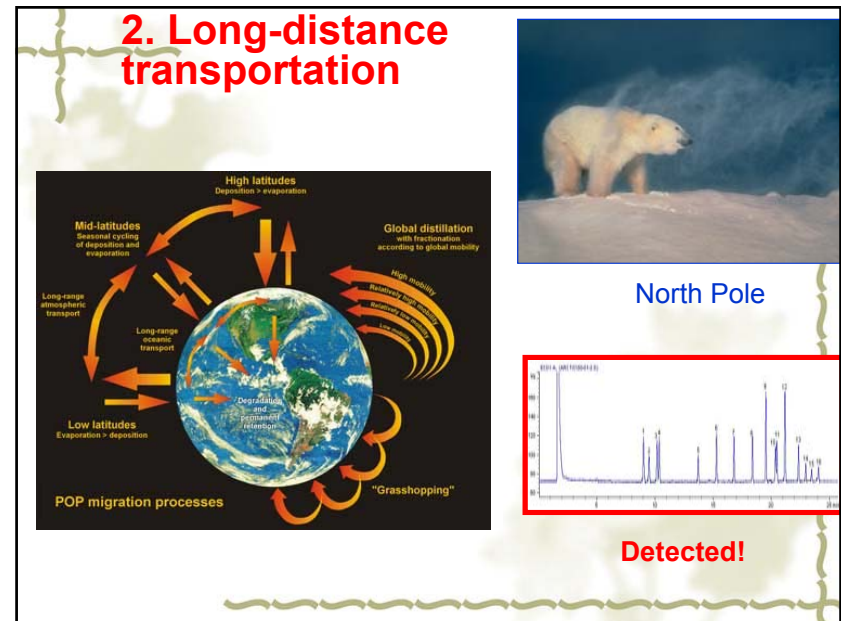
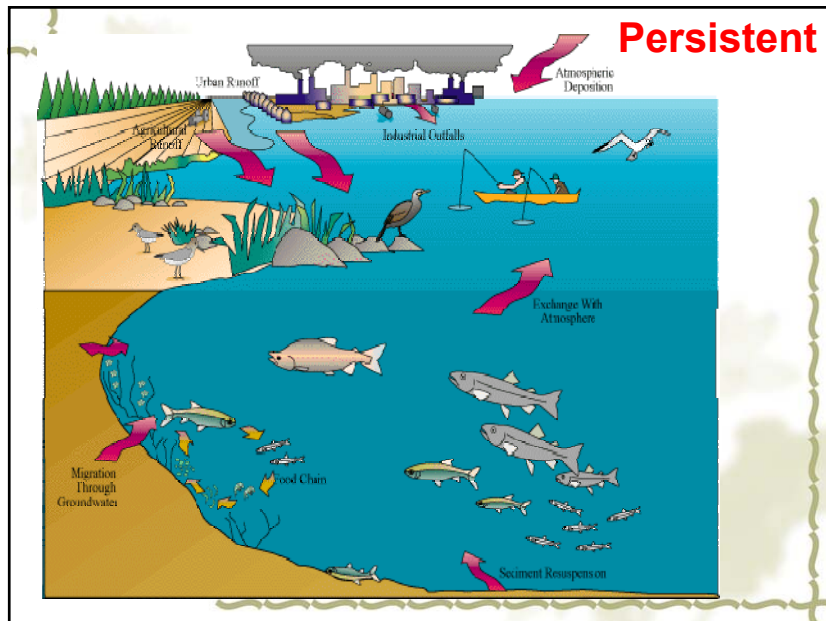
DDT, 滴滴涕

(made by human)

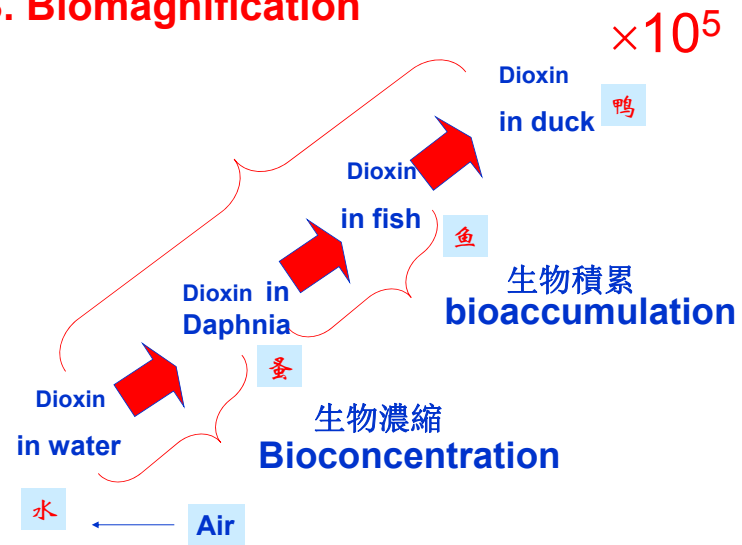


Dioxins, 二噁英

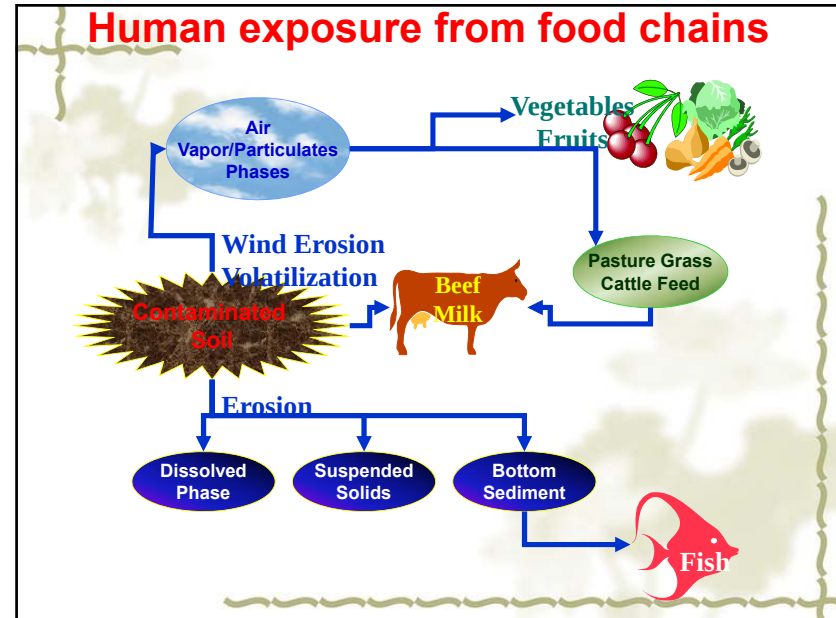
(produced unintentionally)



3. Biomagnification

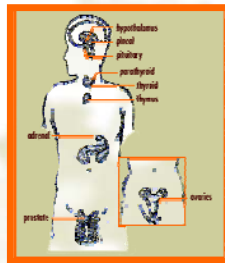


Human exposure from food chains



Adverse effects

- ❖ Cancer
- ❖ Reproductive impairment
- ❖ Developmental & immune system disorders
- ❖ Endocrine disruption
- ❖ Threat of lowered reproductive success
- ❖ Loss of biological diversity





Stockholm
Convention
on POPs
(5/2001)



斯德哥爾摩公約

Stockholm Convention
on Persistent Organic Pollutants

The Stockholm Convention is an important milestone in human & environment protection



The Chinese Government Delegation signed on the convention in May 2001

• Over 180 countries/regions have signed on Convention. China (including Hong Kong SAR) started ratification in Aug. 2004.

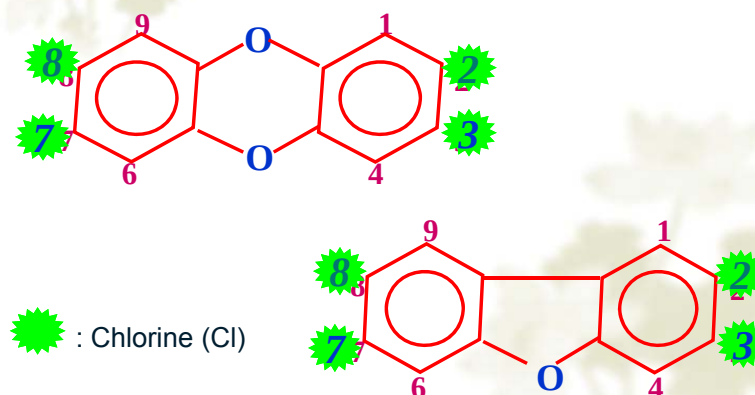
• **Great Challenge** - No integrated data on new POPs; research on POPs is inadequate.

Objectives

- ❖ Objective of the Convention:
Protect human health and the environment from POPs
- ❖ Production and use of intentionally produced POPs:
Elimination of production and use of all POPs;
To achieve this goal, production and use of POPs will be terminated or restricted; in any case, trade will be restricted;
- ❖ Unintentionally produced POPs:
Minimization of all releases of POPs with the goal of ultimate elimination.
- ❖ Monitoring and review every 5 years.

2,3,7,8-Substituted-Dioxins

17 Congeners



Sources



- ❖ Not intentionally produced
- ❖ **Primary:** Combustion processes
 - incineration of municipal waste containing PVC
 - crematory services
 - accidental fires
- ❖ **Others:**
 - burning fuels
 - production and use of chloro-organic chemicals
 - chlorine bleaching of pulp and paper
- **e-Wastes**

Human dioxin exposure

>90% of human exposure occurs via food ingestion -WHO, 2001

- Food of animal origin (based on consumption habits in **Germany**)
 - ↪ 1/3 from milk and milk products
 - ↪ 1/4 from meat and meat products
 - ↪ 1/4 from fish
 - ↪ 1/20 from eggs

Dioxin Case Study - Human

Former Ukraine President Viktor Yushchenko, Dec. 2004



108000 pg/g TCDD in blood, 50000 times above normal

Dioxin Case Study - Foods

Dioxin contamination in Belgium, Jan. 1999

- ❖ Contamination of animals fed from animal feed
- ❖ Poultry, eggs, pigs, cattle prohibited for domestic consumption and export
- 60,000 tons of chickens, pigs, cattle, meat-products were destroyed leading to food crisis
- Major impact on economy of Belgium (loss of >625 million EUR)
- Political crisis: Government was elected out

(<http://dioxin.fgov.be>)



Dioxin case study - air

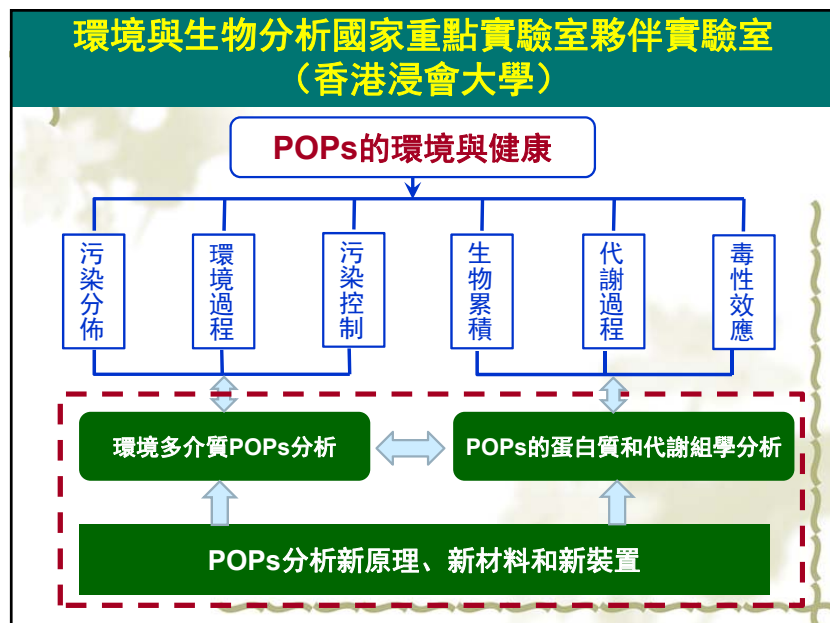
9-11 terrorism attack, USA

- ❖ Measured 23/09/2001-21/11/2001
- ❖ 10-170 pg TEQ/m³ in Sept. (compared to normal level in urban area of North America 0.1-0.2 pg TEQ /m³)
- ❖ **"likely the highest ambient concentration that have ever been reported"**
- USEPA
- ❖ Decreased to normal range in late November

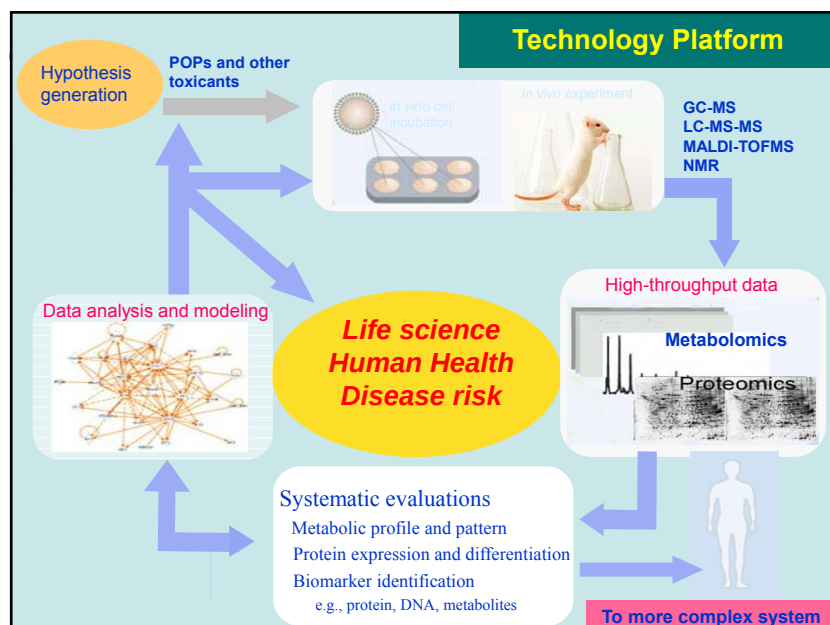


Analytical/Environmental Sciences at HKBU

- Recognized as the best locally and strong internationally
- 1982 UGC approved **M.Sc. in Analytical Chemistry**
- 1998 Chemical Testing Services
- 2002 HKBU-CAS Joint Institute for Environmental & Analytical Sciences
- 2003 Croucher Institute for Environmental Sciences
- 2003 Dioxin Analysis Laboratory
- 2012 UGC approved BSc program of **"Analytical Chemistry and Testing Sciences"**
- 2013 State Key Laboratory of Environmental and Biological Analysis



Cutting-edge Research



Example 1: Dioxin toxicity

Clc1cc2c(c1)oc3cc(Cl)cc(Cl)c3oc2Cl

2,3,7,8-tetrachlorodibenzo-p-dioxin
(TCDD)

- Endocrine disrupting compounds (EDCs)
- Developmental, neurological and immunological effects
- Cancer promoter

Aryl hydrocarbon receptor (AhR) binding

Lin S, Cai Z, et al. *Int. J. Mass Spectrom.* 2011; 301(1-3): 29-36
Lin S, Cai Z, et al. *Mol. BioSyst.* 2011, 7 (6): 1956-65.

Two mouse models

Aryl hydrocarbon receptor (AhR) binding

- ❖ High-affinity AhR
- ❖ C57BL/6J mice (C6)



High-affinity

- ❖ Low-affinity AhR
- ❖ DBA/2J mice (D2)



Low-affinity

Dosing:

20 microgram/kg body weight for consecutive three days

Workflow

Body weight



- ❖ Air conditioning
- ❖ Foods (corn, peanut, oil)
- ❖ Clean water (**no Pb 鉛 contamination**)

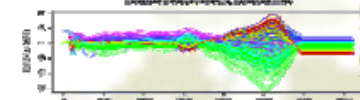
Serum, liver or skeletal muscle homogenized

ESI-Q-TOF MS

XCMS program

Nonlinear retention time alignment
peak matching and extraction

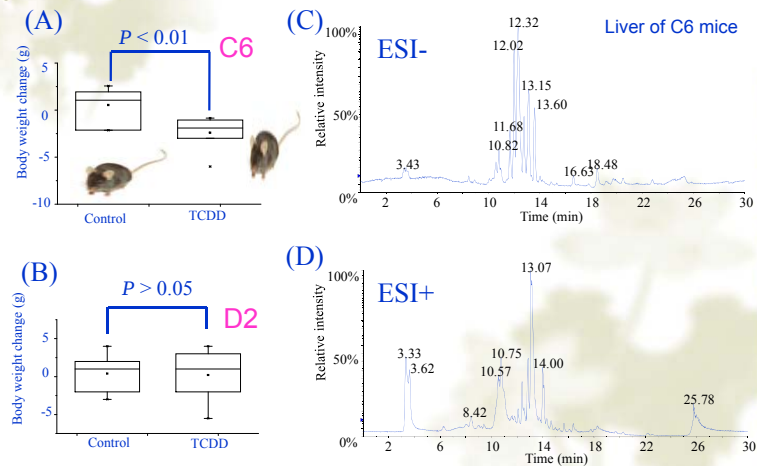
Reversed-phase
LC Column



Unsupervised pattern recognition
PCA (Principal Components Analysis)
Heat map
Z-score plot for visualization

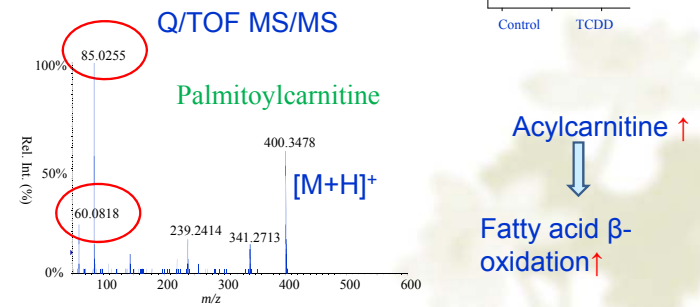


Body weight changes to biomarkers



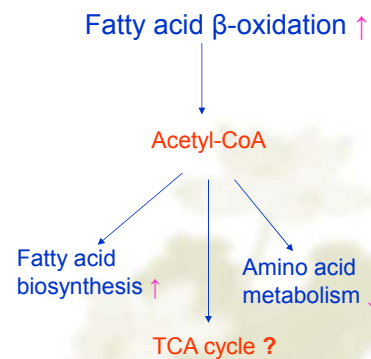
Feature selection and metabolite identification

Significant changes: $P \leq 0.0001$;
 fold-change ≥ 1.5

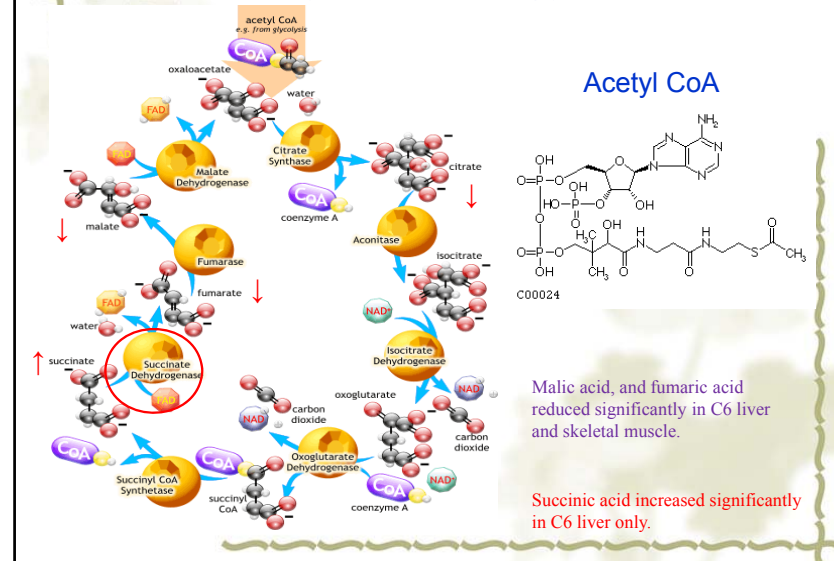


Analysis for TCA cycle

- ❖ UPLC-MS/MS with MRM mode for determination of malic acid, fumaric acid, citric acid/isocitric acid and succinic acid.



TCA cycle – Energy Metabolism



Summary

- ❖ Dioxin exposure may cause metabolic perturbation in both C6 and D2 mice.
- ❖ Fatty acids as well as phospholipids were elevated significantly induced by Dioxin
- ❖ Fatty acid beta-oxidation, fatty acid and lipid accumulation, amino acid and purine metabolism as well as TCA cycle were identified as the targets in AhR-high affinity C6 mice.
 - ⌚ Might be associated with the imbalance energy metabolism
 - ⌚ Metabolic traits might be pinpointed to general pathological conditions rather than a specific disease.

Service to Nation/Region

Stockholm Convention in Asian Region



Final Workshop of First Worldwide UNEP Intercalibration Study on POPs — Asia Region
Hong Kong, 26-28 February 2010



2010 UNEP workshop and training



2002 UNEP Workshop

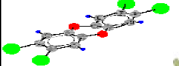
POPs Management – New Developments and Challenges in Implementation of Stockholm Convention, 9-10 April, 2012





 **Hong Kong Baptist University**
Dioxin Laboratory (2003 -)

- **Internationally recognized**
- **HOKLAS Accredited**
- **Research Focus**
 - Environment monitoring
 - Pollution sources
 - Food safety
 - Human health






Case 1: HK Foods and Risk Assessment

- Analyze all foods commonly consumed by HK residents
- Estimate potential dietary exposure to specific contaminants of various subgroups



- Compare with built tolerable intake level based on toxicology

Authorities	Time	Tolerable intake
WHO	1998	TDI=1-4 pg TEQ/kg b.w. day
JECFA	2001	TMI=70 pg TEQ/kg b.w. month
SCF	2001	TWI=14 pg TEQ/kg b.w. week

Dioxins in HK foods

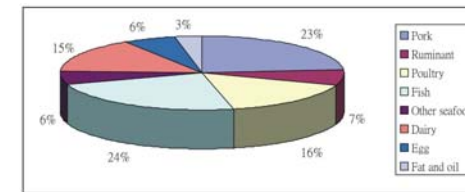
Food	Total TEQ of all composite samples (pg WHO-TEQ 1998/g fat)			Maximum level (pg WHO-TEQ /g fat)	Action level (pg WHO-TEQ /g fat)
	Mean	Median	Max		
Beef and mutton	1.4	1.17	4.03	4.5	2.5
Poultry	0.986	0.957	1.47	4	3
Pigs	0.563	0.548	1.07	1.5	1.1
Fish muscle*	0.65	0.513	2.4	8	6
Raw milk and products	1.27	1.26	2.21	6	4
Hen egg products	2.69	2.61	5.43	6	4
Mixed animal fat	0.268	0.243	0.541	3	2.25

* Fresh weight basis



Risk assessment of dietary intake of dioxin of HK residents

- ❖ By combining food consumption data of H.K. residents, the dietary exposure to dioxins was estimated



Overview of animal origin food intake of an average H.K. resident

(H.K. population-based food consumption survey, final report)

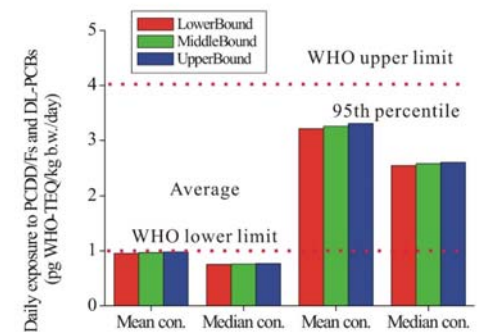
- ❖ Two scenarios : average and high risk group (95th percentile)



Are we safe? assumptions

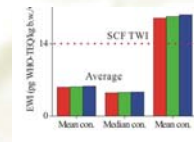
- ❖ Both mean & median of dioxin concentration were used for assessment
- ❖ Mean & 95th of food consumption used
- ❖ Food subgroup adjusted

We are safe, to some extent



Estimated daily intake of dioxin like compounds

High risk subgroup is in danger.

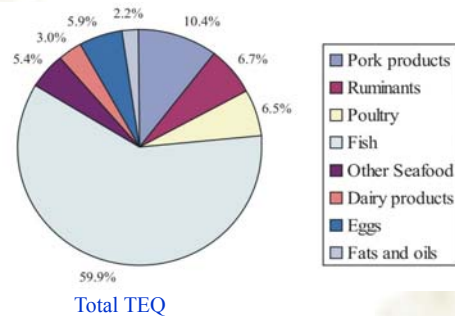


Weekly intake

Food group contribution of average residents- be careful of



Mean concentration



Case 2: Disneyland Crisis



❖ Hong Kong Disneyland

- Shipyard operated 1964-2001 (Penny Bay)
- 30000 cubic meters of dioxin contaminated soils

Soil decontamination



Off-site treatment:

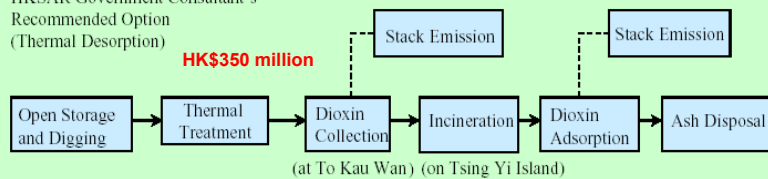
Penny's Bay

To Kau Wan

Finished: April 2003

HKSAR Government Consultant's
Recommended Option
(Thermal Desorption)

HK\$350 million



Thermal desorption for dioxin-contaminated soil



•Action level: 1 ppb I-TEQ

•Clean-up target: 1 ppb I-TEQ

•Operated from July, 2003 to April 2004

Thermal desorption is used to extract the contaminants from the soil by using hot water and alcohol.

Independent Assessment

- ❖ To provide independent expert review on the effectiveness for the operation
 - ↻ handling and transportation
 - ↻ disposal
- ❖ To assess the effectiveness of incineration
 - ↻ stack emission
 - ↻ fly and bottom ash samples
- ❖ To evaluate the impact of incineration on ambient air dioxin levels

Dioxins in Air of Hong Kong

location		Dioxin Concentration (pg I-TEQ/m ³)		
		Dec,2003	Jan, 2004	Average
Hong Kong (Tsing Yi)	Ching Wah Court	0.056	0.090	0.073
	Cheung Wang Estate	0.049	0.100	0.075
	Cheung On Estate	0.087	0.039	0.063
	Tivoli Garden	0.072	0.066	0.069
	Lai King Estate	0.057	0.045	0.051
	Central	0.05		
	Tsuen Wan	0.06		
The United States (Columbus)		0.05		
Air Standard in Japan		0.6		

< 0.1 pg I-TEQ/m³ (normal urban level in North America)

It is safe, from Dioxins



Independent assessment was accepted by community.

Acknowledgement

- Kwok Chung Bo Fun Charitable Fund
- Hong Kong Baptist University Foundation
- Dioxin Analysis Laboratory
- State Key Laboratory of Environmental and Biological Analysis
- United Nation Environmental Program
 - ❖ Representative from countries in the Asia-Pacific region
 - ❖ International consultant team for the Report
- HKBU Research Committee
- Research Grant Committee of Hong Kong
- Students, post-doc, staff and colleagues

