Drainage Service Department-
Research and Development Forum 2012
Day 2: 28 Nov 2012 Wastewater Treatment

Persistent Organic Pollutants & Emerging Chemicals of Concern: Sources, Fates and Effects

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Different Era of Chemical Revolution

- TNT – 1900
- Bakelite – 1922
- Penicillin – 1928
- PCBs – 1929
- Polystyrene - 1931
- Alkylbenzene sulfonate (detergent) – 1933
- DDT – 1939
- Toxaphene – 1942
- Tetracycline and Chlordane – 1948
- Erythromycin - 1948,
- Polyurethane – 1952

(Trussell, 2009)

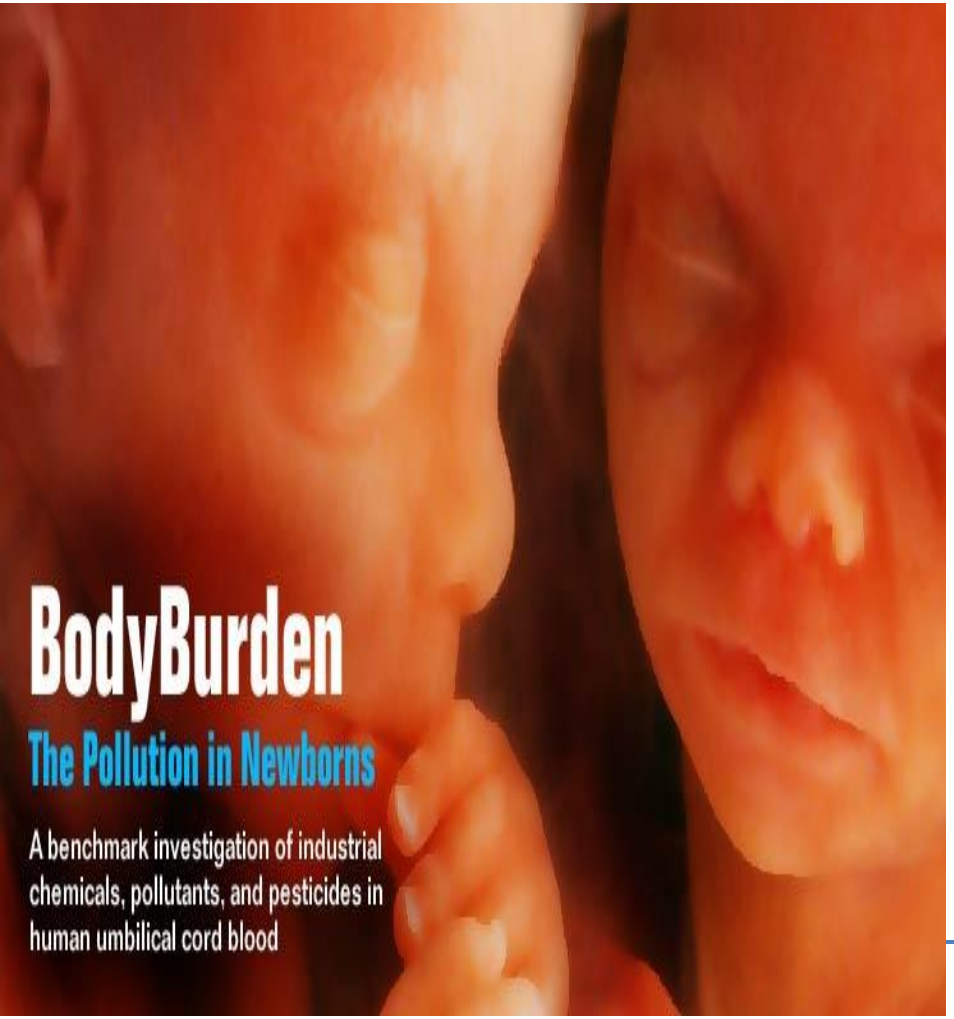
New Chemicals (some statistics)

- **As of 4/18/2007**
  - **> 30 million (31,322,549)** organic and inorganic substances (excluding proteins & nucleotides) have been registered
  - **About 14 million (13,780,301)** are commercially available
  - **< 0.5 million (245,316)** are inventoried or regulated substances
- **Two years later**
  - **> 5 million** new chemicals have been registered
  - **About 5 million** additional chemicals are commercially available
  - **Only 5,316** additional substances have been added to inventoried/regulated lists

（Equivalent to 0.1% of new or commercially available chemicals）

Source: http://www.cas.org/cgi-bin/cas/regreport.pl
Chemical Abstracts Service (CAS) Registry

EWG (Environ Working Group), based on investigation at 2 major laboratories: an average of 200 industrial compounds & pollutants (a total of **287** chemicals) found in 10 newborn babies



-**Organochlorine pesticides** (DDT, dieldrin, etc)

-**Chemicals** used in a wide range of **consumer products** (perfluoro-chemicals, brominated fire retardants, PCBs)

-**Chemical pollutants** from **waste** & **fossil fuel combustion** (polyaromatic hydrocarbons, polychlorinated & polybrominated dioxins/furans, polychlorinated naphthalenes, mercury)

Sources of Emerging Contaminants

Residential wastewater

Agriculture

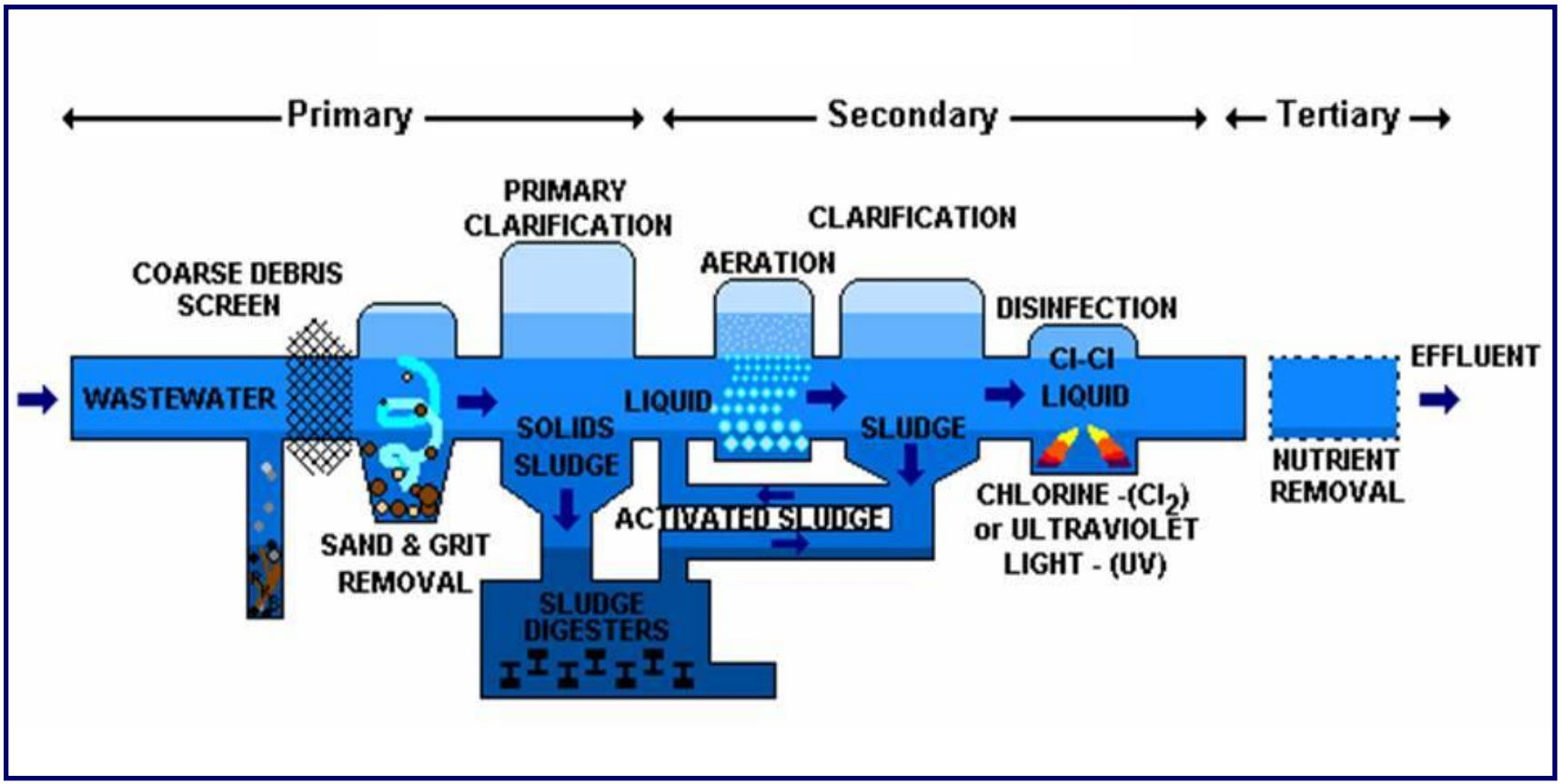
Pathways to Nature

- **Directly into the sewage system**
  - **Excreted medicine**
    - -Unmetabolized parent compounds
    - -Partially metabolized compounds
    - -Altered compounds
  - **Unused or unwanted medicines**
  - **Manufacturing metabolites**
- **Aquatic environment**
- **Landfill leachate**

Residential lawns

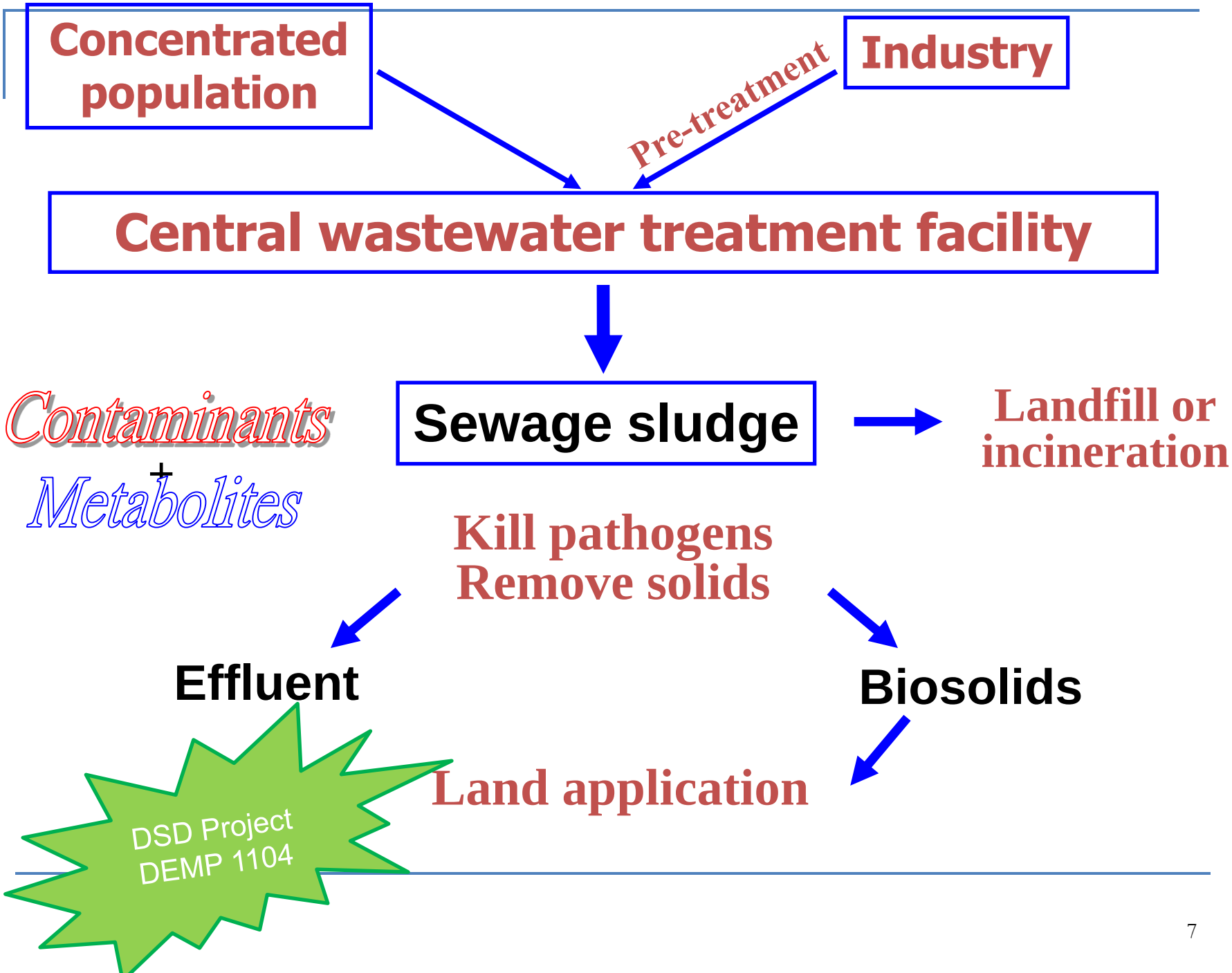
Consumer products

Wastewater Treatment Facility



How Can Pharmaceutical Waste Enter The Environment?

- **95%** of antibiotics are unaltered & excreted into the environment
- **54%** of people throw medicines into the trash
- **35%** of people flush medicines down the toilet


Concentrated population
Industry
Pre-treatment
Central wastewater treatment facility
Contaminants
+
Metabolites
Sewage sludge
Landfill or incineration
Kill pathogens
Remove solids
Effluent
Biosolids
Land application
DSD Project
DEMP 1104

Environmental/Human Health Impacts

Chapman P (2006). *ETC* 25: 1445-7

- Feminization of fish, birds, reptiles
- Intersex males (males with ova present in their testes) in amphibians and fish
- Gynandromorphism (both male and female characters) in daphids
- Abnormal development in fish and birds
- Biomarkers for exposure do not translate into quantifiable adverse effects

- Very little data on human health effects
- Unknown effects of mixtures & minute concentrations, with effects at lower levels
- Interfere with or mimic natural hormones, estrogen, testosterone
- Disruption in reproduction (e.g., lowered sperm count), development, and/or behavior
- Developing fetuses and those with suppressed immunity may be particularly vulnerable
- Potential risks to public health & safety have yet to be determined

Reasons for Concern?

- They have existed in the environment as long as they have been used commercially
- Not only new compounds, but any pharmaceutical or personal care products (PPCP), and new use of existing chemicals
- May degrade quickly, but with constant input
- Difficult to quantify due to low concentrations (PPT) & chemical mixtures
- Widely varying sensitivities amongst wildlife receptors
- Exposure risks for aquatic organisms are much larger than those for humans
- Effects can be reversible
- Potential for cumulative & synergistic effects from multiple exposures
- They are not included in routine monitoring programs, & no regulatory limits have been set
- There is insufficient information concerning long-term exposure in aquatic systems

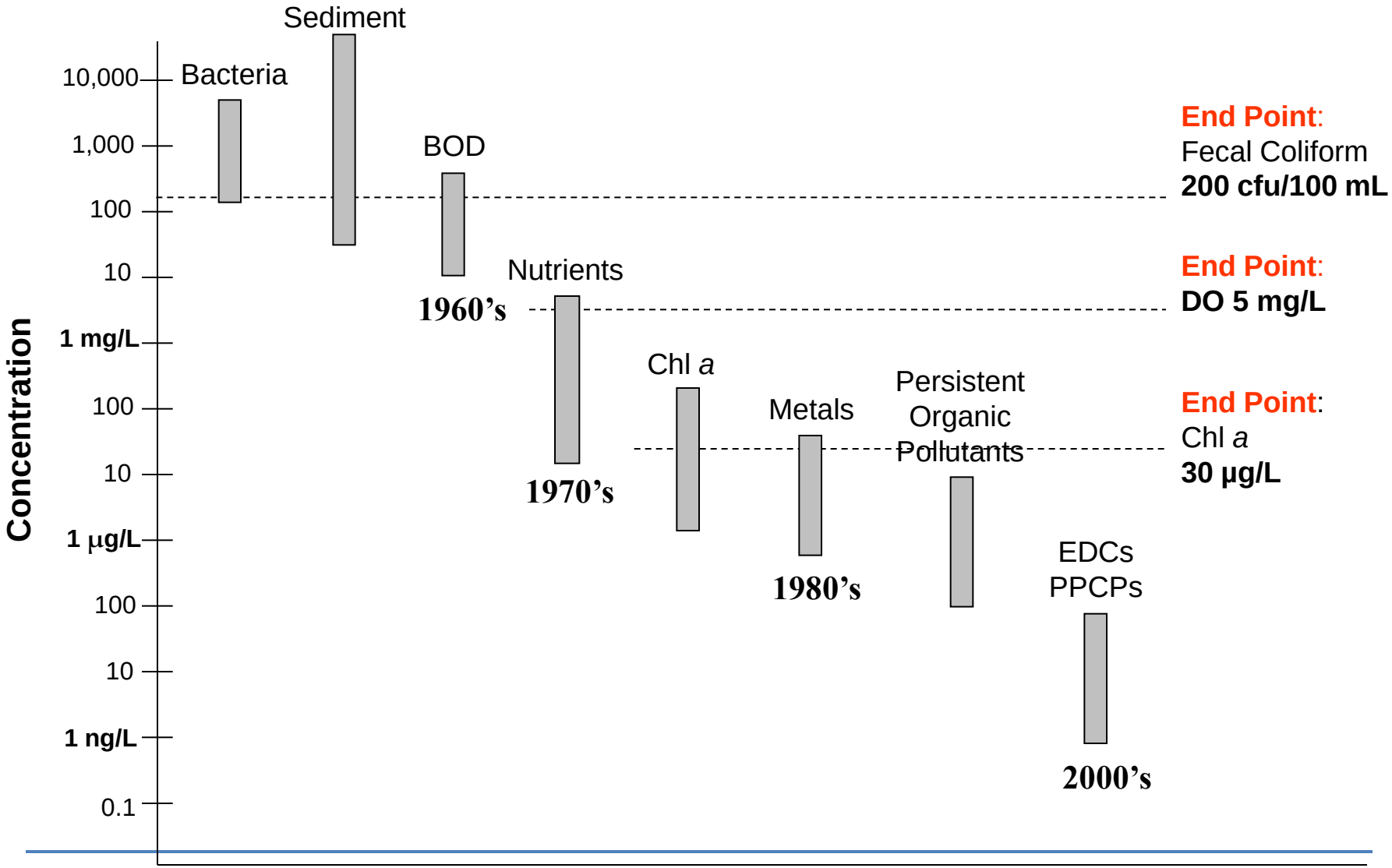
Chapman P (2006). Editorial: Emerging Substances – Emerging Problems. *ETC* 25: 1445-7

Environmental Monitoring

- **Early days**: pathogenic organisms, E. coli, N and P, chlorophyll a, dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD)
- **Chemical pollutants**: heavy metalloid/metals (As, Cd, Pb, Hg)
- **Priority pollutants**: total organic carbon (TOC), trace organics :114 priority pollutants, including a). volatiles, b). based-natural extractables, c). acid extractables, d). pesticides
- **Disinfection by-products**: chlorine used in disinfection of drinking water reacts with natural organic mater – organic compounds
- **Volatile organic solvents (VOC) in groundwater:** e.g., benzene, trichloroethylene, etc
- **Persistent Organic Pollutants (POPs):** DDT, PCB, etc
- **Emerging Chemicals of Concern:**

A Historic Perspective:

Types of Contaminants and Their Levels in Receiving Waters



(W Lung, Department of Civil & Environmental Engineering, University of Virginia)

A World-Wide Concern –

A Recent Project Supported by UNEP/GEF

Hindrik Bouwman, Ming Hung Wong, Ricardo Barra

Emerging Chemicals Management Issues in Developing Countries and Countries with Economies in Transition

- To support the Global Environment Facility (GEF) **immediate goal in its chemicals program**

  - "to promote the **sound management of chemicals** throughout their life-cycle in ways that lead to the **minimization of significant adverse effects on human health and the global environment**".

- The drafting group, with the assistance of STAP (GEF), **identified a preliminary list of Emerging Chemicals Management Issues (ECMIs)**

  - based on **numerous policy & guidance documents, combined knowledge, & active screening of recent literature**.

Emerging Chemicals Management Issues Identified

(with no order of precedence)

Compound/ Class Based:

1) PAHs
2) Arsenic
3) Bisphenol A
4) Alkylphenols
5) Parabens
6) Phthalates
7) PBDEs
8) TBTs
9) PFOA/PFOS
10) Heavy Metals

Effect Based:

1) Endocrine Disruption

Product Based:

1) Pb in Paints
2) Artificial Fertilizers
3) Cd Fertilizers
4) Pharmaceuticals &
5) Personal Care Products
6) Illicit Drugs
7) Food Additives – Melamine in milk

Process Based:

1) E-waste
2) Ammunition, Propellants, Military Equip, & Environ Chem Legacy of War & Conflict
3) Mine Wastes/Drainage
4) Sewage Sludge/Biosolids - for Land Application
5) Open Burning – with emphasis on open burning of biomass

Strategic Approach to International Chemicals Management

-A policy framework to foster the sound management of chemicals

-Initial examination of priority setting by National Stakeholders
-Development of a STAP advisory document to GEF, in cooperation with SETAC

SAICM Side Event:

Introduction to Emerging Chemicals Management Issues in Developing Countries and Countries with Economies in Transition:

Initial examination of priority setting by National Stakeholders

Development of a STAP advisory document to the GEF, in cooperation with SETAC

The immediate goal of the Global Environment Facility (GEF) through its present chemicals program is **to promote the sound management of chemicals throughout their life-cycle in ways that lead to the minimization of significant adverse effects on human health and the global environment.**

The GEF's Scientific Technical Advisory Panel (STAP) recognizes the last two decades' rapid increase in new chemicals, uses, or products, fueling or fueled by a concomitant increase in demand, increased trade, and expansion of manufacturing of chemicals into Developing Countries and Countries with Economies in Transition (CEIT). This period has also seen a rapid implementation of multilateral environmental agreements (MEAs) to meet the expanded chemicals management demands.

In this context, the Strategic Approach to International Chemicals Management (SAICM) acts as the focus for a globally effective and sustainable chemicals management process to help respond to the ever-increasing range of chemicals in global use.

Speakers include

Hindrick Bouwman, *STAP Chemicals Panel Member*
Ricardo Barra, *Consultant to STAP*
Ming H Wong, *Consultant to STAP*
Michael Mozur, *Global Executive Director, SETAC*

The STAP Chemicals Panel member, along with the Society of Environmental Toxicology and Chemistry (SETAC) and colleagues of the scientific community have focused on Emerging Chemical Management Issues (ECMIs), defining them for purposes of advising the GEF on any potential or recognized human health and/or environmental effects associated with chemical(s) whose management is not, or only partially addressed by, existing MEAs.

Based on the results of a chemicals prioritization survey of developing country and CEIT respondents, SETAC members and other experts, the STAP is developing an advisory paper for the GEF Council to identify, evaluate and prioritize ECMIs in relation to the likely chemical management needs of these countries, such that additional resources and support from the GEF will anticipate, prevent, reduce and/or minimize adverse impacts on human health and the environment within the chemicals focal area.

In this event, the GEF STAP Chemicals expert, SETAC Global Executive Director, and other internationally renowned scientists will lead a discussion on the results of their work to date.

Where: *Hall 1 (Annex B)*

When: *Friday, November 18, 14.00h to 15.00h*

Catering will be provided

Scientific and Technical Advisory Panel

An independent panel of scientists that advises the Global Environment Facility

UNEP

GEF Guidance on Emerging Chemicals Management Issues in Developing Countries and Countries with Economies in Transition

Scientific and Technical Advisory Panel

An independent group of scientists which advises the Global Environment Facility

gef

UNEP

Table 1: Regional and all-regional ECMIs ranked on Aggregate concern

ECMI	Central & South America	Africa	Asia	Eastern Europe	Oceania	**All regions - Oceania**	**All regions + Oceania**
Heavy metals	1	1	1	1	3	**1**	**1**
PAHs	3	2	2	4	2	**2**	**2**
Mixture effects	2	7	6	2	15	**3**	**4**
Open burning	5	5	3	3	1	**4**	**3**
Endocrine disruption	4	12	4	7	12	**5**	**6**
Sewage	6	10	12	6	5	**6**	**5**
Inorganic fertilizer	8	9	13	5	7	**7**	**7**
Arsenic	10	11	5	10	9	**8**	**9**
E-waste	13	3	7	14	7	**9**	**8**
PPCPs*	7	8	15	11	14	**10**	**11**
Mine waste	11	14	11	8	10	**11**	**10**
Lead in paints	17	4	8	15	16	**12**	**13**
Illicit drugs	9	6	18	19	17	**13**	**14**
Cadmium in fertilizer	12	15	10	16	10	**14**	**12**
Food additives	15	13	14	13	21	**15**	**16**
Phthalates	16	17	16	9	20	**16**	**17**
Bisphenol A	19	20	9	20	18	**17**	**19**
Organotins	18	21	17	12	12	**18**	**18**
Marine debris	14	19	19	21	4	**19**	**15**
Alkylphenols	20	18	20	21	18	**20**	**21**
Ammunition/conflict	22	16	22	18	6	**21**	**20**
Nanoparticle/material	21	22	21	17	22	**22**	**22**

**Pharmaceuticals and personal care products*

Common Contaminant "Lingo"

Daughton (2005) *Renewable Resources J*, 23: 6-23

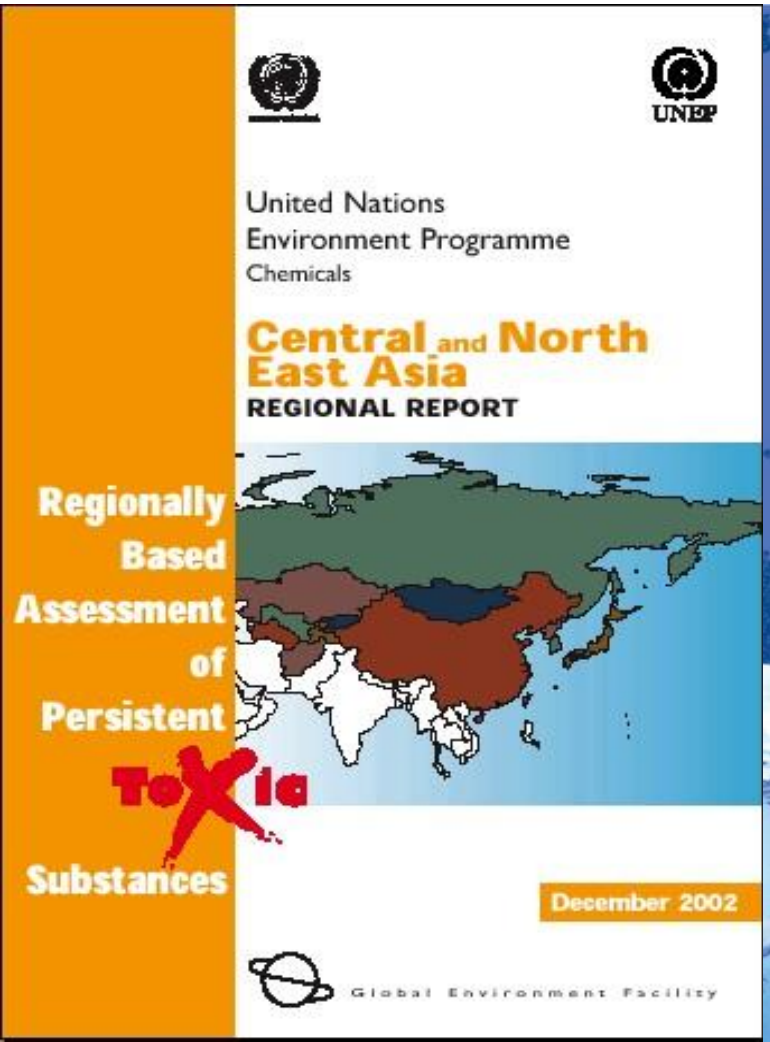
Chemical Group	Grouping Method
EDC (Endocrine Disrupting Chemical)	toxicological mode of action or endpoint
PBT (Persistent, Bioaccumulative, Toxic) **POP (Persistent Organic Pollutant)**	environmental properties
OWC (Organic Wastewater Contaminant)	location of occurrence
PPCP (Pharmaceuticals and Personal Care Product)	type of intended usage
Priority Pollutant	regulation
ECC (Emerging Compound of Concern)	novelty, fad, timeliness, or new concern
Xenobiotics	foreign versus endogenous
HPV (High Production Volume) chemical	quantity (manufactured/imported in US ≥1 million pounds/year)
POHO (Pollutant Of Human Origin)	source or origin

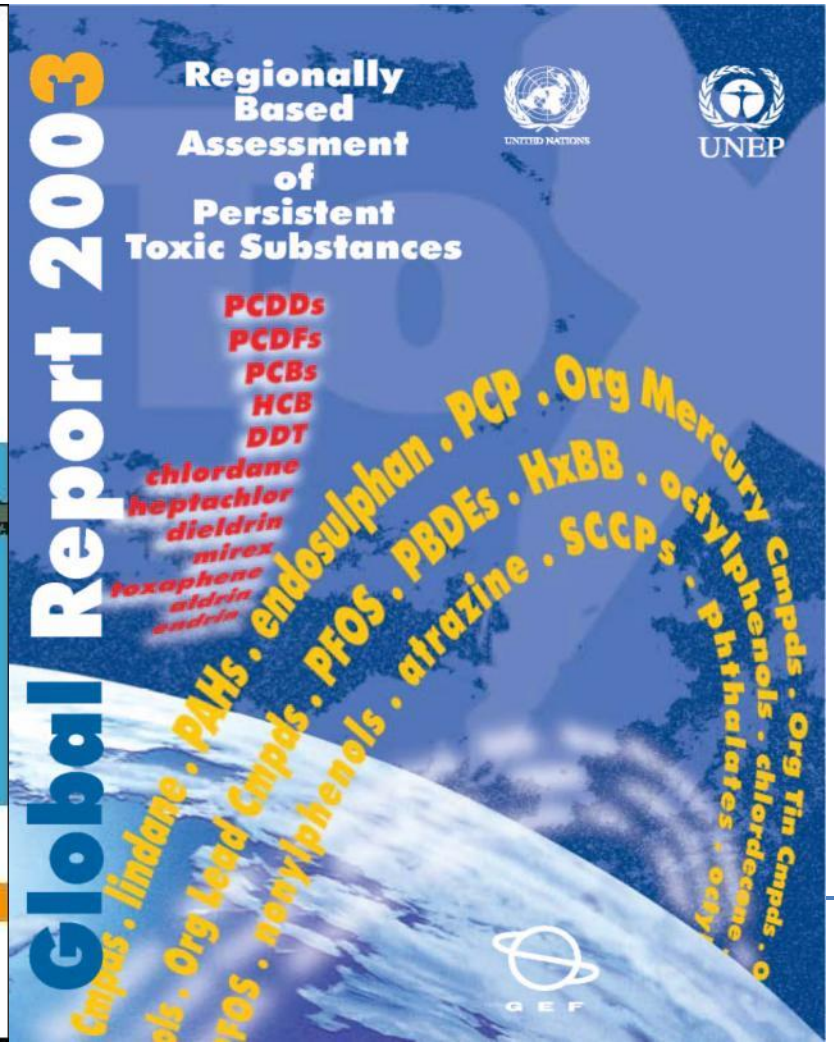
- **many additional categories**
- **use depends on context, author, audience, date of publication**

Regionally Based Assessment of Persistent Toxic Substances (PTS) 2000-2003

UNEP-Chemicals & GEF (Global Environmental Facility)

http://www.chem.unep.ch/pts



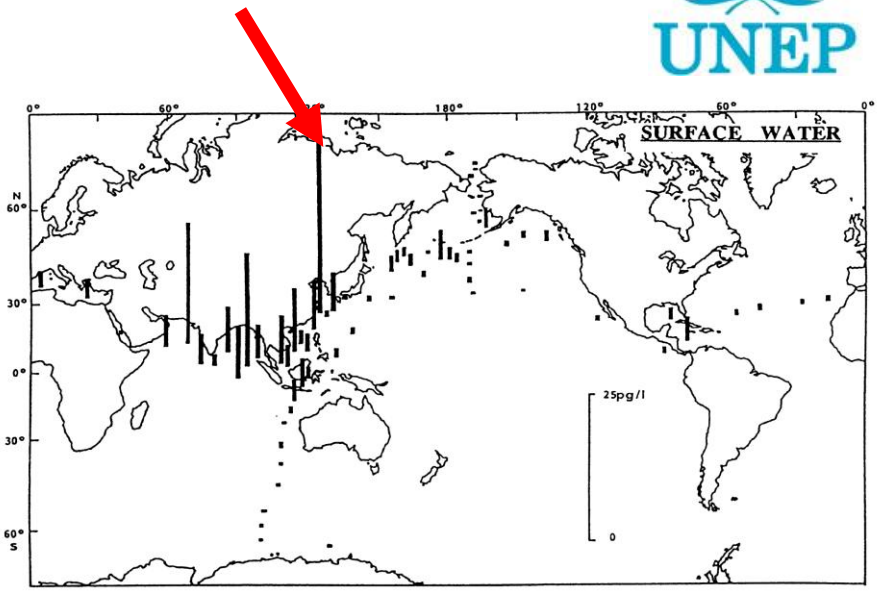


Pearl River Delta

One of the World's Mega Deltas (5,000 inhabitants/km²)

Highest record: near Macao eastern coast

UNEP



Global distribution of total DDT concentrations in surface seawater

(Iwata et al, 1993)

Hong Kong: 7.5 M population, land area 1046 km²

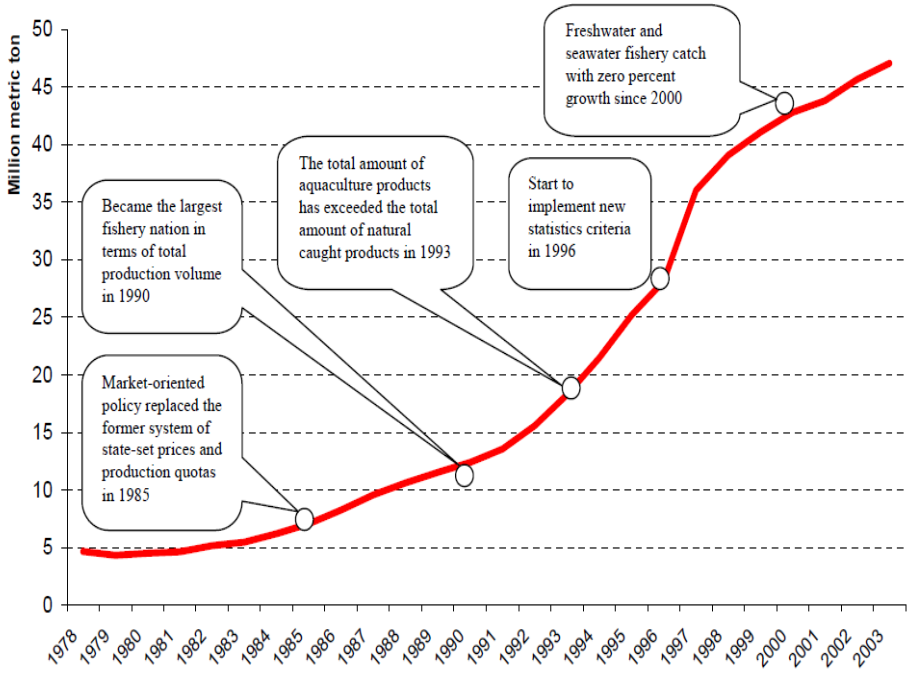
Information Extracted by News Media

- Deng WJ…., Wong MH (2006). ***Atmos Environ***
- Deng WJ…., Wong MH (2007). ***Environ Int***
- Peng XL…., Wong MH (2007). ***Environ Model Assess***
- Choi MPK…., Wong MH (2008). ***Chemosphere***
- Choi MPK…., Wong MH (2009). ***Chemosphere***

- Kong KY…., Wong MH (2005). ***Water Res***
- Cheung KC, Leung HM, Wong MH (2007). ***Arch Environ Contam Toxicol***
- Cheung KC, Leung HM, Wong MH (2007). ***Chemosphere***

Fishery Industry in China (1978-2003)

- China - the largest total seafood production volume in the world;
- Aquaculture contributes 65% to the total fishery production
- Guangdong Province ranked 2nd - 13.63% (1st one is Shandong Province- 14.43%)



Polyculture:
mulberry-dike-pond system + waste the major E source

Monoculture:
under higher density + high protein feeds

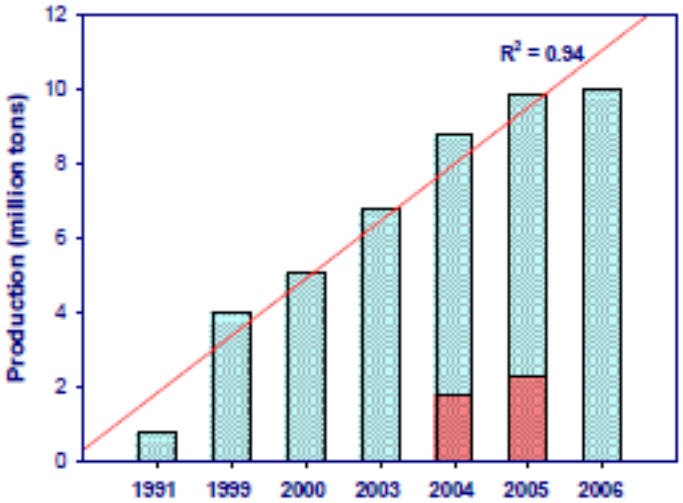
Major Mariculture Zones

Trash Fish as Feed for Grouper

Two Types of Fish Feeds

Trash fish – mainly wild, various species, with low commercial value, due to low quality, small size, with low consumer preference.

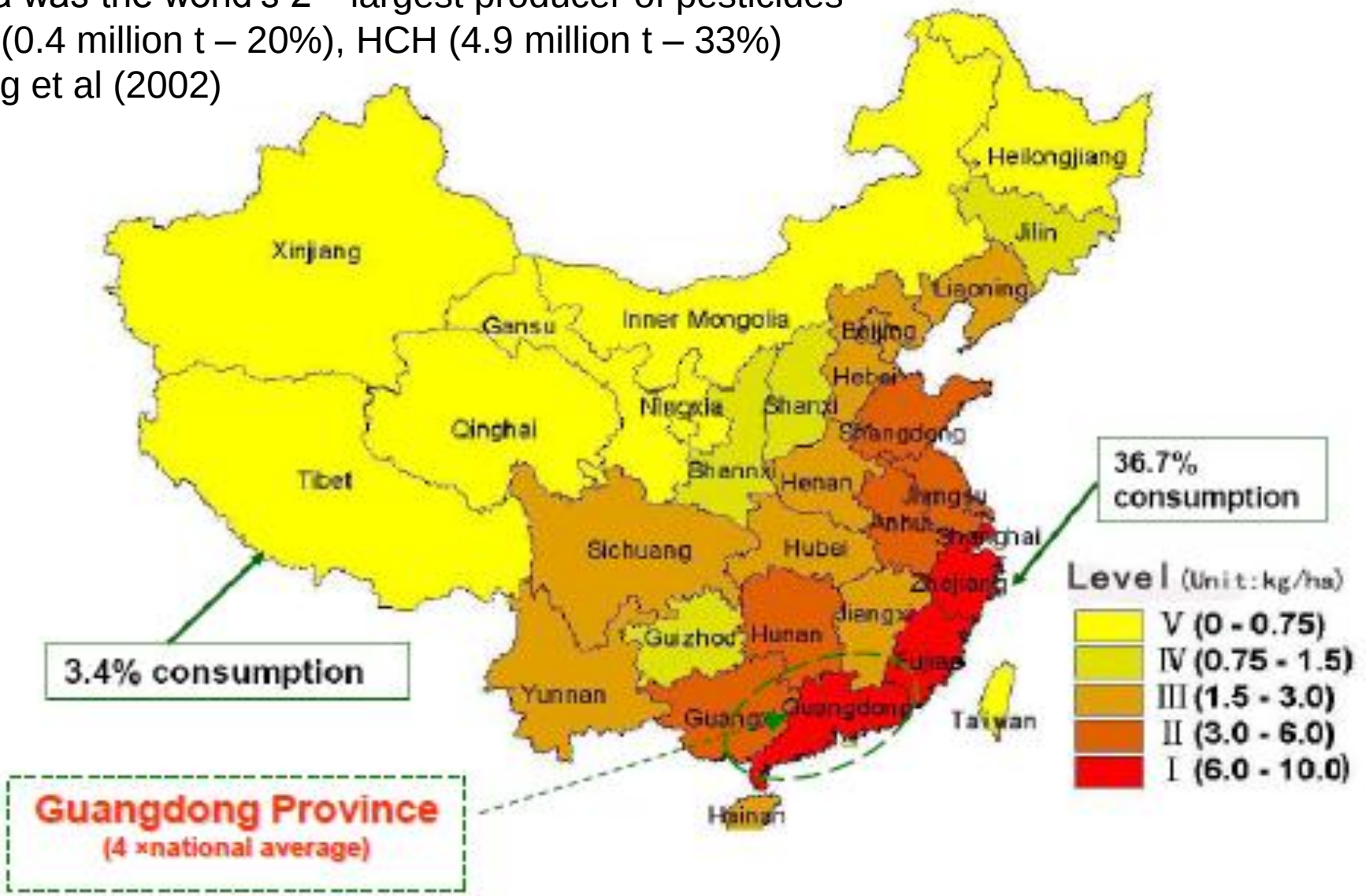
Compound feed (fish meal) - has not been widely used until recent years.



State of World Fisheries & Aquaculture, 2006

Consumption of Pesticides in China

a was the world's 2nd largest producer of pesticides
(0.4 million t – 20%), HCH (4.9 million t – 33%)
g et al (2002)



Guangdong Province
(4 ×national average)

http://www7.nationalacademies.org/sustainabilityroundtable/POPs_Pollution_in_C

Locality of E-Waste Processing Sites

Ni and Zeng, *ES&T*, 2009

Annual loading of PBDEs from e-waste (t/yr):
Domestic: 5548, Imported: 70607-176518, Total: 76155-182066
Ni, Zeng et al, ET&C (2010)

Electronic-Waste- Transboundary Movement

- Not In My Back Yard **(NIMBY)** attitude ⇨
- **80%** of all discarded computers are exported to Asia
- Of these, **90%** are sent to China ⇩

E-waste has evolved into a complex social and global problem with deep-rooted issues

Acid Stripping of Chips & Printed Circuit Boards

HNO_3

HCl

Cl_2

SO_2

(Photos by CIES, 2004)

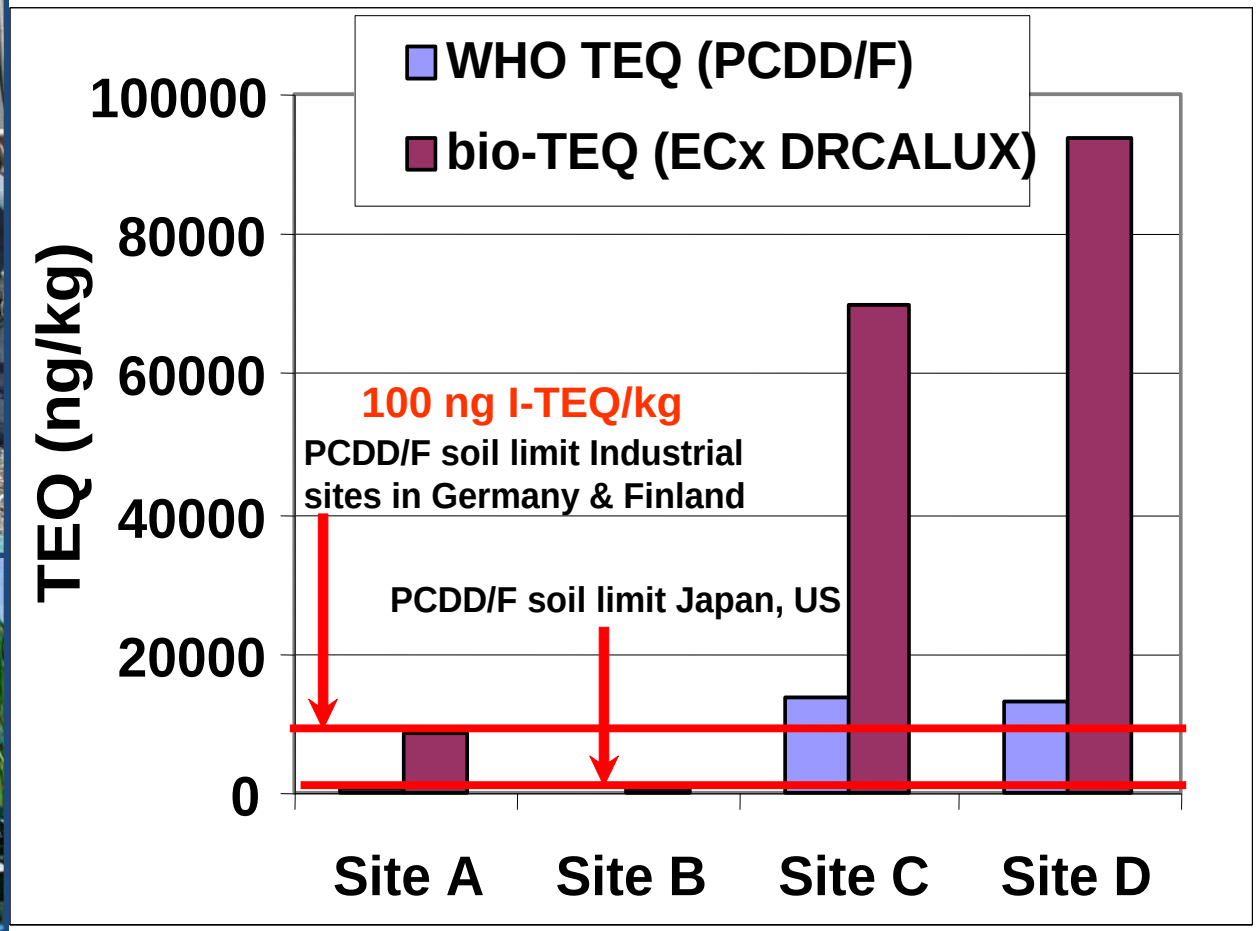
Open Burning of E-Waste – Air pollution

PCDD/Fs
PBDD/Fs
PBDEs
PAHs
PCBs
Heavy Metals

- Cu acts as catalyst for the formation of PCDD/Fs during combustion of PVC
- Burning of insulated wires generates 100x more PCDD/Fs than domestic waste (Gullet et al 2007)

(Photos by CIES, 2004)

PCDD/F in Contaminated Soil



DR-CALUX® = Dioxin Responsive Chemical-Activated LUciferase gene eXpression: a cell-based assay (quantitative approach)

Food Consumption Survey

Semi-quantitative food intake questionnaires & face-to-face interviews

A. 饮食习惯 (Food Consumption Survey)

请选择下列左侧图中所示食物的饮食**总**次数和**总**数量，**每份份量如图中所示**：

范例


菜芯


青菜


芥兰


油麦菜


芹菜

请选择左侧图中所示食物的饮食**总**次数和**总**数量，**每份份量如图中所示**：

怀孕前

每周吃 **2 次**菜芯、**1 次**青菜，**1 次**芥兰，**1 次**芹菜，每样每次各吃 **1 份**，所以总计**每周**吃 **5 份**。

☐ 每日 ☑ 每周 ☐ 每月

☐ 0 份 ☐ 1 份 ☐ 2 份 ☐ 3 份

☐ 4 份 ☑ 5 份 ☐ 6 份 ☐ 6 份以上

怀孕期

每日吃 **1 次**菜芯，每一次吃 **2 份**；**1 次**油麦菜，每次 **1 份**，所以总计**每日**吃 **3 份**。

☑ 每日 ☐ 每周 ☐ 每月

☐ 0 份 ☐ 1 份 ☐ 2 份 ☑ 3 份

☐ 4 份 ☐ 5 份 ☐ 6 份 ☐ 6 份以上

鱼类


鲫鱼


鲤鱼


草鱼


大头鱼

怀孕前

☐ 每日 ☐ 每周 ☐ 每月

☐ 0 份 ☐ 1 份 ☐ 2 份 ☐ 3 份

☐ 4 份 ☐5 份 ☐ 6 份 ☐6 份以上

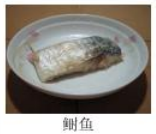
怀孕期

☐ 每日 ☐ 每周 ☐ 每月

☐ 0 份 ☐ 1 份 ☐ 2 份 ☐ 3 份

☐ 4 份 ☐5 份 ☐ 6 份 ☐6 份以上


带鱼


鲫鱼


黄花鱼/黄鱼

怀孕前

☐ 每日 ☐ 每周 ☐ 每月

☐ 0 份 ☐ 1 份 ☐ 2 份 ☐ 3 份

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怀孕期

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☐ 4 份 ☐5 份 ☐ 6 份 ☐6 份以上

B. 个人信息调查表 (Socio-Demographics Questionnaire)

采样负责人姓名：_____ 采样人职业：_____

采样日期 乳汁：____年____月____日 样品编号：_____

头发：____年____月____日 样品编号：_____

胎盘：____年____月____日 样品编号：_____

（一） 基本信息

1. 姓名：_____
2. 出生日期：____年____月____日 身高：____厘米 体重：____斤
3. 自我感觉目前身体状况如何：
   ☐ 很好 ☐ 较好 ☐ 一般 ☐ 差 ☐ 很差
4. 在台州居住：____年
5. 以前是否曾在台州以外地区长久居住（超过半年以上）？
   ☐是（请详细回答） ☐否（请答第 6 题）
   居住时间：____ 年____月 至 ____ 年____月，居住省份：_____
6. 常患疾病
   ☐ 头痛、头晕
   ☐ 耳鸣
   ☐ 肾结石
   ☐ 慢性支气管炎、哮喘、鼻炎、咽喉炎等呼吸道疾病
   ☐ 过敏性皮炎、接触性皮炎
   ☐ 浅表性胃炎、胃溃疡
   ☐ 十二指肠溃疡、肠梗阻、胰腺炎
   ☐ 其他，请注明：_____
7. 家族病史：
   ☐高血压 ☐冠心病 ☐糖尿病 ☐肿瘤 ☐其他，请注明：____

（二） 怀孕记录

怀孕次数：____次 生育次数：____次 流产次数：____次

怀孕前正常体重：____斤 怀孕期间体重：____斤

此次怀孕周数：____周 以前母乳育婴：____次(婴)

以前用母乳育婴共：____月 此次母乳育婴：____周

（三） 工作

从事工作是否与电子垃圾回收处理或大型机电设备回收处理有关？

☐ 有关（请往下作答） ☐ 无关（请答第（四）部分）

具体工种_____ 从事时间_____

工作条件： ☐ 吸入异味气体

☐ 皮肤暴露接触 ☐ 皮肤间接接触

☐ 长期接触 ☐ 偶尔接触

Estimated Daily Intakes of POPs – Adults & Infants

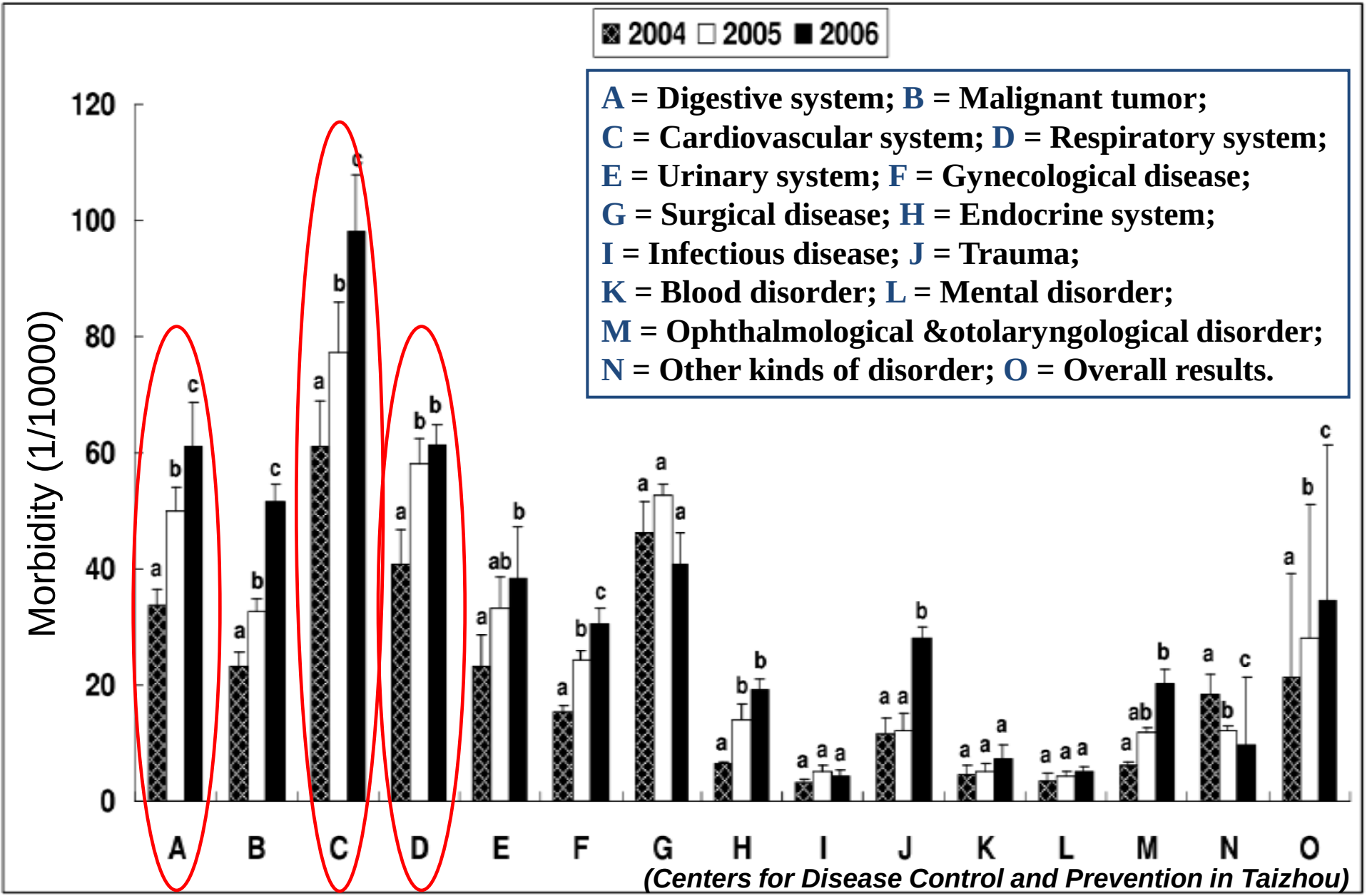
(Chan et al, 2007; Chan, 2008; Leung et al, 2009; Xing, 2008)

Estimated Daily Intake	Population group	Guiyu	Taizhou	Lin'an
ΣPCDD/Fs (pg-TEQ/kg body wt/day)	Adult [a]	1.95 ± 1.25[a]	0.37 ± 0.36[b]	0.03 ± 0.03[c]
	Breast-fed infant	NA	103 ± 67.7[a]	45.8 ± 36.2[b]
Σ_7PBDEs (ng/kg bw/day)	Adult [b]	931 ± 772[a]	44.7 ± 26.3[b]	1.94 ± 0.86[c]
	Breast-fed infant	461 ± 423[a]	346 ± 559a*	7.01 ± 3.95[b]
Σ_{37}PCBs (ng/kg bw/day)	Adult [b]	5.36 ± 4.60[b]	92.8 ± 77.5[a]	7.31 ± 4.73[b]
	Breast-fed infant	46.6 ± 76.9[c]	1779 ± 2303[a]	568 ± 529[b]

NA = Not available; [a] = exposure from fish consumption; [b] = exposure from 9 food groups

- EDI of PCDD/Fs, PBDEs & PCBs significantly higher ($p<0.05$) than RfD for adults & infants.
- **TDI of PCDD/Fs by Taizhou & Lin'an infants both exceeded WHO TDI (1-4 pg WHO-TEQ/kg bw/day) by 25 & 11 times.** EDI for Guiyu women of BDE-47 (584 ng/kg bw/day) exceeded RfD of 100 ng/kg/day for BDE-47 (US EPA), based on developmental neurotoxicity. The maximum EDI value for BDE-47 for breast-fed Taizhou infants was 534 ng/kg body wt/day, also exceeded the RfD for BDE-47.

Epidemiological Data from Taizhou (2004-2006)



Regulations Concerning EEE (EU)

(1) The Waste Electrical & Electronic Equipment (Amendment) Regulations 2007 (WEEE Directive 2002/96/EC)

- Came into force on Jan 1, 2008
- Aims to reduce both the amount of WEEE being generated & encourages stakeholders to reuse, recycle & recover materials, & to improve the environmental performance of relevant businesses that manufacture, supply, use, recycle & recover EEE

(2) The Restriction of the Use of Certain Hazardous Substances in EEE (RoHS) Regulations 2006 (Directive 2002/95/EC)

- Prohibits the use of PBDEs (penta-BDE & octa-BDE), polybrominated biphenyls (PBBs), Pb, Hg, Cd, Hexavalent chromium - exceeding set maximum concentration values in new EEE products, after July 1, 2006

Global and National Co-operation

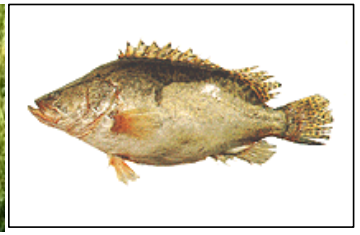
- Holistic approach - systematic governance & detailed guidelines on a nation-wide basis is needed
- E-waste is a global challenge
  - International cooperation is needed to tackle transboundary movement of e-waste
  - Article 10 of Basel Convention (cooperation)
- Share technical knowledge, improving & harmonizing technical standards, codes of practices & technologies for safe, efficient & effective management of e-waste
  - StEP Initiative - coordinated by the UNU

It is essential to close the loophole – E-waste is not clearly defined
Basel Convention (legal loophole) – export of whole products is permitted to other countries as long as it is not used for recycling

10 Freshwater species

Orecochromis mossambicus (Tiliapia)

Ctenopharyngodon idellus (Grass carp)

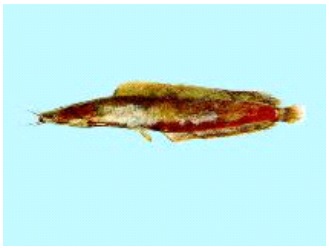


Siniperca chuats (Mandarin fish)

Mugil cephalus (Grey mullet)

Monopterus albus (Rice field eel)

Cirrhinus molitorella (Mud carp)



Clarias fuscus (Catfish)

Channa Maculata (Spotted snakehead)

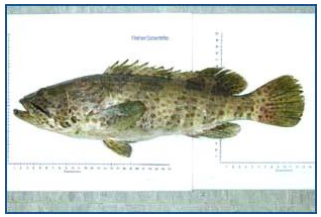
Channa Asiatiea (Small snakehead)

Aristichthys nobilis (Big head)

10 Marine species

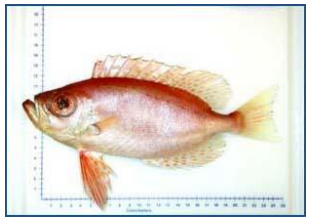
Acanthopagrus latus (Yellowfin seabream)

Nemipterus virgatus (Golden threadfin bream)

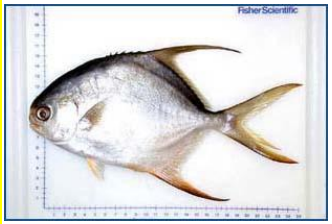


Epinephelus coioides (Orange-spotted grouper)

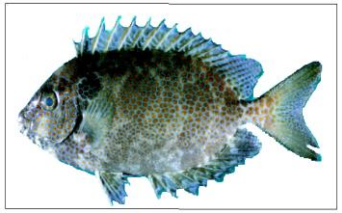
Epinephelus bleekeri (Bleeker's grouper)



Priacanthus macracanthus (Bigeye)



Trachinotus blochii (Snubnose pampano)



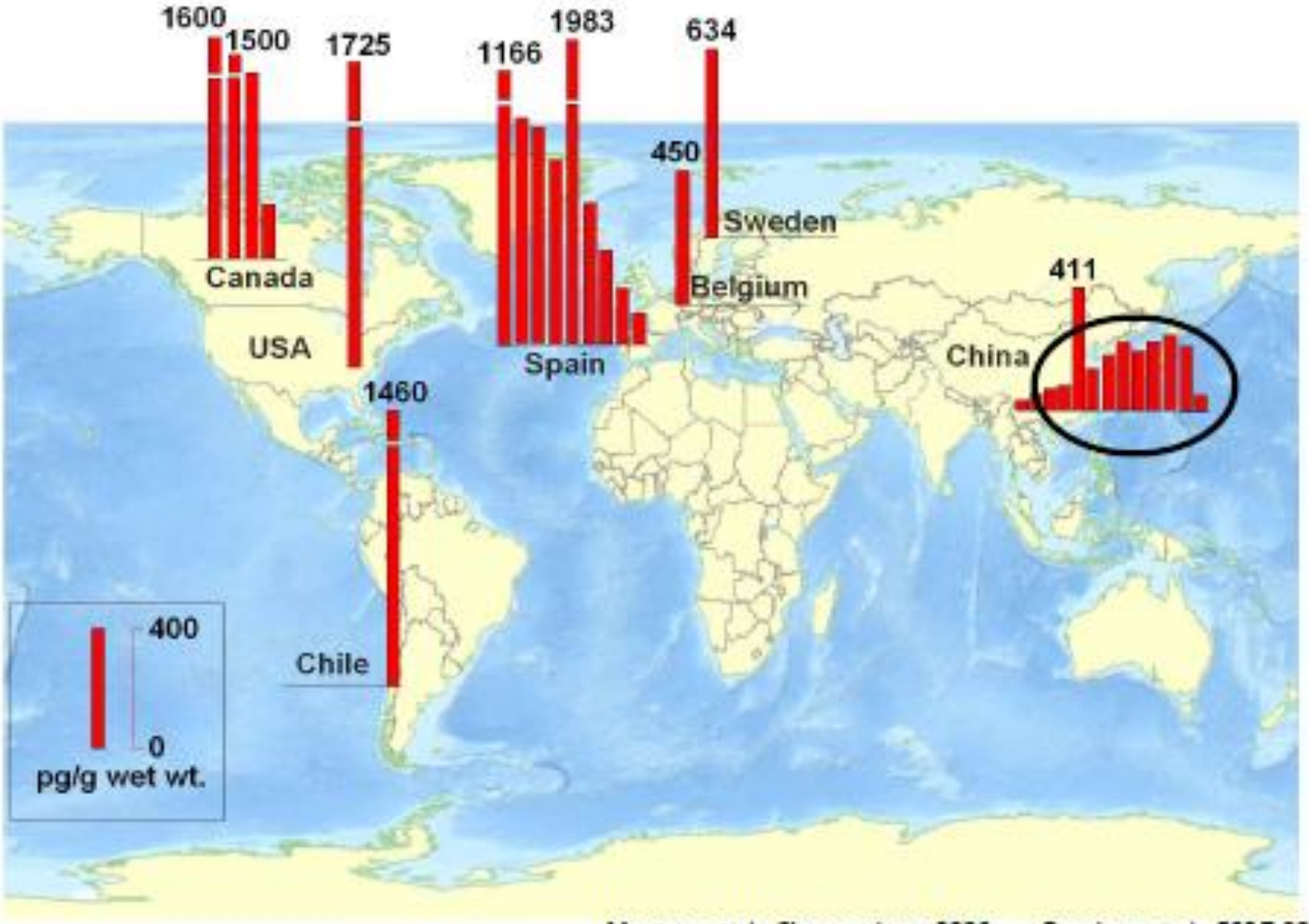
Siganus punctatus (Goldspotted rabbitfish)

Platycephalus indicus (Bartail flathead)

Pseudosciaena crocea (Yellow croaker)

Cynoglossus robustus (Tongue sole)

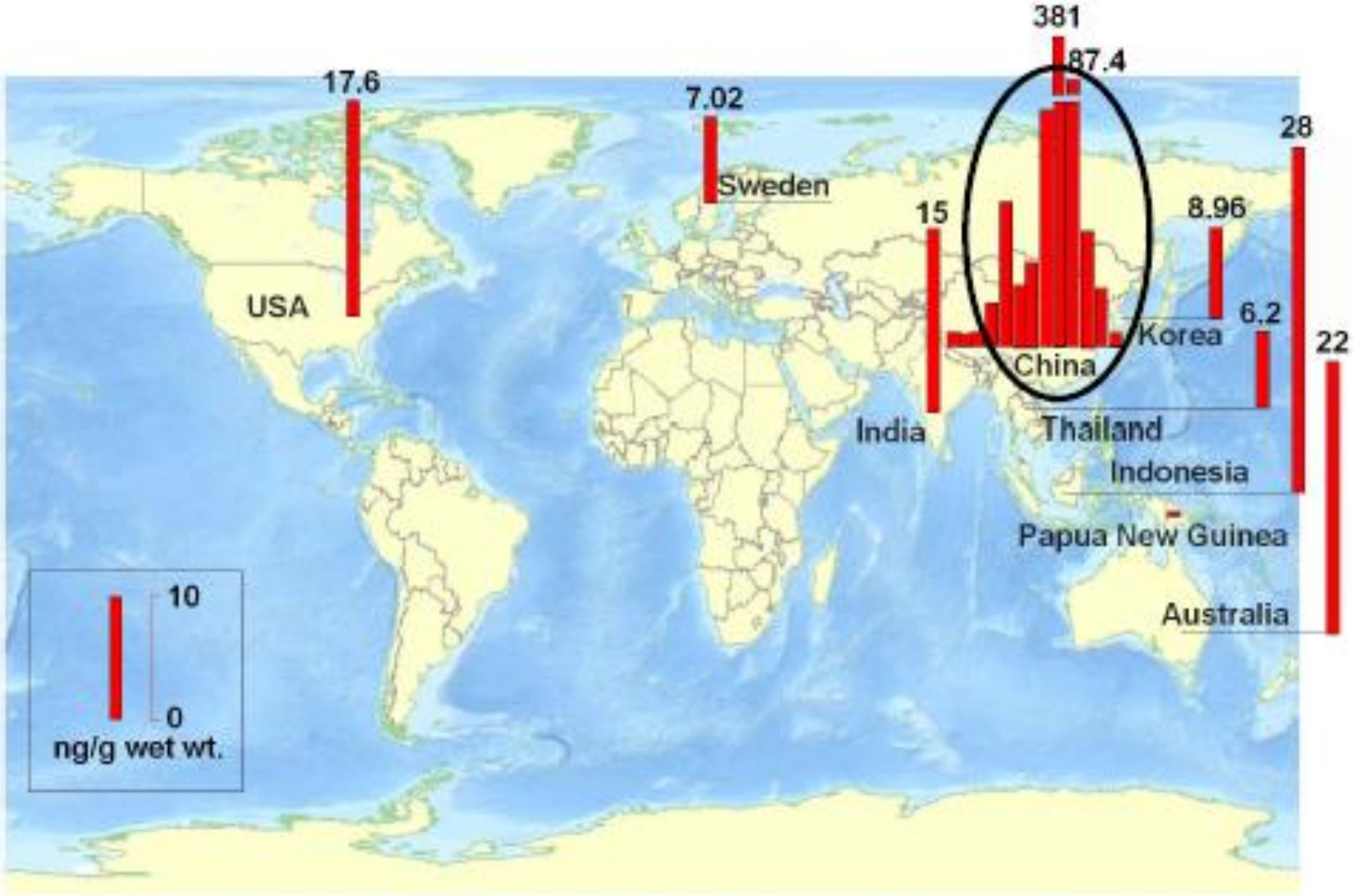
PBDE Levels in Global Edible Fish



Montory et al., *Chemosphere*, 2006 Domingo et al., *ES&T*, 2006

Tittlemier et al., *J. Agric. Food Chem.*, 2004 Voorspoels et al. *Environ. Int.*, 2006 Schecter et al., *ES&T*, 2004

DDT Levels in Global Edible Fish



Kannan et al. *ES&T*, 1995 Sapozhnikova et al. *Chomsphere*, 2004 Darnerud et al. *Food Chem. Toxicol.*, 2006

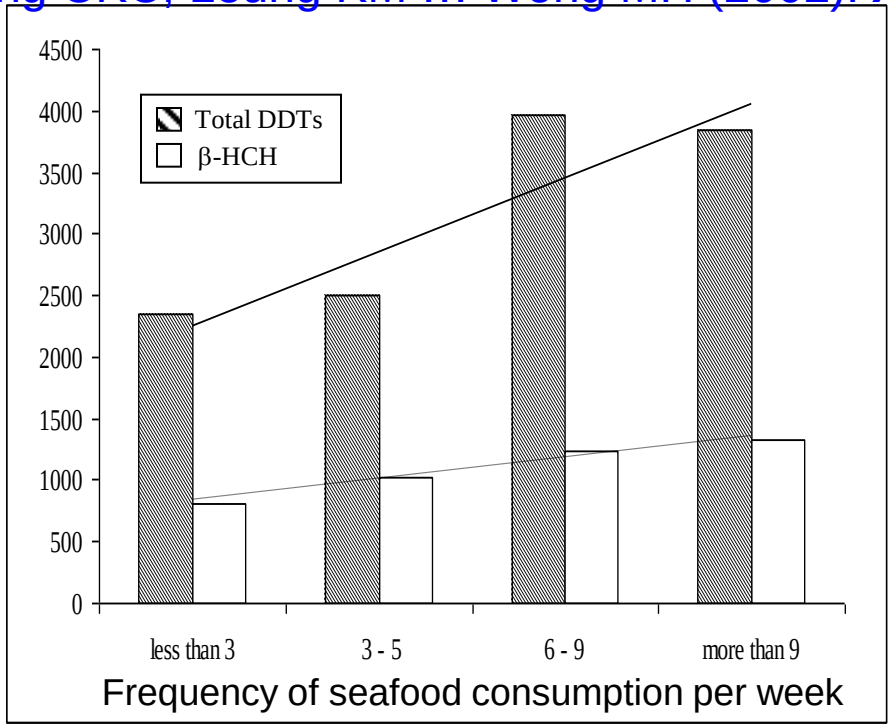
POPs in Food Items Available in HK

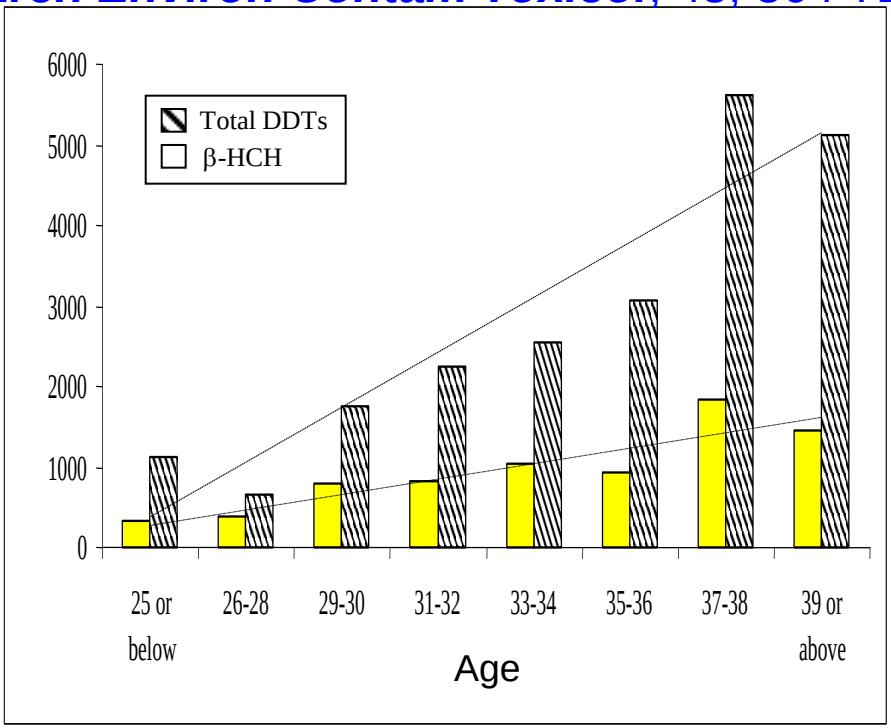
Qin YY, Leung CKM, Leung AOW…..Wong MH (2011) *Chemosphere* 82: 1329-36

	Food Items	PAHs	HCHs	DDTs	PCBs	PBDEs
				ng/g wet wt		pg/g wet wt
Milk	Coconut milk	17.5±4.91	3.02±1.51	5.92±1.23	n.d.	19.3±5.53
	Carnation evaporated milk	22.4±13.7	3.62±1.76	3.14±0.45	n.d.	14.8±4.26
Meat	Goose liver	47.3±6.63	13.4±4.13	25.1±7.16	4.20±3.01	479±77.0
	Chicken skin	43.4±5.16	11.7±6.10	14.6±5.84	3.07±1.62	158±27.2
	Chicken breast	40.5±6.29	10.8±4.28	15.6±6.54	3.16±1.94	154±30.5
Wine	White wine	7.55±2.03	2.98±0.39	n.d.	n.d.	8.07±2.33
	Red wine	7.71±0.72	3.38±0.56	n.d.	n.d.	4.25±1.23
Oil	Corn oil	27.6±16.1	3.86±1.73	8.02±3.74	2.40±0.78	34.9±7.25
	Mustard seed oil	24.9±16.2	5.97±1.80	9.51±0.47	2.72±0.42	29.4±4.84
	Olive oil	24.0±4.27	5.98±1.01	7.96±1.93	2.41±0.26	36.4±5.96
	Peanut oil	17.0±5.01	4.68±1.13	8.54±0.82	2.91±1.28	38.8±4.68
	Fish oil	40.9±13.0	8.81±1.48	12.7±2.02	4.40±2.48	82.3±13.7
	Flaxseed oil	22.9±10.9	3.93±1.97	9.24±0.96	1.84±0.55	35.1±6.45
Nut	Pistachio	24.2±14.2	7.01±0.88	10.2±2.36	1.47±0.19	56.6±11.7
	Sunflower seeds	29.5±18.1	7.26±0.32	10.3±5.09	1.96±0.08	49.6±10.7
	Pumpkin seeds	26.3±9.72	5.13±0.51	6.30±1.68	1.12±0.12	39.9±9.06
	Hawaii nutlet	29.9±24.8	8.93±0.81	16.9±4.65	2.73±0.41	53.3±10.4
	Almond	21.7±13.3	7.85±0.18	15.6±3.84	2.61±0.32	55.9±14.0
	Cashew	23.9±11.4	7.73±0.89	13.6±2.36	1.86±0.27	30.5±5.75
	Walnut kernel	24.2±13.6	6.29±1.15	19.1±6.20	3.20±0.71	28.0±4.99
	Peanut	27.6±12.7	7.22±0.83	14.4±9.31	2.54±0.74	61.5±10.2

Levels of DDT/PCB in Human Milk Related to the Age of Donors & Frequency of Fish Consumption

Wong CKC, Leung KM … Wong MH (2002). ***Arch Environ Contam Toxicol***, 43, 364-72.





- **Dietary food intake is the major route of body burden of POPs**
- **Consumption of fatty fish elevated DDT level in human milk**
- **May impose adverse health effects on our next generation**

Collaboration with Dr Leung, Director of *In Vitro* Fertilization Clinic

PAHs, OCPs, PCBs, PBDEs in Human Blood Plasma Related to Seafood Diet Consumption

Collaboration with Dr Lin, Director, Red Cross, HK

Qin YY, Leung CKM, Lin CK …Wong MH (2011) *Environ Sci Tech 45*: 1630-7

Pollutants	Congeners	Seafood consumption/week	<3	4-6	7-8	>9
		Num	51	25	20	13
PAHs	Fluorene	ng/g lipid	104±41.7a	117±49.3ab	130±70.2ab	142±63.7b
	PAHs		1191±279a	1240±439a	1341±228a	1366±496a
OCPs	pp-DDE		746±320a	801±251a	811±331a	899±399b
	pp-DDT		58.3±27.9a	63.9±23.3a	61.9±35.9a	86.2±37.1b
	DDTs		810±342a	887±275a	873±329a	957±414b
PCBs	PCB126		0.53±0.11a	0.54±0.19a	0.57±0.20ab	0.67±0.34b
	PCBs		97.4±19.1a	98.6±20.3a	99.8±24.0a	99.6±17.9a
PBDEs	PBDEs		5.67±1.66a	5.02±1.39a	4.93±1.21a	4.93±1.11a
Heavy metals	As	μg/L	0.47±0.13a	0.47±0.19a	0.50±0.17a	0.53±0.20b
	Hg		0.79±0.19a	1.08±0.40a	1.31±0.44b	1.63±0.24b

- Values are presented in mean ± standard deviation, with n=3
- Values followed by the same letter in the same row are not significantly different at the 0.05 probability level according to Duncan's Multiple Range Test

PAHs, OCPs, PCBs, PBDEs in Adipose Tissues of Patients with Uterine Leiomyomas - Seafood Diet

Collaboration with Dr Leung, Director of *In Vitro* Fertilization Clinic

Qin YY, Leung CKM …Wong MH (2010) *Environ Sci Pollut R* 17: 229-40

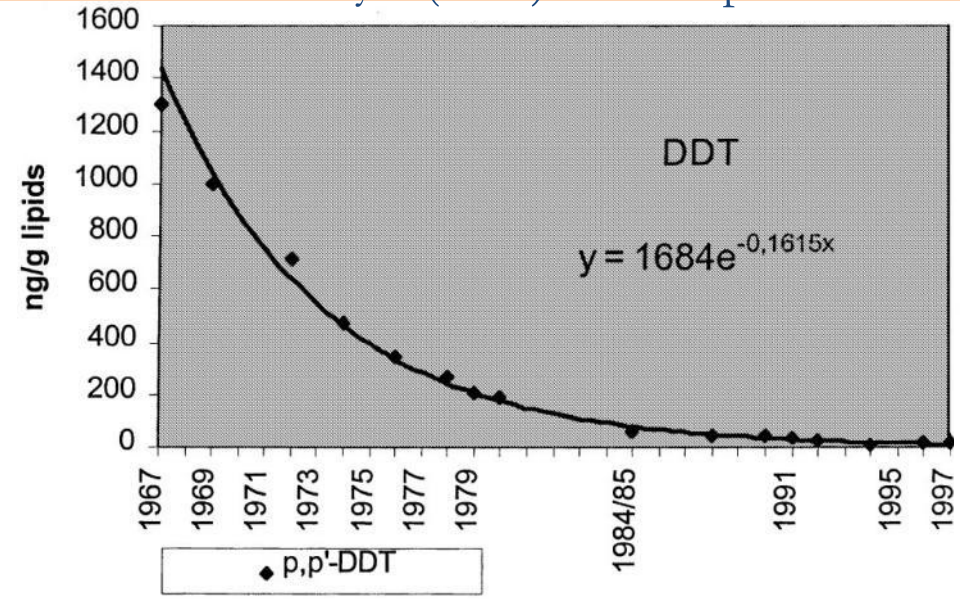
Seafood consumption/week		Patient	<3	4-7	>8	Control group	<3	4-7	>8
POPs		No.	6	9	9		6	5	8
PAHs			1737±1117a	1853±791a	1922±791a		580±195a	1117±348a	1011±571a
HCHs			217±34.4a	319±78.3b	303±68.2b		136±73.7a	96.4±16.4a	90.7±48.9a
DDTs	ng/g fat		1541±562a	2161±547b	2245±750b		1128±913a	1233±437a	1343±523a
PCBs			198±91.7a	174±96.9a	204±67.1b		94.8±41.0a	119±46.1a	158±57.3b
PBDEs			12.5±2.84a	15.2±7.70a	11.4±2.00a		3.61±0.75a	8.54±5.92a	4.17±1.62a
Heavy metals		No.	5	8	7	Control group	6	5	8
As			0.57±0.09a	0.57±0.19a	0.63±0.08a		0.22±0.07a	0.34±0.18a	0.45±0.21b
Hg	µg/kg fat		9.28±1.63a	9.02±1.06a	9.10±2.64a		5.55±1.82a	5.84±1.49a	7.56±1.44b
Pb			4.10±0.99a	5.25±0.96b	5.52±0.85b		3.48±0.70a	3.38±2.42a	3.28±1.33a

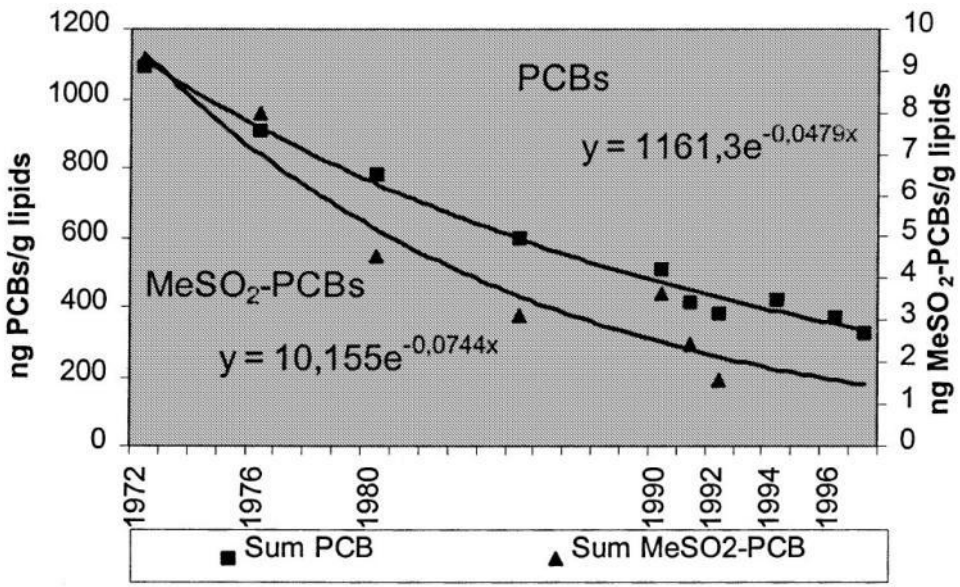
- Values are presented in mean ± standard deviation, with n=3
- Values followed by the same letter in the same row are not significantly different at the 0.05 probability level according to Duncan's Multiple Range Test

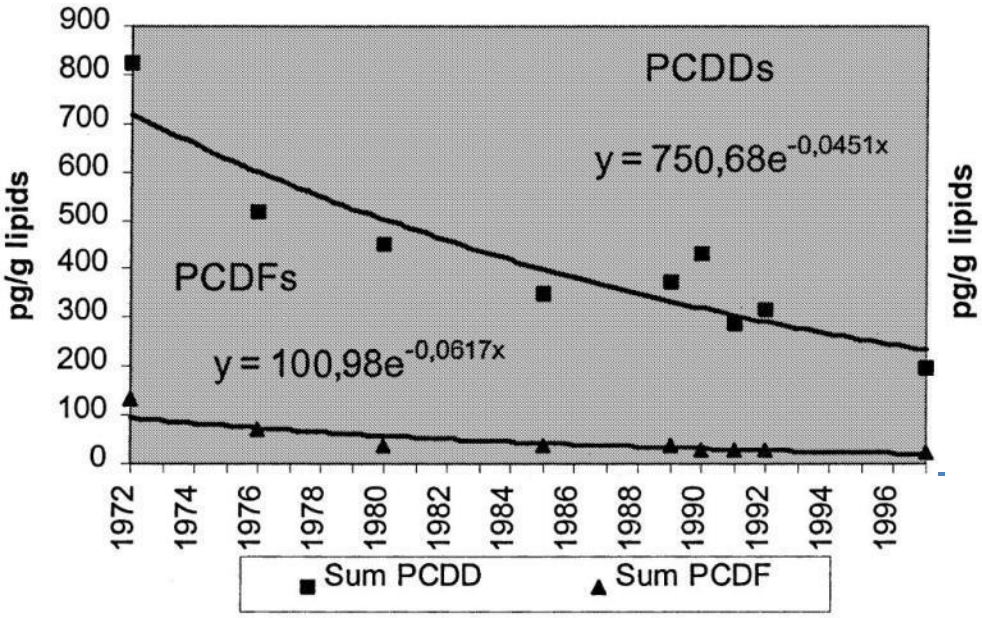
Patients accumulated significantly *higher* (p<0.01 or 0.05) DDTs, HCHs, PCBs, PAHs, PBDEs, As, Cd, Pb & Hg in adipose tissues, compared with healthy females

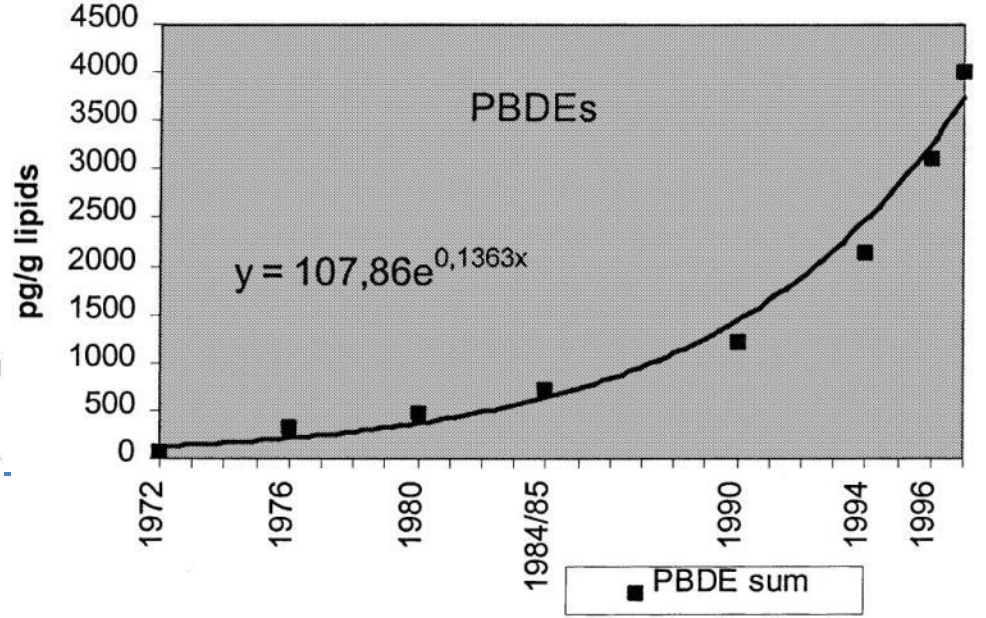
DDT, PCBs, PCDDs & PBDEs in Human Milk – Stockholm Region (expressed as an exponential curve)

Noren & Meironyte (2000) Chemosphere 40: 1111-23









Basel Convention, Rotterdam Convention

- **Basel Convention** - Control of Transboundary Movements of Hazardous Wastes & Disposal
- Adopted in 1989 - developed country companies dumping hazardous wastes in developing countries
- Entered into force 5 May 1992
- To date it has 172 Parties
- It covers hazardous wastes that are explosive, flammable, poisonous, infectious, corrosive, toxic or ecotoxic.

(Barbados, March 2009)

- **Rotterdam Convention** - Prior Informed Consent (PIC) Procedure for Certain Hazardous Chemicals & Pesticides in International Trade
- Adopted in 1998 - dramatic growth in chemicals trade
- Entered into force 24 Feb 2004
- To date it has 130 Parties
- It covers pesticides & industrial chemicals that have been banned or severely restricted for health or environmental reasons

(Geneva, 30 September 2009)

The Stockholm Convention on POPs

Pesticides	Industrial Chemicals	Unintended By-products
Aldrin	PCBs	Dioxins
Chlordane	Hexachlorobenzene	Furans
DDT		
Dieldrin		
Endrin		
Heptachlor		
Hexachlorobenzene		
Mirex		
Toxaphene		

- Adopted in 2001
- Entered into force 17 May 2004
- To date it has 166 Parties

10 New POPs

1. Pentabromodiphenyl ether (PBDE)
2. Chlordecone
3. Hexabromobiphenyl
4. Lindane
5. Perfluorooctane sulfonate
6. Octabromodiphenyl ether (PBDE)
7. Pentachlorobenzene
8. Short-chained chlorinated paraffins
9. Alpha hexachlorocyclohexane
10. Beta hexachlorocyclohexane

Most POPs are covered by all 3 conventions.

Many pesticides are subject to the 3 conventions.

The Need to Monitor these Toxic Chemicals in STW

- Existing conventional STWs were not designed for treating these toxic chemicals.
- These chemicals will find their way into the aquatic environment, through sewage effluent discharge, use of effluent for crop irrigation & application of sludge on land.
- Most of these chemicals are highly toxic, causing environmental & health problems (e.g., endocrine disrupting effects)
- Aquatic organisms: known adverse effects, lowering biological diversity, & some chemicals could be biomagnified through food chains
- Human beings: potential health risks through consumption of contaminated seafood/shellfish

Removal Efficiency of Toxic Chemicals by Sewage Treatment Works (DEMP 11/04)

Project Objectives

- To evaluate the removal efficiency of sewage treatment works (STW) on toxic chemicals such as heavy metals, POPs, emerging chemicals of concern, antibiotics & hormones.

- To determine the profiles of specified toxic chemicals in STW and their concentrations in the sewage sludge samples produced.

Targeted Pollutants

As, Cd, Pb, Cr, Cu, Ni, Sb, Sn, Zn, Total-Hg, Methyl-Hg

OCPs	Hexachlorobenzene, Chlordane (cis- and trans-chlordane, cis- and trans-nonachlor, Oxychlordane), Heptachlor (Heptachlor, Heptachlor epoxide), DDT (p,p'-DDE, -DDD, DDT and o,p'-DDE, -DDD, -DDT), Mirex, Dieldrin, Endrin, Aldrin
PCBs	1, 8, 18, 28, 29, 44, 50, 52, 66, 77, 81, 87, 101, 104, 105, 108, 114, 118, 123, 126, 128, 138, 153 , 154, 156, 157, 167, 169, 170,180, 187, 188, 194, 195, 201, 206 and 209
PBDEs	BDE3, BDE15, BDE28, BDE47, BDE99, BDE100, BDE153, BDE154, BDE183, BDE196, BDE197, BDE206, BDE207, and BDE209
PAHs	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-C,D)pyrene, benzo(g,h,i)perylene, dibenz(a,h)anthracene
Bisphenol A	Bisphenol A
Perfluorinated compounds	Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA)
Antibiotics	Tetracycline, ciprofloxacin and erythromycin
Hormones	Estrone, estradiol, estriol, ethinylestradiol and testosterone

SEWAGE TREATMENT WORKS EVALUATED

- Stonecutters Island STW: Primary treatment only

  Chemically enhanced primary treatment

  ($FeCl_3$ and cationic polymer as flocculation coagulants)

- Shatin STW: Primary and secondary treatment

  Plain settling primary treatment and biological secondary treatment (aerobic for solution & anaerobic for sludge)

SAMPLING POINTS

@ **Stone Cutter Island-STW** :

- **CS** (crude sewage, primary influent)
- **FE** (final effluent)
- **Sludge cake**

Sampling Dates

(1) 11/11/2011

(2) 12/12/2011

(3) 19/12/2011

(4) 6/2/2012

(5) 13/2/2012

@ **Shatin-STW :**

- **CS** (crude sewage, primary influent)
- **PE** (primary effluent)
- **FE** (final effluent)
- **ML** (mixed liquor activated sludge, this material was used as FE-PM @ Stone Cutter Island-STW due to the difficulty to obtain enough PM from Shatin-STW, it is a good approximation)
- **DS** (digested sludge)
- **Sludge cake**

Experimental Design

- All liquid samples were separated into
  LP (liquid portion) and PM (particulate matter)
- All solid materials were freeze-dried
- The LP, PM and cake samples were analyzed to obtain data in ng/L for LP and ng/g (dw, dry weight) for solid.

Major Equipment

- Mercury Analyzer, Methyl-Mercury Analyzer
- ICP-MS (for very low level of heavy metals)
- GS-MS (for volatile POPs)
- HPLC-MS-MS (for nonvolatile POPs)

Special Feature of the Experimental Design

- The STWs' operation data were utilized for flow analysis:
- Sewage Flow: in Thousand Cubic Meter (TCM) = 1000 m^3/day
- Sludge Produced: in tonne =1000 kg/day
- % solid in cake
- Total Suspended Solid (TSS) in Crude Sewage (CS), Primary Effluent (PE), Final Effluent (FE)

STWs Operation Parameters

Operation Parameter	Stonecutters Island - STW	Shatin - STW
Sewage Flow	1,362,000 – 1,411,000 m^3/day	216,000 – 224,000 m^3/day
Sludge Produced	581,000– 631,000 kg/day	115,000 – 125,000 kg/day
Sludge (% solid)	35.0 % – 36.0 %	30.2 % – 30.7 %
Dry Cake (g) per L of sewage flow	0.148 g/L – 0.167 g/L	0.159 g/L – 0.172 g/L
CS, TSS	230 mg/L – 390 mg/L	260 mg/L – 340 mg/L
PE, TSS	NA	77 g/L – 131 mg/L
FE, TSS	38 mg/L – 42 mg/L	8.3 mg/L – 9.3 mg/L

Flow Analysis Table

Erythro-mycin Flow	CS-LP (ng)	CS-PM (ng)	CS-Tot (ng)	FE-LP (ng)	FE-PM (ng)	FE-Tot (ng)	Remo. FE(%)	Cake (ng)	Account able (%)
14-Nov 11	105.35	8.82	114.17	127.00	0.65	127.65	(11.81)	3.70	115.05
12-Dec 11	99.05	5.75	104.80	78.70	1.18	79.88	23.78	5.17	81.15
19-Dec 11	244.00	5.05	249.05	234.00	1.63	235.63	5.39	5.23	96.71
6-Feb 12	279.00	16.19	295.19	317.00	4.28	321.28	(8.84)	5.93	110.85
13-Feb 12	603.00	6.84	609.84	654.50	1.47	655.97	(7.57)	1.58	107.82
Average	266.08	8.53	274.61	282.24	1.84	284.08	(3.45)	4.32	105.02
STDEV	204.88	4.51	204.96	227.84	1.41	228.15	14.74	1.74	13.64

Combined test data for LP (ng/L), PM (ng/g, dw) and cake (ng/g, dw)
Operational data from STWs
The flow analysis for each heavy metal and each organic pollutant

Removal Efficiency (RE)

Sorption Property

→Physical Removal

Crude sewage (CS) to Particulate Matter (PM)

- VS: > 90%
- S: 60-90%
- M: 20-60%
- L: <20%

Biodegradation Property

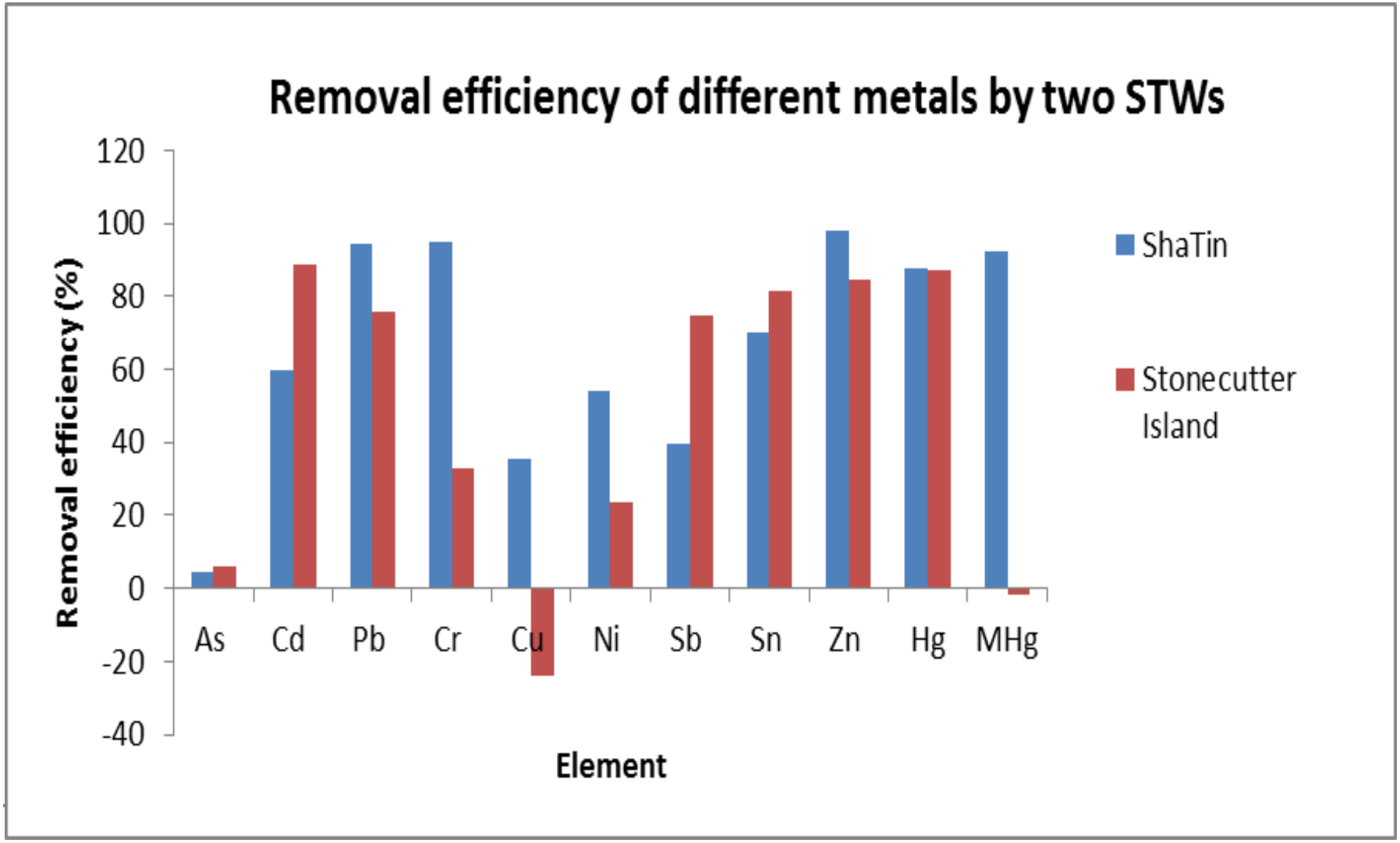
→Secondary Treatment

Primary to Secondary Treatment & % accountable (% AC)

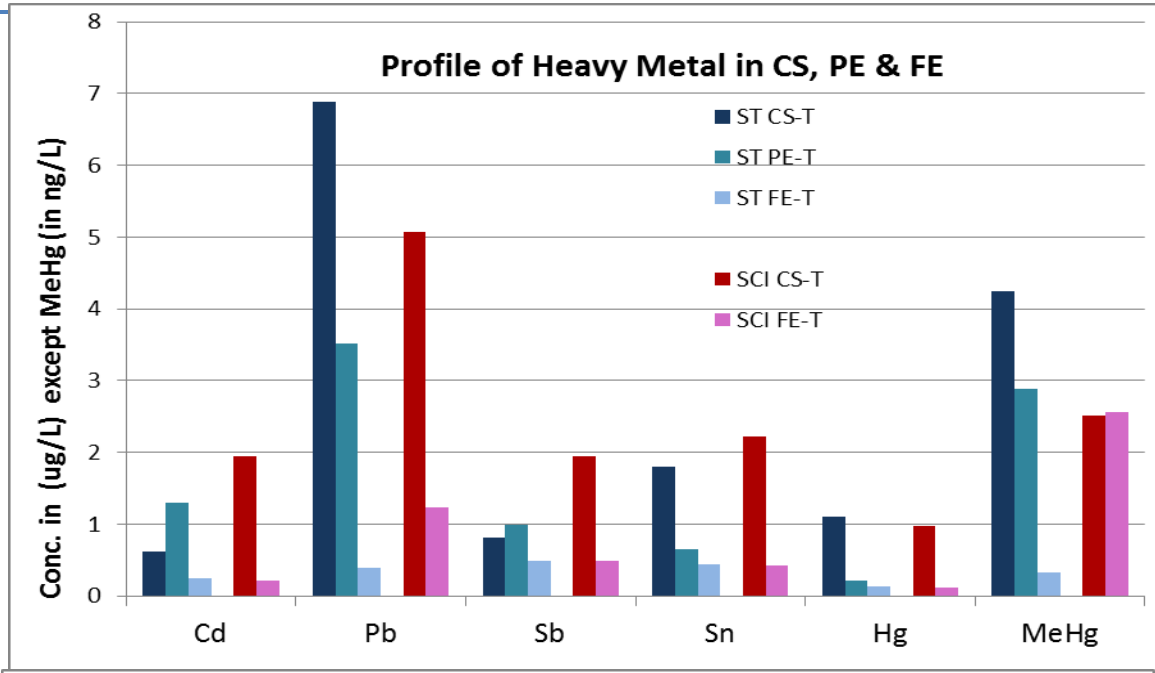
- VS: >50%, <20% AC
- S: >50%, <40% AC
- M: >15%, <85% AC
- L: <15% , >85% AC.

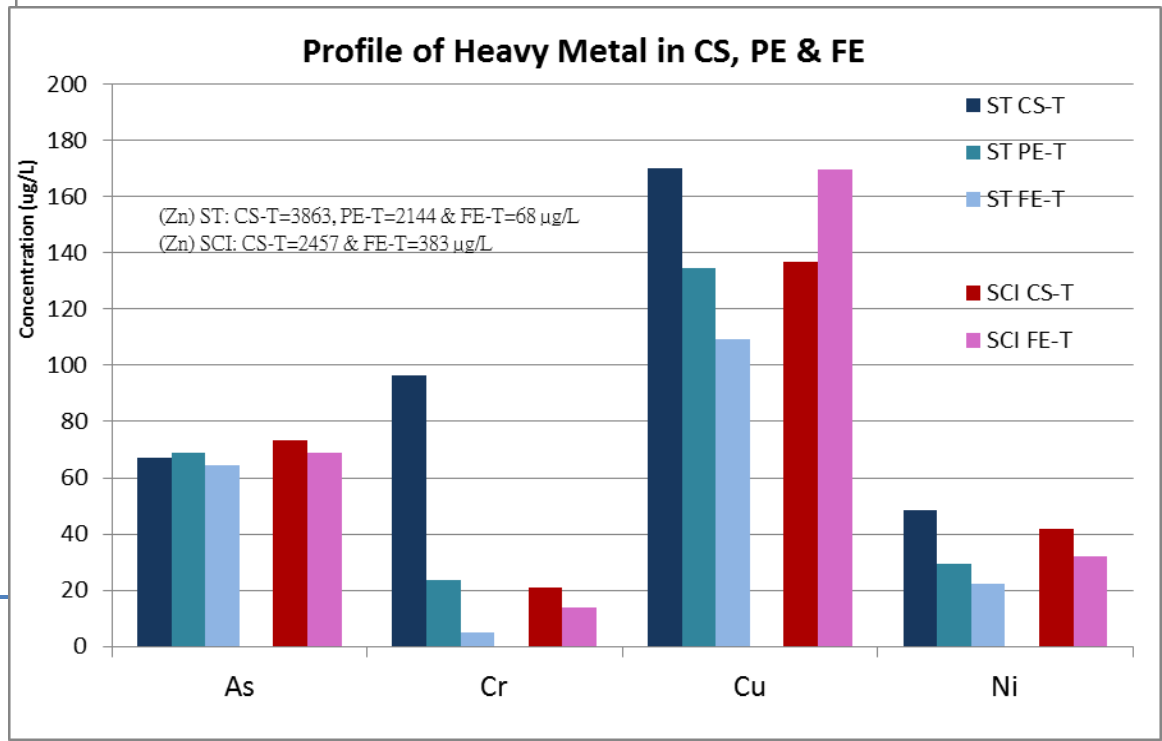
L (low) , M (medium), S (strong), VS (very strong)

Removal Efficiency for Heavy Metals



Profiles

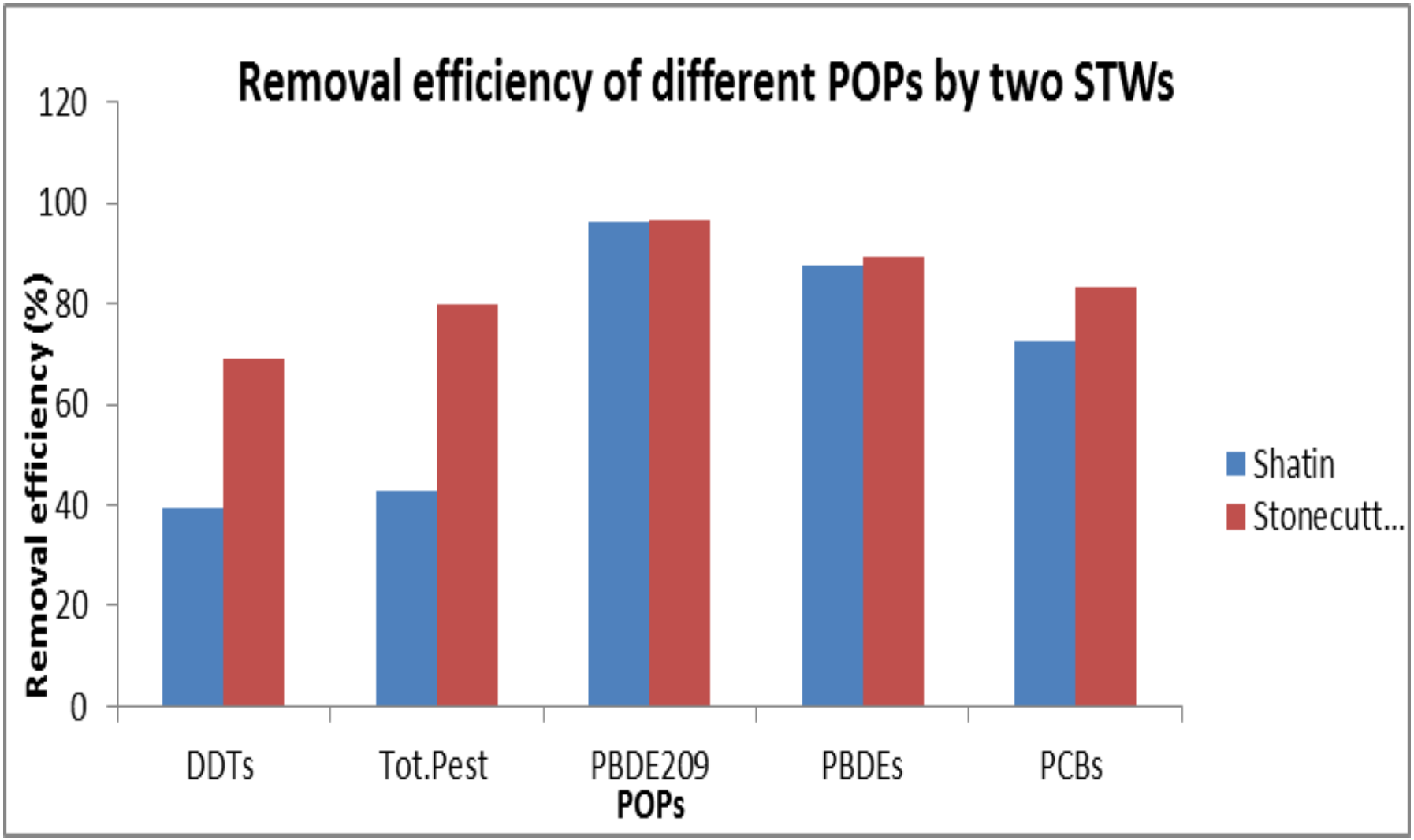

Profile of Heavy Metal in CS, PE & FE
Conc. in (ug/L) except MeHg (in ng/L)
0
1
2
3
4
5
6
7
8
ST CS-T
ST PE-T
ST FE-T
SCI CS-T
SCI FE-T
Cd
Pb
Sb
Sn
Hg
MeHg


Profile of Heavy Metal in CS, PE & FE
Concentration (ug/L)
0
20
40
60
80
100
120
140
160
180
200
(Zn) ST: CS-T=3863, PE-T=2144 & FE-T=68 µg/L
(Zn) SCI: CS-T=2457 & FE-T=383 µg/L
ST CS-T
ST PE-T
ST FE-T
SCI CS-T
SCI FE-T
As
Cr
Cu
Ni

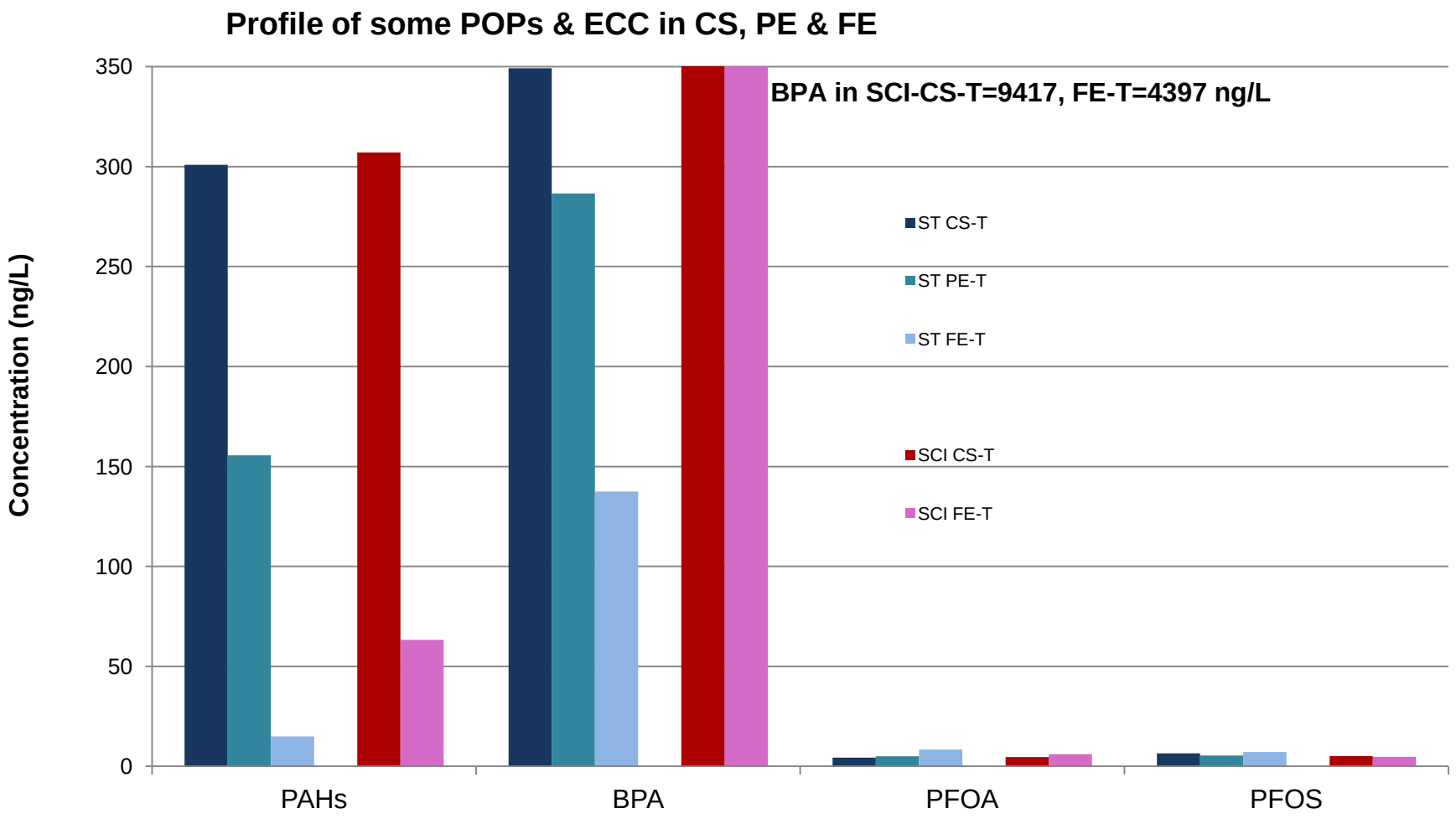
Heavy Metals: USEPA and China Limits

	SCI cake	ST cake	ST-DS	ST-ML	USEPA Class A	USEPA Class B	China pH<6.5	China pH>6.5
As	20	15	8	8	41	75	75	75
Cd	3	1	1	5	39	85	5	20
Cr	161	214	185	37	NA	NA	600	1000
Cu	225	265	172	169	1500	4300	800	1500
Hg	1	2	2	1	17	57	5	15
Ni	68	74	67	32	420	420	100	200
Pb	35	21	14	16	300	840	300	1000
Zn	755	1046	6988	3050	2800	7500	2000	3000
PCBs	0.254	0.043	0.148	0.055	NA	NA	0.2	0.2

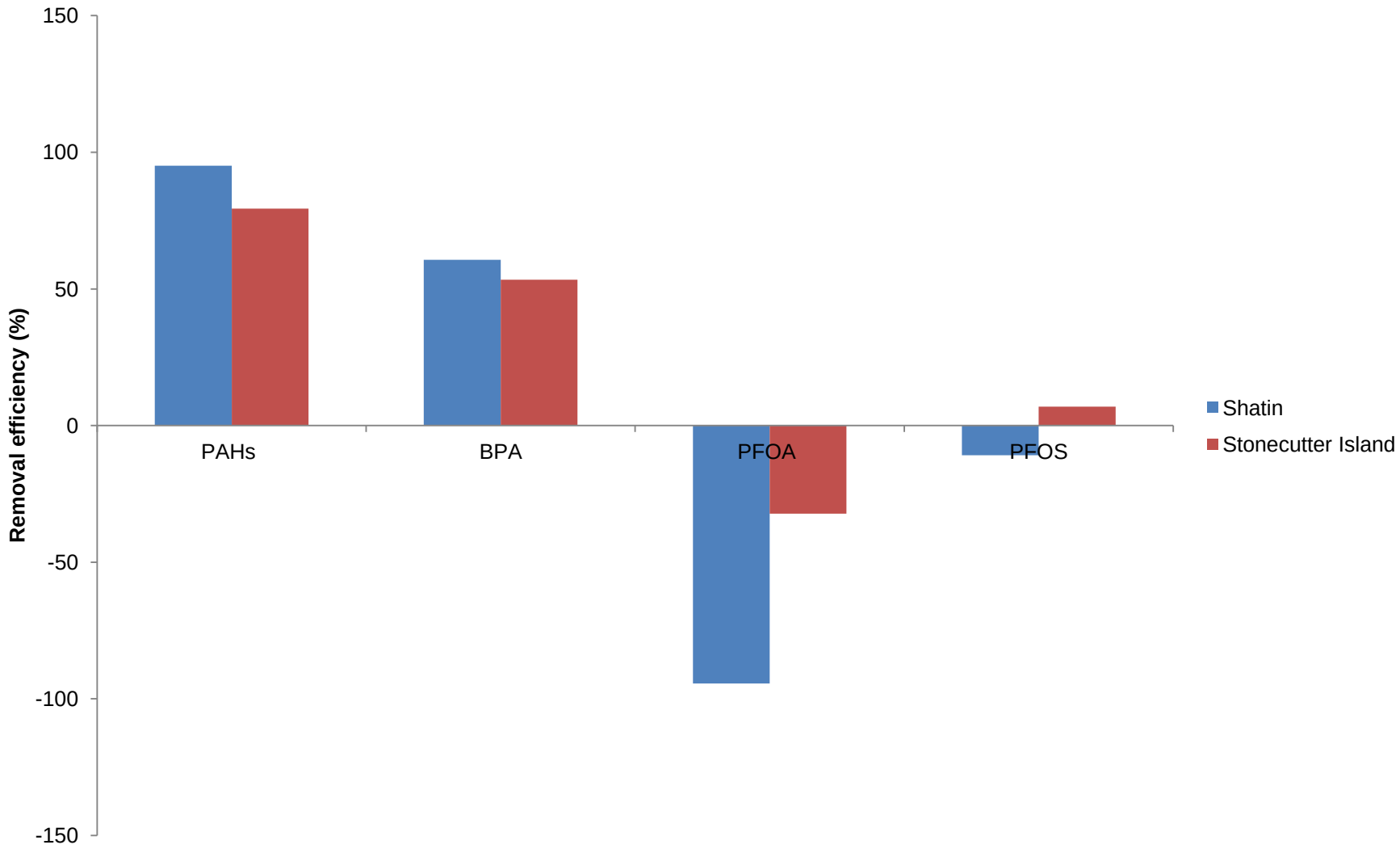
Removal Efficiency of POPs



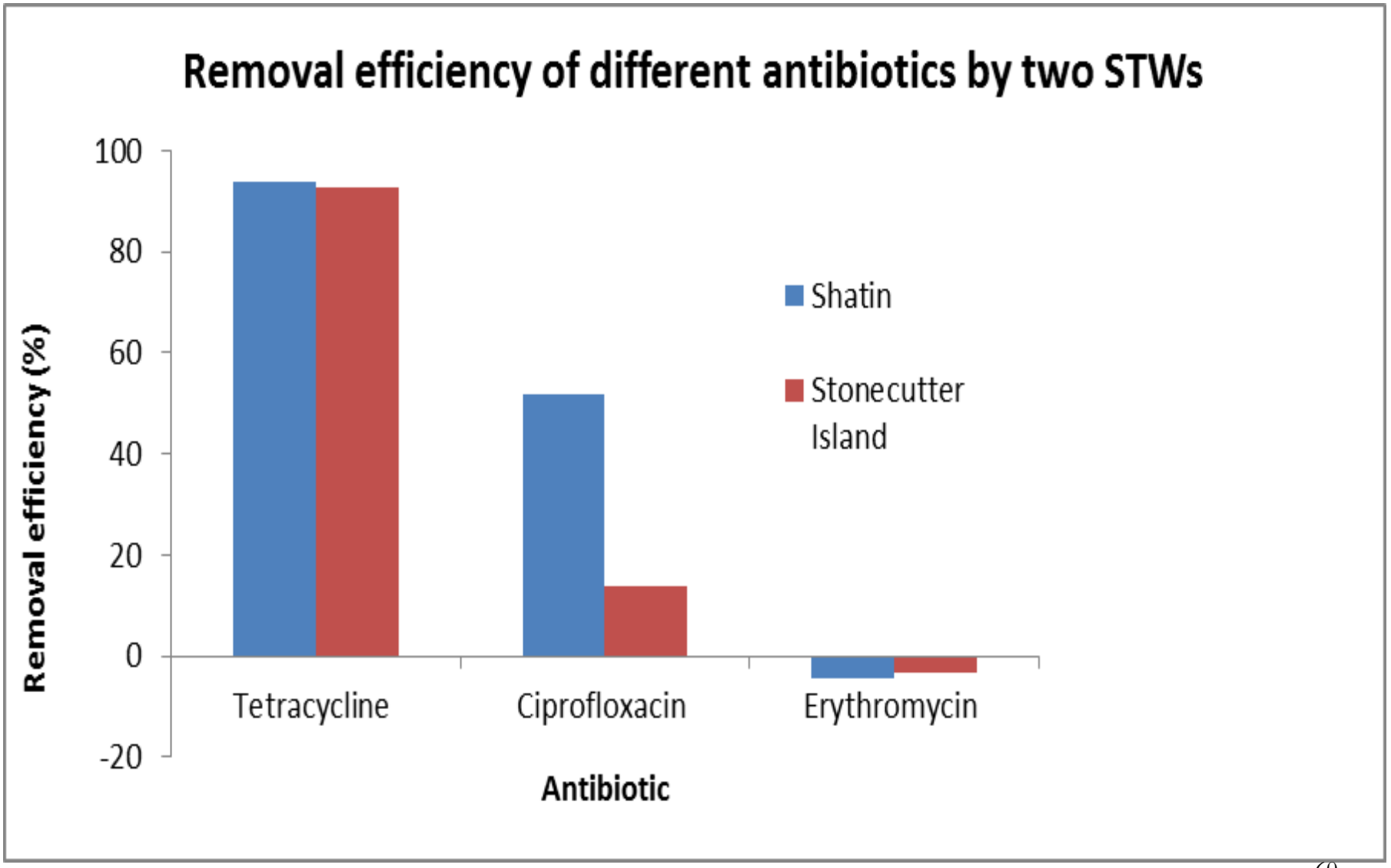
Profile of Some Organic Pollutants



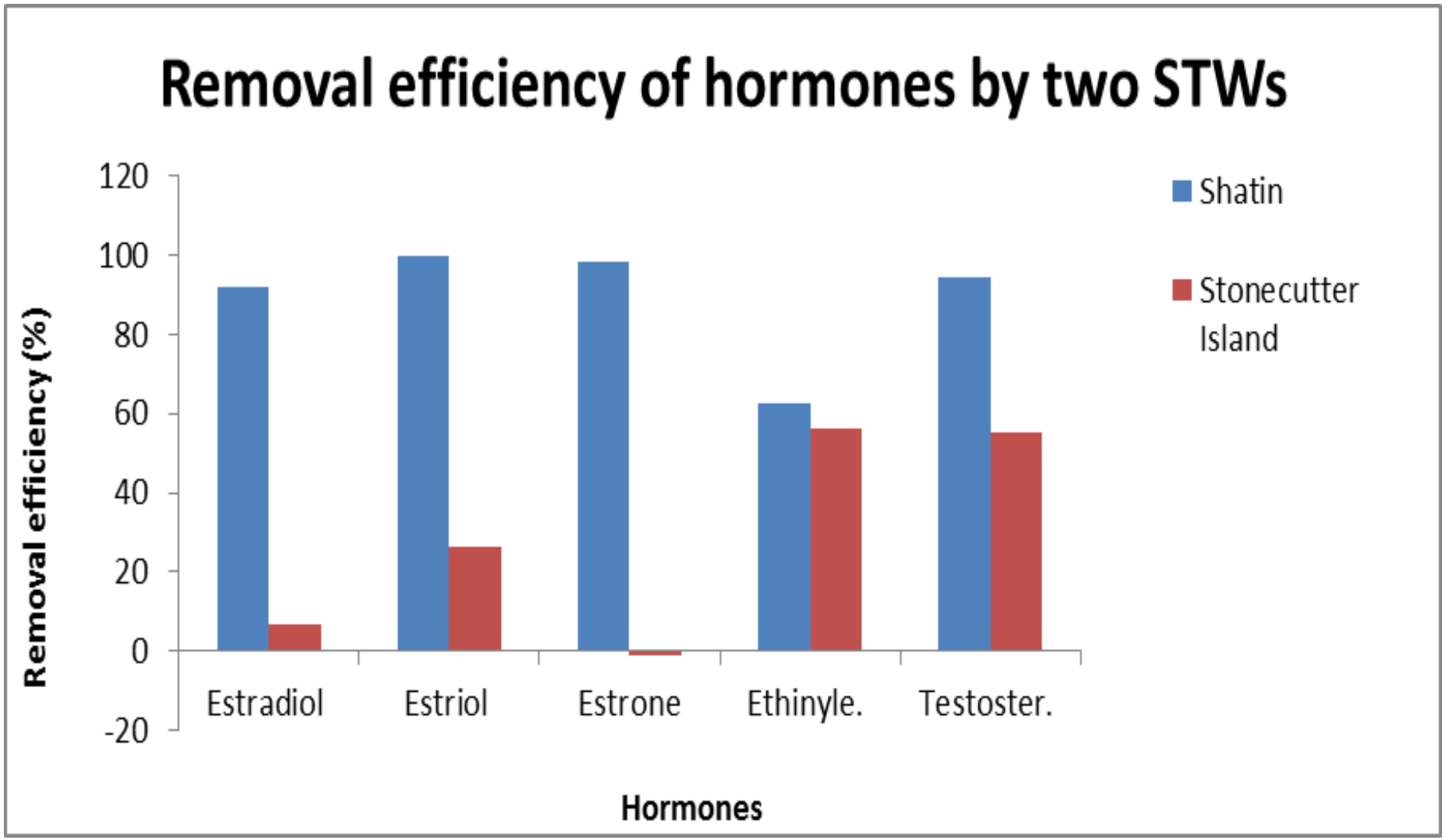
Removal Efficiency of Some Organic Pollutants



Removal Efficiency of Antibiotics



Removal Efficiency of Hormones



Major Findings

1. We demonstrated a well defined way to assign (i) sorption property and (ii) biodegradation property, with each pollutant rated accordingly.
2. Compounds with L (low sorption property) and L (low biodegradation property), such as arsenic, erythromycin, PFOA and PFOS, had minimal removal.
3. Removal efficiency varied a lot among compounds or elements, which can be separated into the following five groups:

Major Findings

(i) Strongly removed and degraded by *secondary* treatment, such as Methyl-mercury, Ciprofloxacin, estradiol, estriol, and estrone.

(ii) More effectively treated or degraded with chemically enhanced primary treatment (*CEPT*) system, such as DDTs, Total pesticides and BDE209.

(iii) Some removal in *both* treatment systems such as most of the heavy metals, PBDEs, PCB, PAH, bisphenol A, tetracycline, and testosterone.

(iv) *None* of the STWs was effective on treating certain pollutants such as arsenic, PFOA, PFOS and erythromycin.

(v) Non-conclusive due to low concentrations -*below* detection limits such as PCB-126 and ethinylestradiol.

Conclusion

- CEPT primary treatment process at SCI-STW is very effective in removing heavy metals (such as Pb, Cr, Sb, and Sn) as compared to ST-STW with primary and secondary treatments.
- For the removal of organic pollutants, ST-STW trapped more DDTs, total chlorinated pesticides, PBDEs & BDE209 into sludge cake.
- There are organic pollutants noticeably degraded during biological processes- such as estradiol, estriol, estrone, testosterone & ciprofloxacin.

Recommendations

- **This project (DEMP 1104) has successfully evaluated the removal efficiency and the profile of specified toxic chemicals in influent, effluent and sludge cake.**
- **Further studies using such approach (separating into liquid portion and particulate matter) to obtain more completed data on pollutant flow instead of the traditional approach (not separating LP and PM from the sewage sample).**
- **BDE209 was considered as relatively inert in the sewage system. However, our observation of BDE209 removal in CEPT process would deserve further studies.**
- **For the removal of a pollutant with L Sorption & L Biodegradation ratings, the removal of such pollutants will require advanced treatment, such as reverse osmosis, ozone treatment, etc.**

Overall Conclusion and Future Prospects

(1) Monitoring/predicting the Fate of Emerging Chemicals –

-Difficult (low concentrations, complex compounds & metabolites, unknown chemical properties & biological effects),

-Previous experience with similar compounds -pesticides, PCBs, dioxins, etc- Basic chemical principles expected to apply

(2) Promising Technologies to be Used in Sewage Treatment -

Oxidation, Ozonation, Activated carbon, Reverse osmosis, etc,

-Should focus more on "Pollution Prevention"

(3) Establishing Public Policy-

-Should consider:

- Combined effects of exposure to many different sources of damage (e.g., synergistic effects of different toxins)
- Different sensitivities of members of the population
- Effects of chronic as well as acute exposures

Thank You

- Special Equipment Grant, RGC, HK
- Croucher Foundation, HK
- UNEP- POPs Global Monitoring Network
- State Key Laboratory on Marine Pollution Control (City U/Xiamen U)