Environmental Applications of Cyclodextrins

Fields of Environmental Applications

Emission control by air filtration

- Solvent vapor
- Iodine vapor
- Cigarette smoke
- Dioxin of incinerators

Waste water treatment

- Binding of PAHs, PCBs, phenols, tensides, softeners, residual drugs

Soil cleaning

- Soil washing
- Intensification of bioremediation and phytoremediation
- Electrokinetic removal of contaminants

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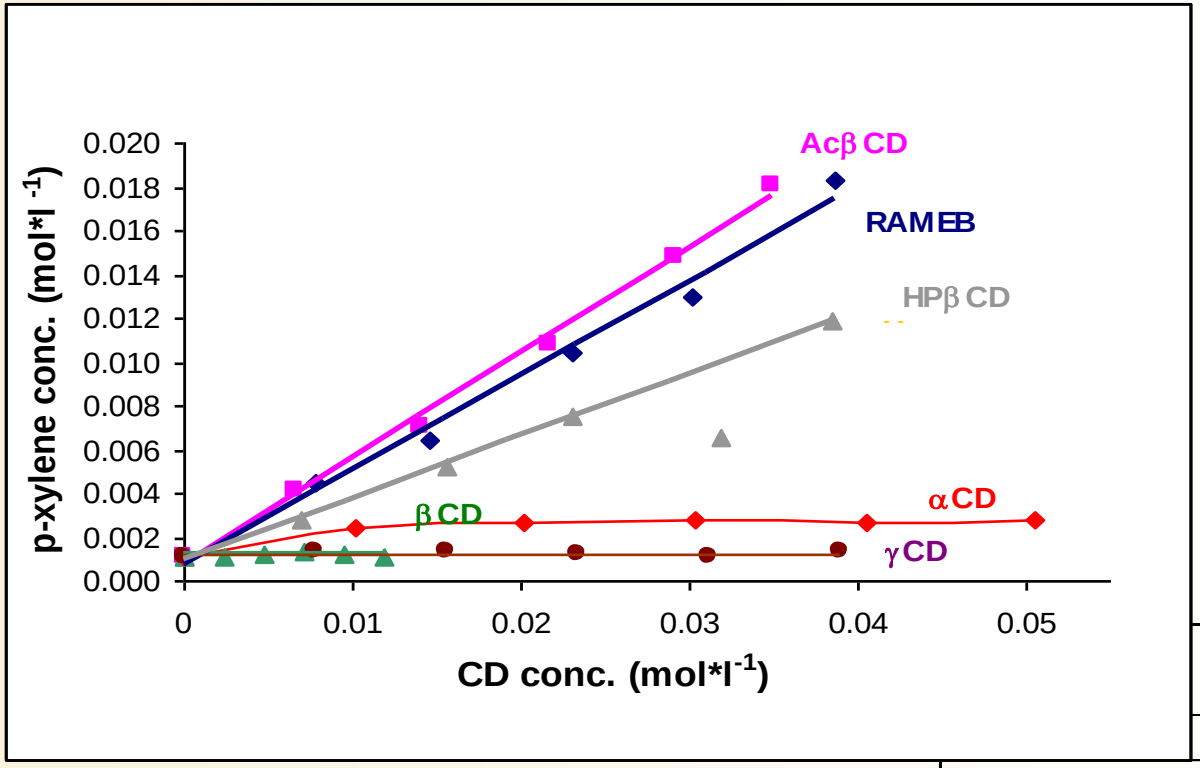
Soil and Groundwater Treatment

Technologies

Ex situ	In situ
Soil washing, extraction	
Chemical transformation	
Biodegradation	
Phytoremediation	
Electrokinetic remediation	

Solubility enhancement



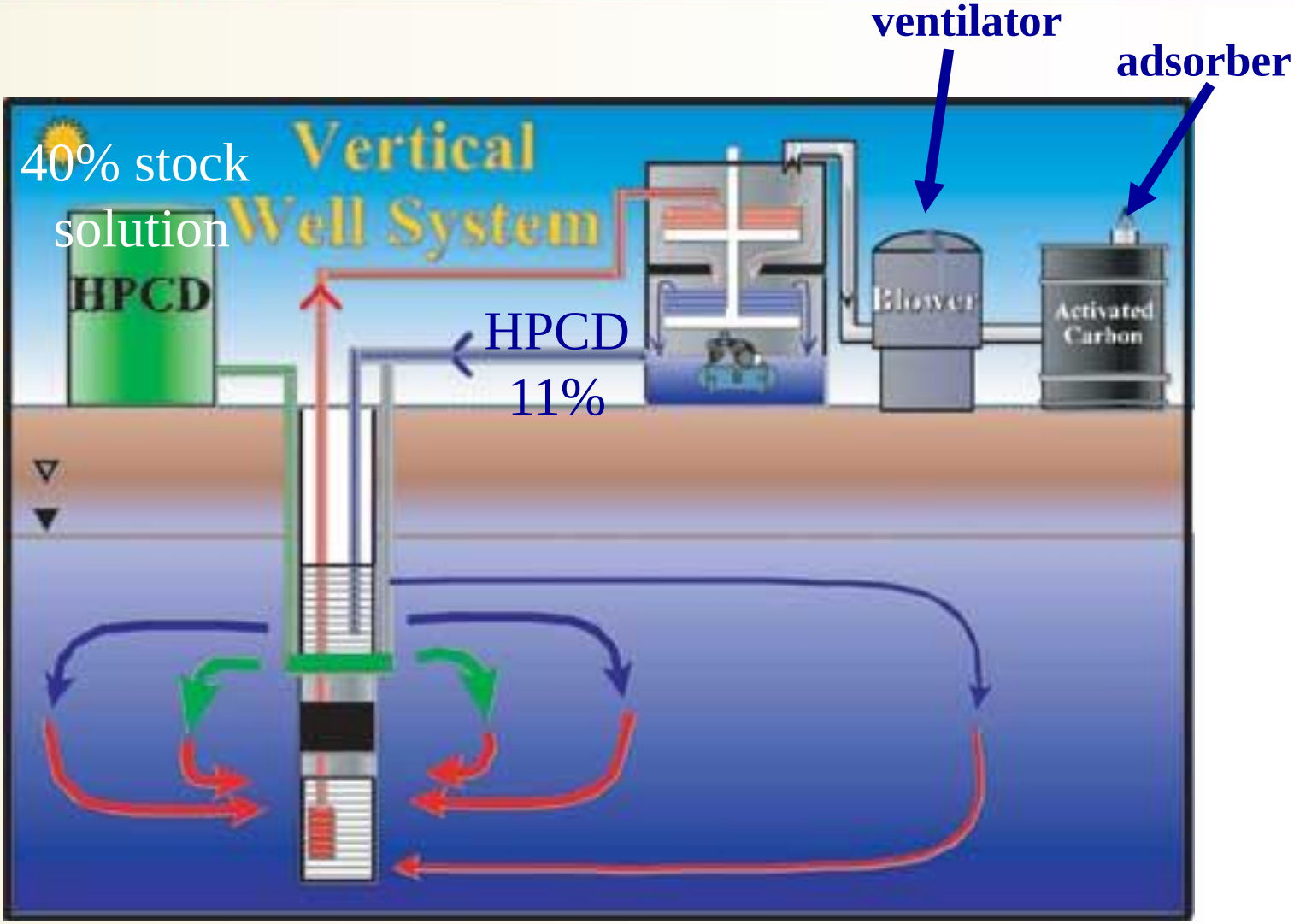
Solubility of p-xylene in CD solutions

Reduced partition into octanol (soil)

	$LogK_{ow}$	$LogK_{oCD}$	
	in water	in 10% solution of	
		HPBCD	RAMEB
p-chlororaniline	1.82	1.22	1,13
p-chlorophenol	2.39	1.61	1,45
toluene	2.92	2.20	2,12
1,2-dichlorobenzene	3.45	2.47	2,35
1-mehyl-naphthalene	3.79	2.58	2,34
pentachlorophenol	4.16	3.00	2,84
phenanthrene	4.67	3.02	2,47

Scheme of the *in situ* soil flushing technology

TCE contamination



Blanford W. J., Barackman, M., Boving, T. B., Klingel, E., Brusseau, M. (2000) *Ground Water Monit. Remediation*. pp. 58-66.

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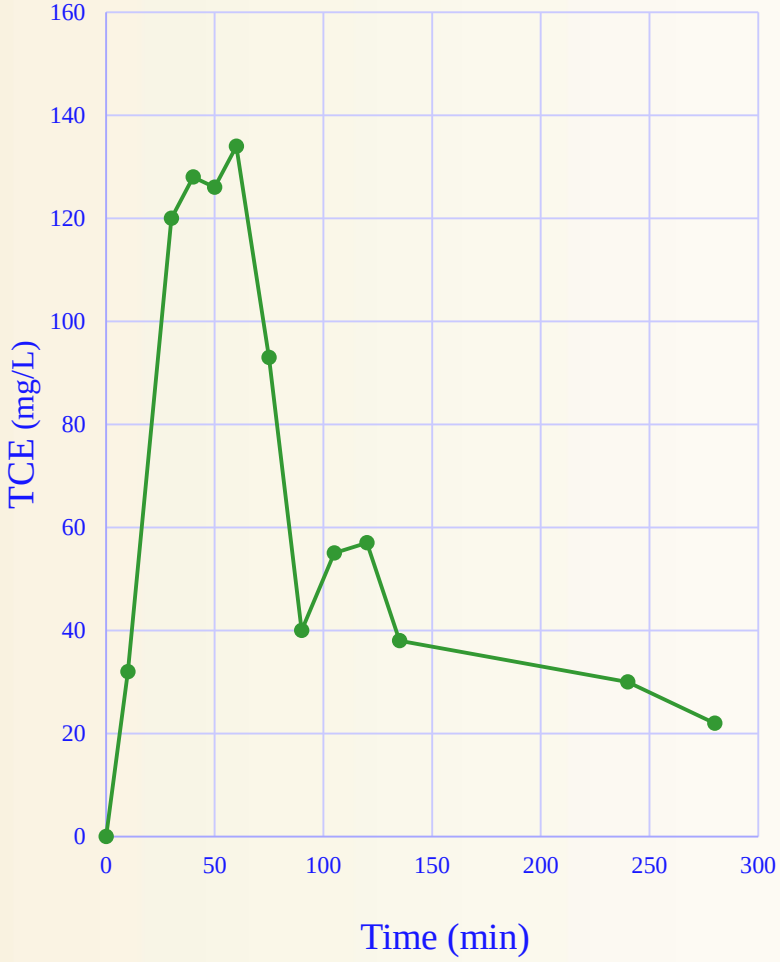
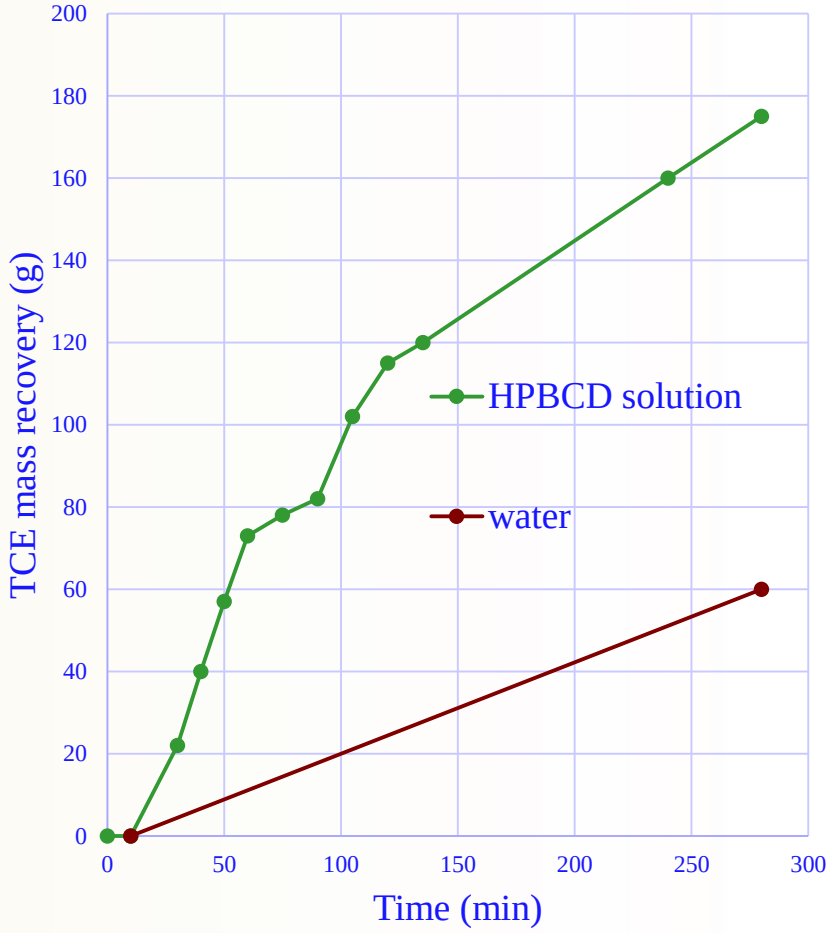
Soil flushing experiment in Arizona, US

Soil washing with HPBCD solution ("push-pull"system)

In situ field experiment at a military airport in Utah, USA



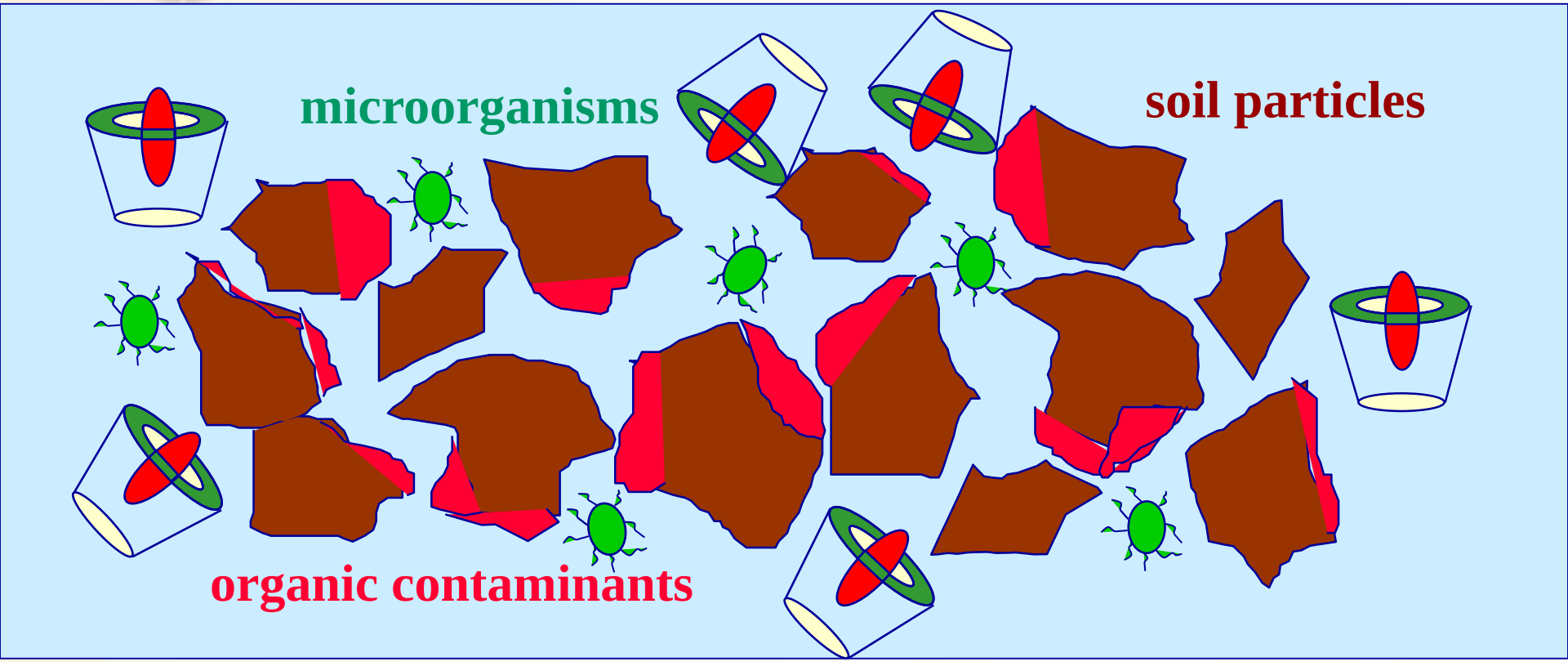


Tick, G.R., Lourenso, F., Wood, A.L., Brusseau, M.L. (2003) *Environ. Sci. Techn.* **37**, 5829-5834

Treatment of the solution containing contaminant/CD complexes

CD is beneficial	CD is inhibitory
Biodegradation	Adsorption
Chemical oxidation	Stripping
Chemical reduction	Distillation
	UV degradation

How CDs help in bioremediation?



The contaminants are adsorbed on soil particles.
The microorganisms live in the biofilms (aqueous phase of the soil)

Enhancement of solubility and bioavailability

Demonstration in field experiment

Former fuel station at an agricultural site
Contaminants: diesel and engine oil

Technology:

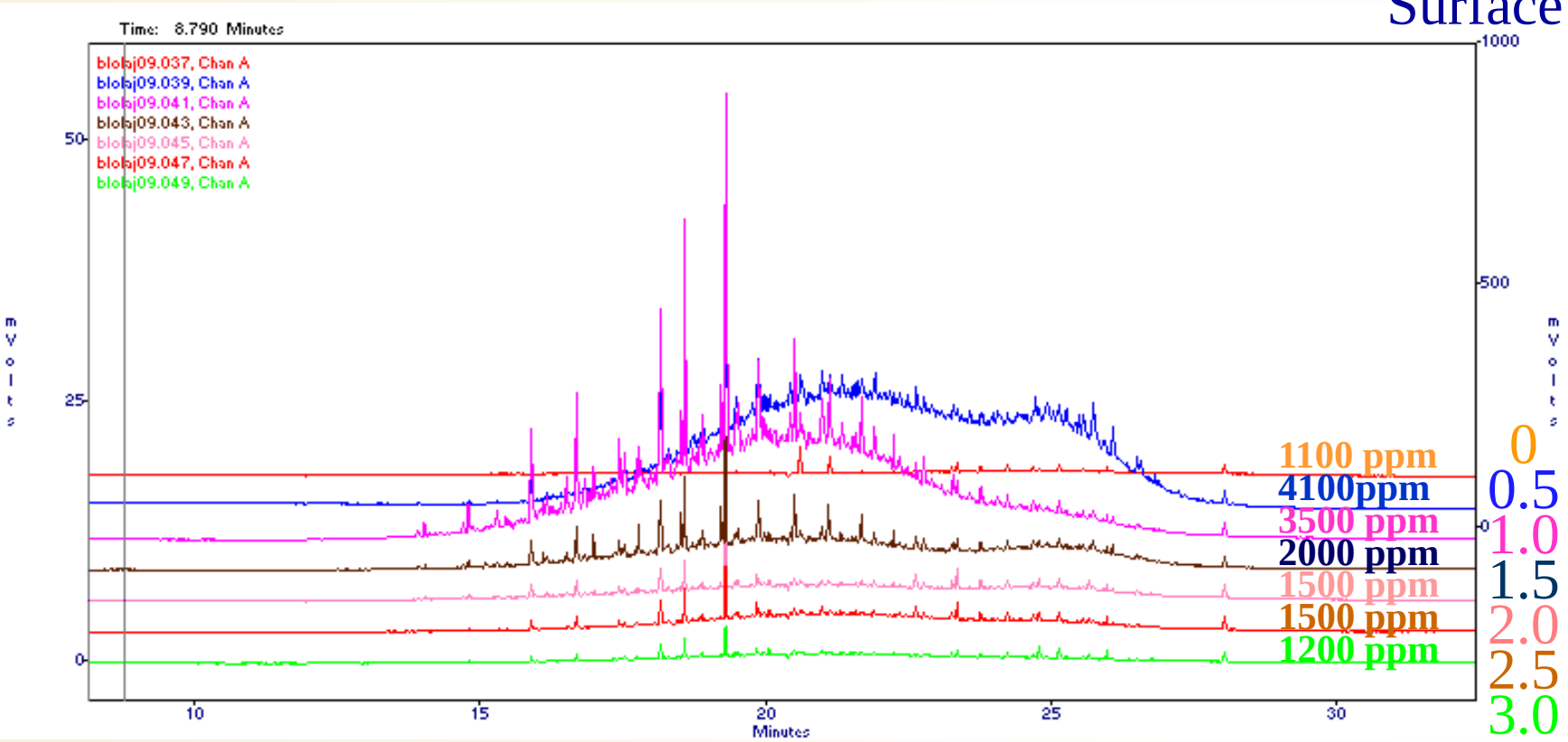
1. In situ ventilation
2. Ex situ physical treatment of groundwater
3. Periodical flushing with RAMEB/nutrients (push-pull)

C:N:P 100:10:1

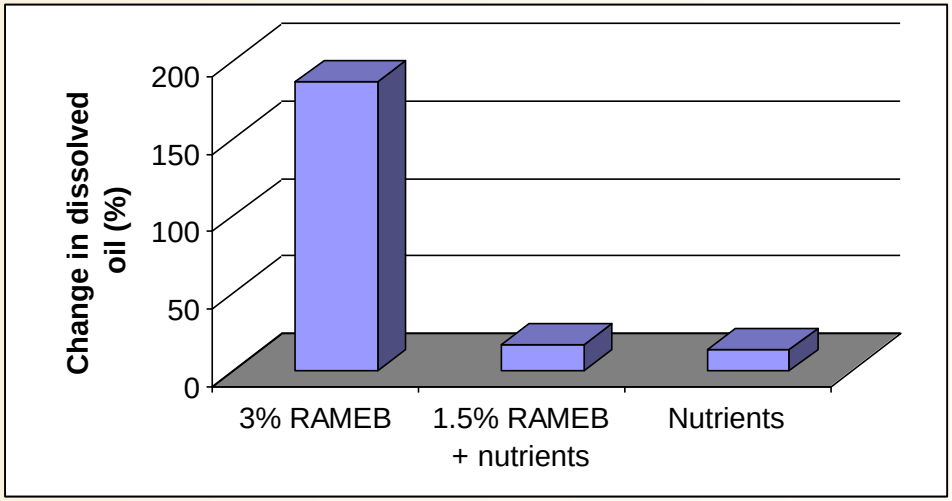
Technology monitoring:
Frequent analysis of soil gas and ground water
Soil sampling at the beginning and end

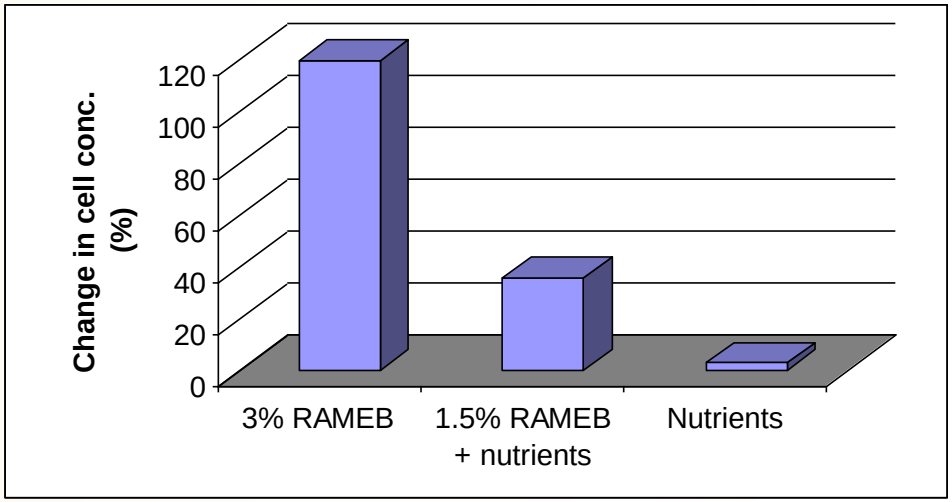
Oil content in the soil layers (GC chromatograms)

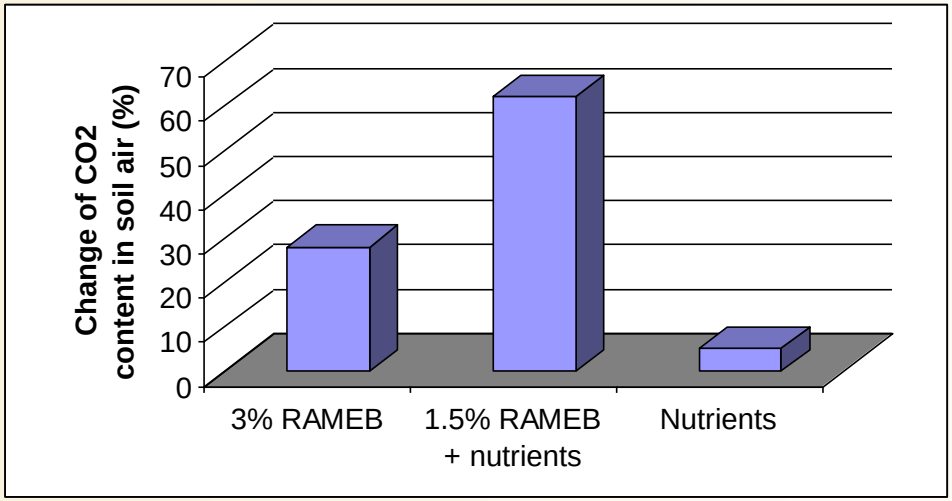
Depth from Surface (m)



Results of field demonstration (Comparison of 3 subsequent treatments) Monitoring of soil phases

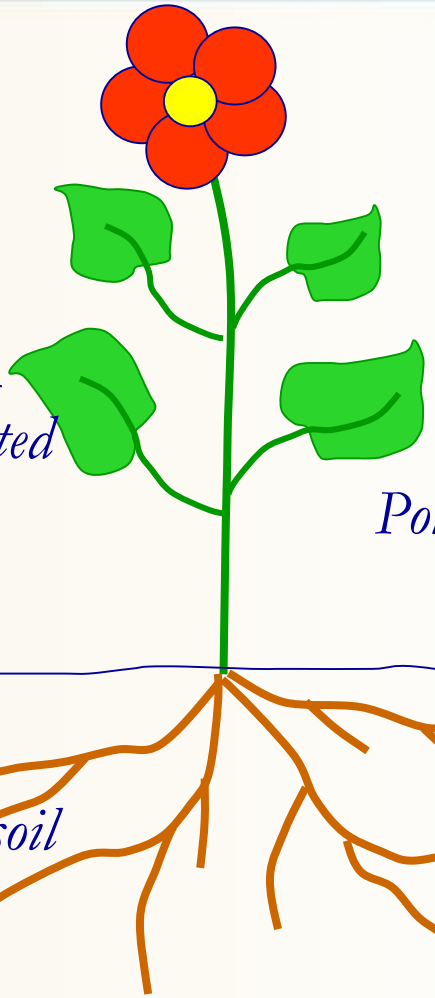






Extractable hydrocarbons (mg/kg)	
Before treatment	10.000 - 29.000
After treatment	<1000 - 3000

Phytoremediation technologies



Phytovolatilization
Pollutant is accumulated and volatilized

Phytoextraction
Pollutant is accumulated

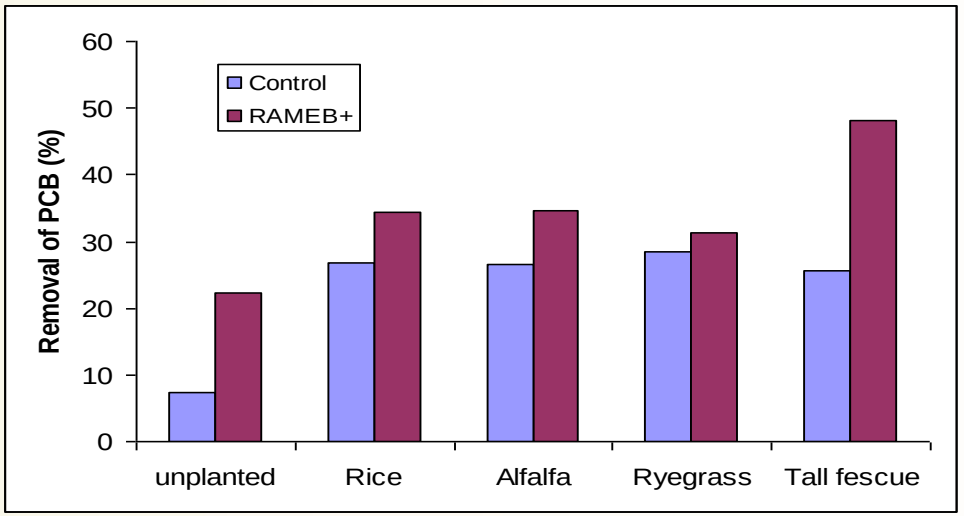
Phytodegradation
Pollutant is accumulated and degraded by the plant

Phytostabilization
Pollutant is immobilized in the soil

Phytostimulation
Pollutant is degraded by the microbes living in the rhizosphere

Soil contaminated with polychlorinated biphenyls, PCBs

- 4 plants: rice, alfalfa, ryegrass (*Lolium*), tail fescue (*Festuca*) planted on the soil contaminated with electronic waste
- 3% RAMEB addition
- On the effect of RAMEB enhanced shoot and root elongation (improved bioavailability of nutrients)
- Enhanced number of bacteria and fungi in the rhizosphere
- Decreased PCB-content in the soil



Shen et al.: J. Hazard. Mater. 172, 1671-1676 (2009)

Fate of CDs in the soil

Biodegradation of CDs according to standard test (OECD 302b)

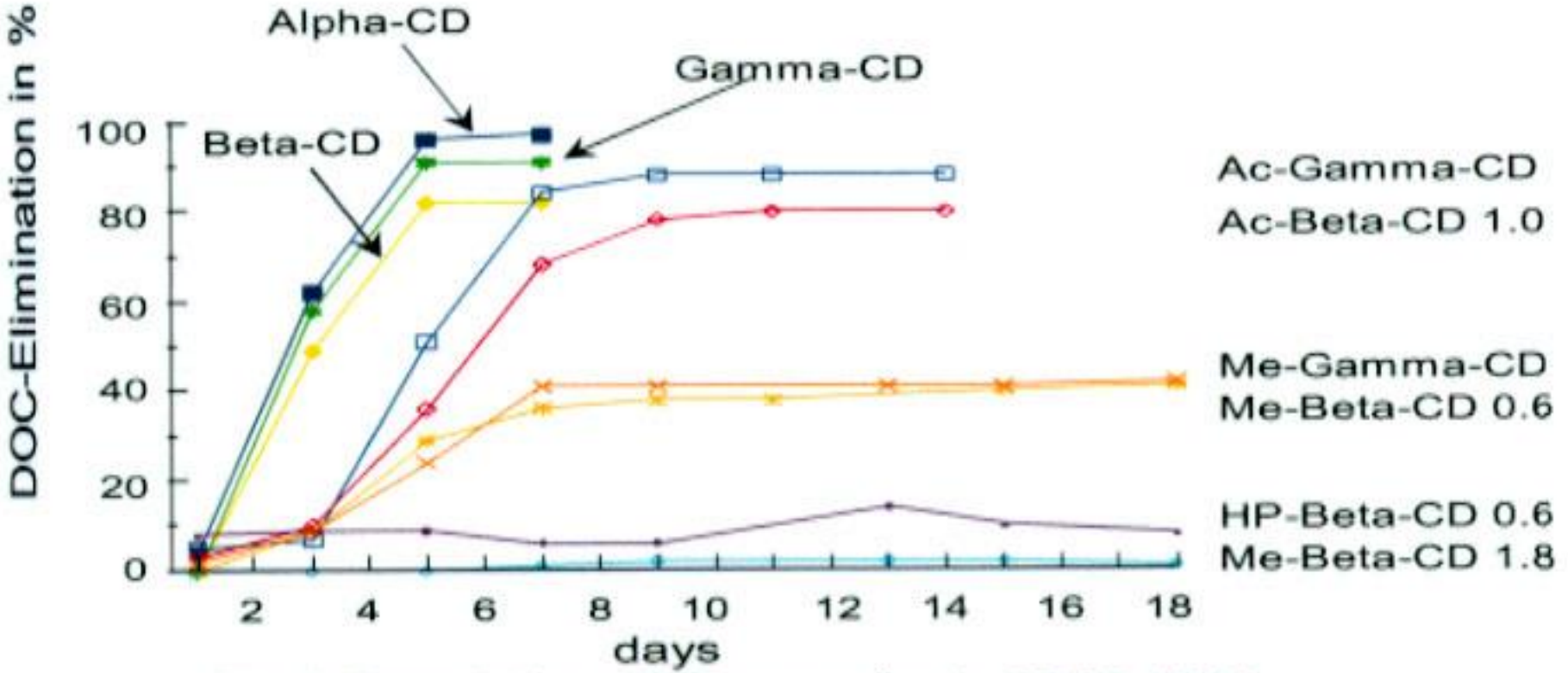
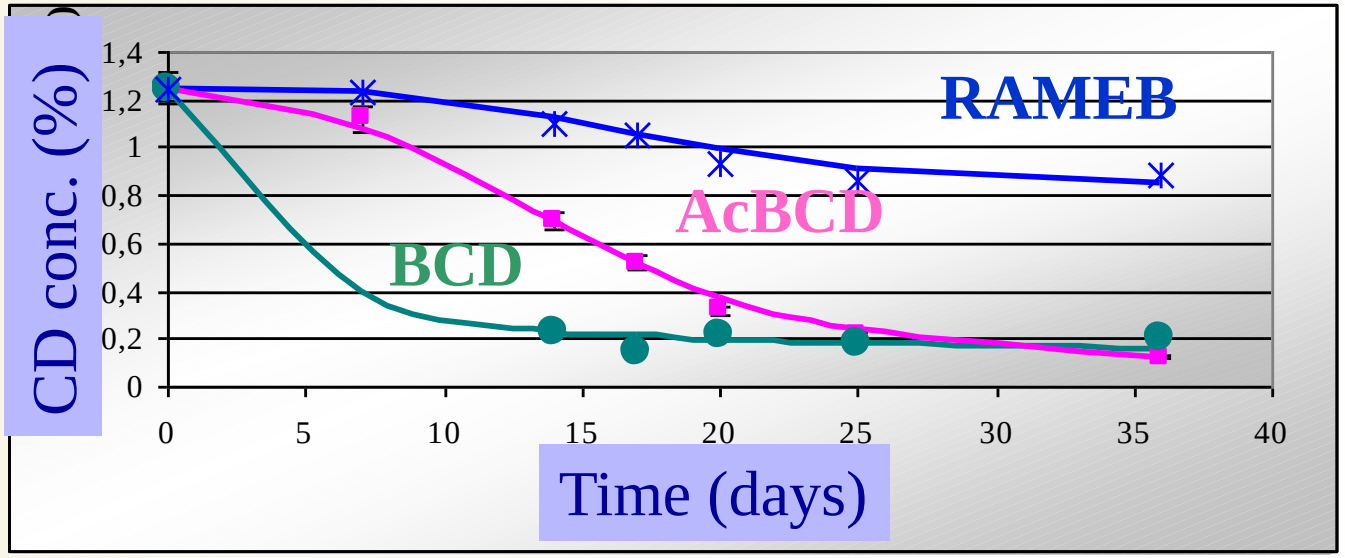
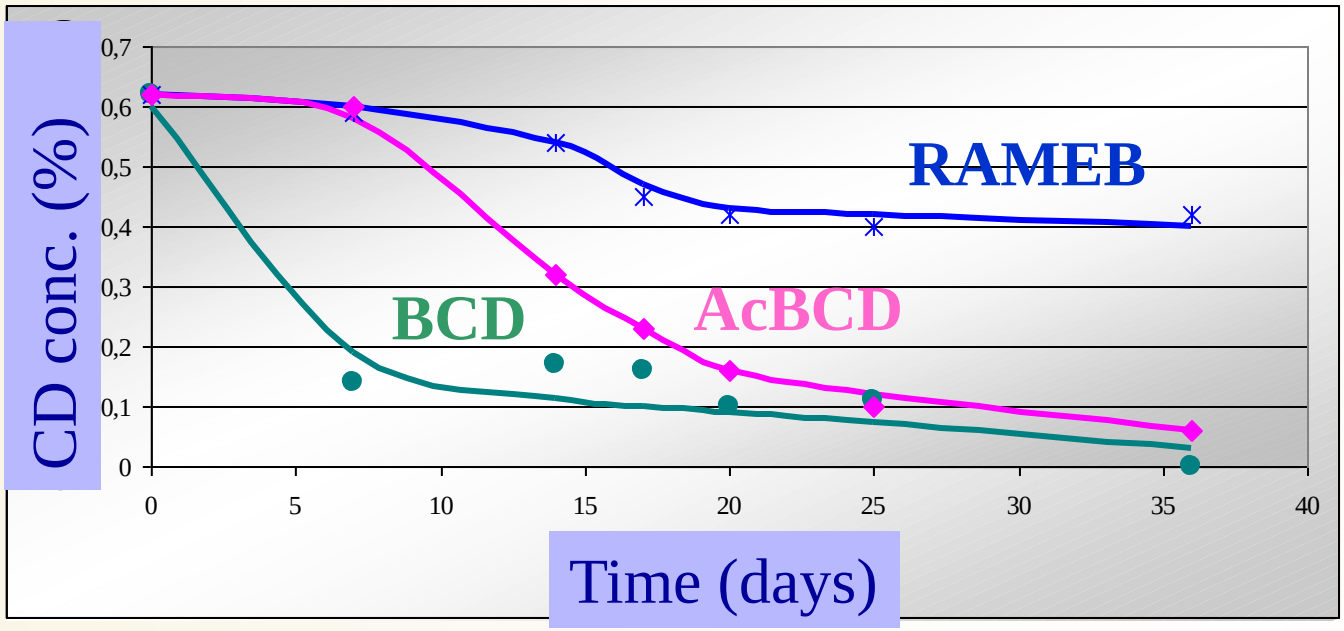


Fig. 1: Degradation of CDs according to OECD 302B

Antlsperger, G., Schmid, G.: Toxicological comparison of Cyclodextrins, Wacker Chemie website

Biodegradability of CDs in soil contaminated with 20000 ppm transformer oil (laboratory experiment)





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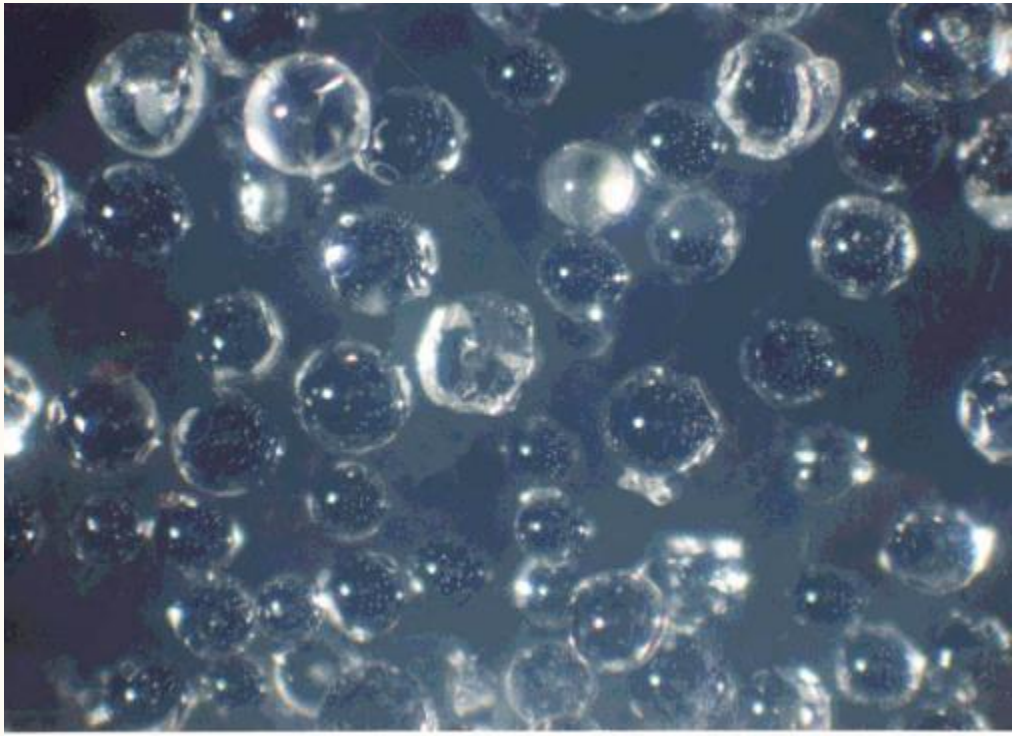
Waste Water Treatment

Immobilization of the dissolved pollutants



Drug residues in the drinking water?

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Source of emerging pollutants:

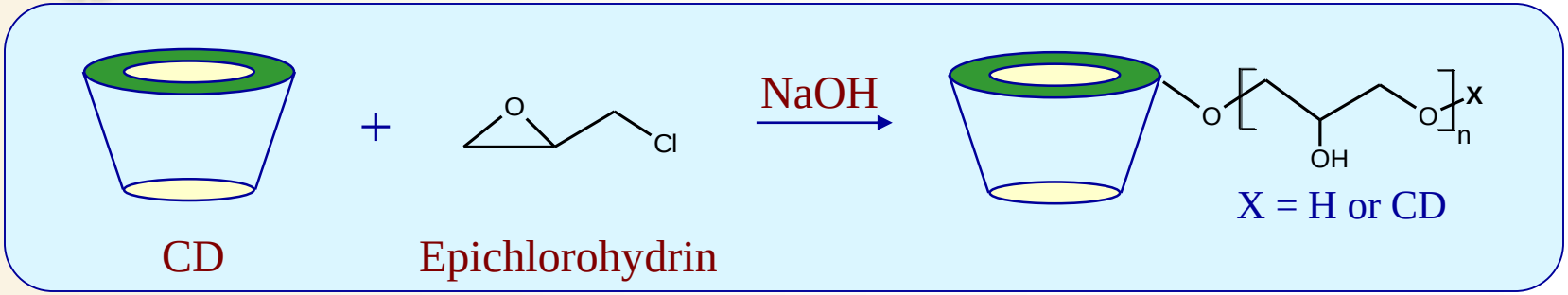
- Drugs (human and veterinary) excreted from the body
- Cosmetics, household chemicals
- Agrochemicals
- Industrial auxiliaries
- Nutrient supplements

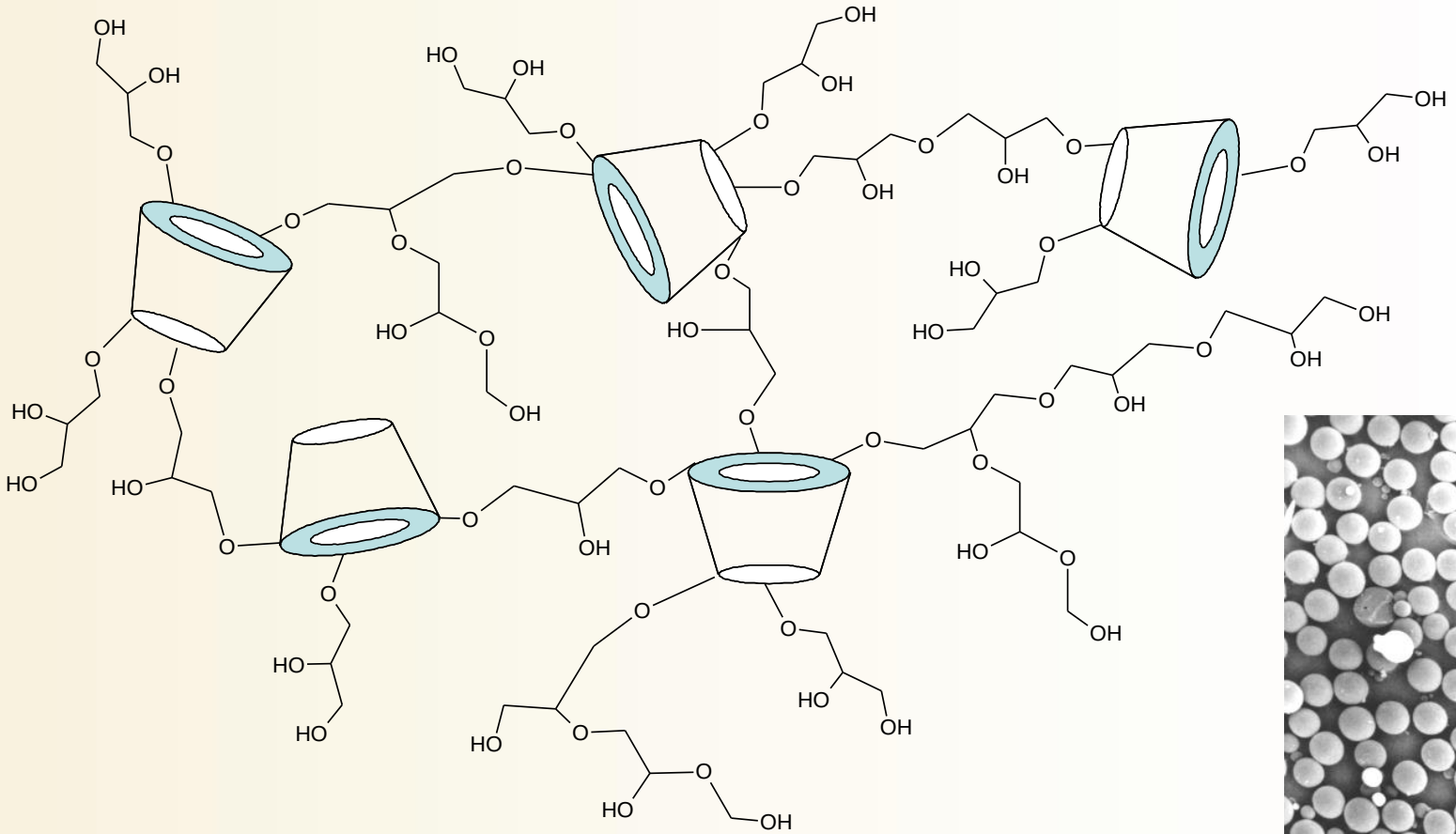
Emerging pollutants

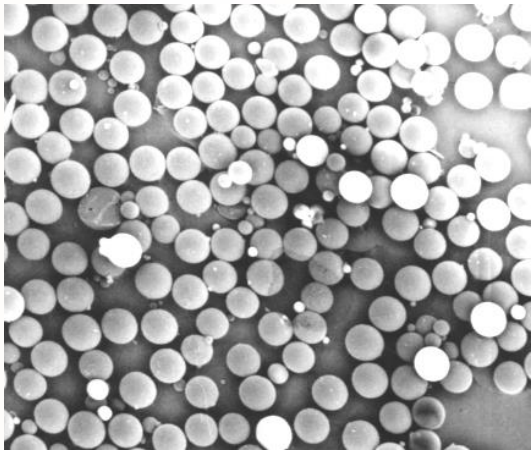
- Not destroyed by the microbes in the conventional biological treatment of sewage water; no biodegradation in the environment
- Sophisticated analytical techniques for measuring ppb and ppt level (**emerging pollutants, EP** = the pollutants detectable)
- Long term consequences on the environment and human health

Further treatment of the purified waste water is necessary

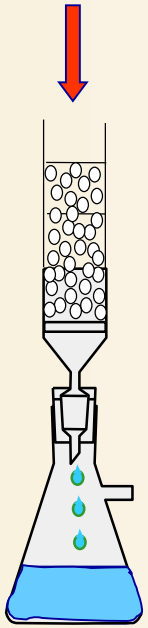
Cyclodextrin bead polymer





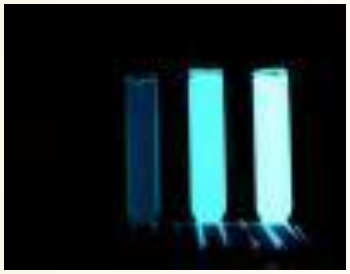


Sorption of Bisphenol A (BPA) followed by ecotoxicity test

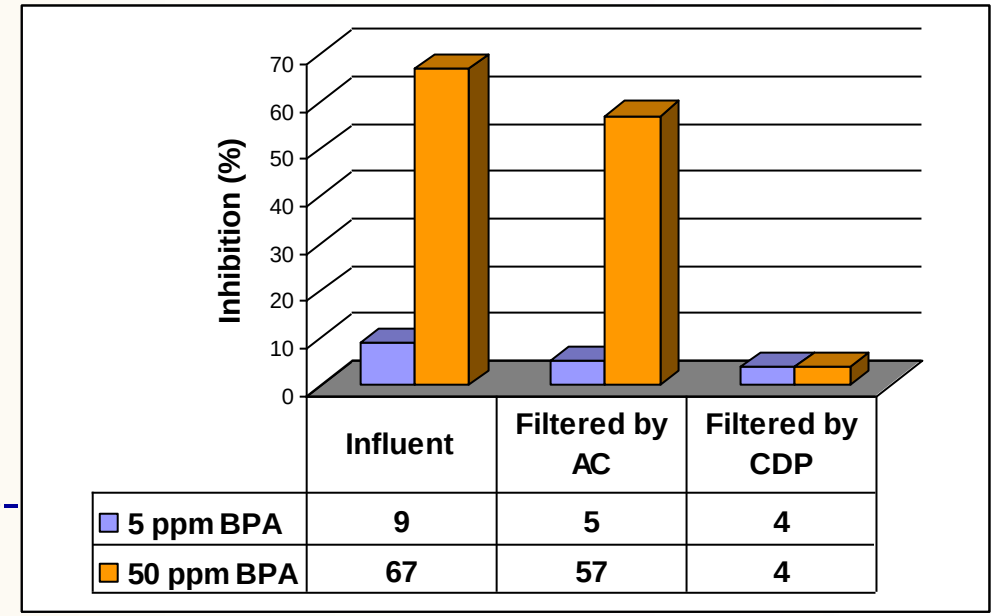


1 g sorbent

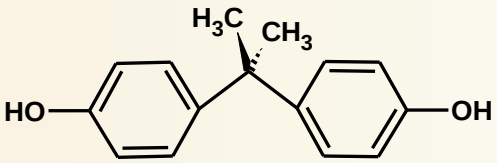
400 mL solution



Vibrio fisheri Bioluminescence-inhibition test



Good correlation with GC-MS



Influent (400 mL)	BPA sorbed [mg/g]		BPA removal [%]	
	CDP	*AC*	*CDP*	*AC*
5 ppm BPA	2.0	0.13	100	6.5
50 ppm BPA	20.0	2.1	100	10.5

Pilot plant experiment

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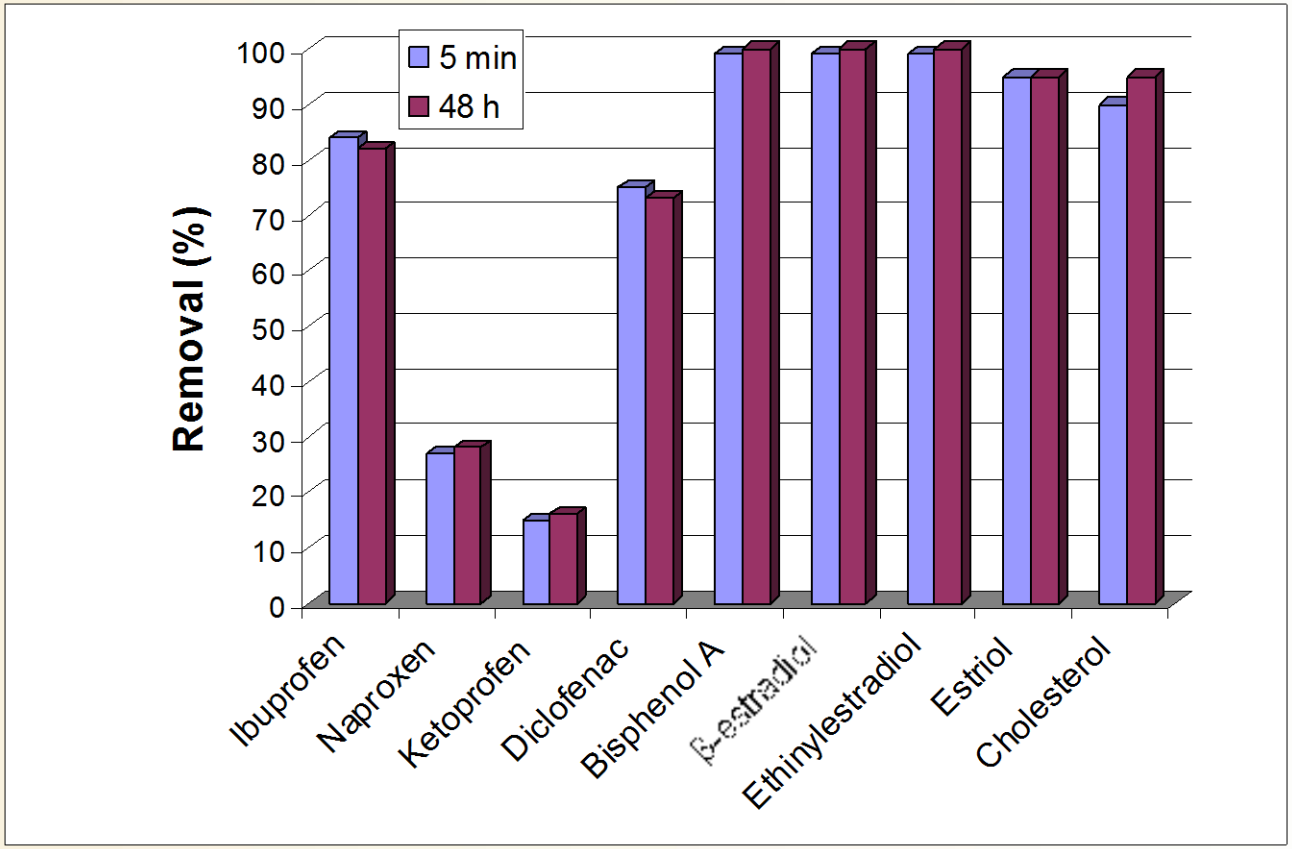
300 L purified wastewater spiked with pollutants at 5 ppb level

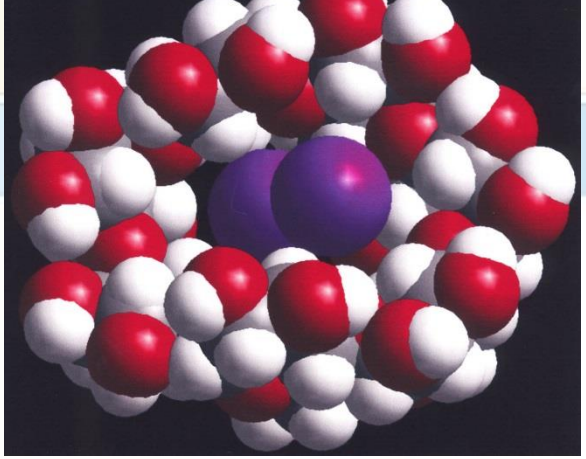
1 kg cyclodextrin bead polymer

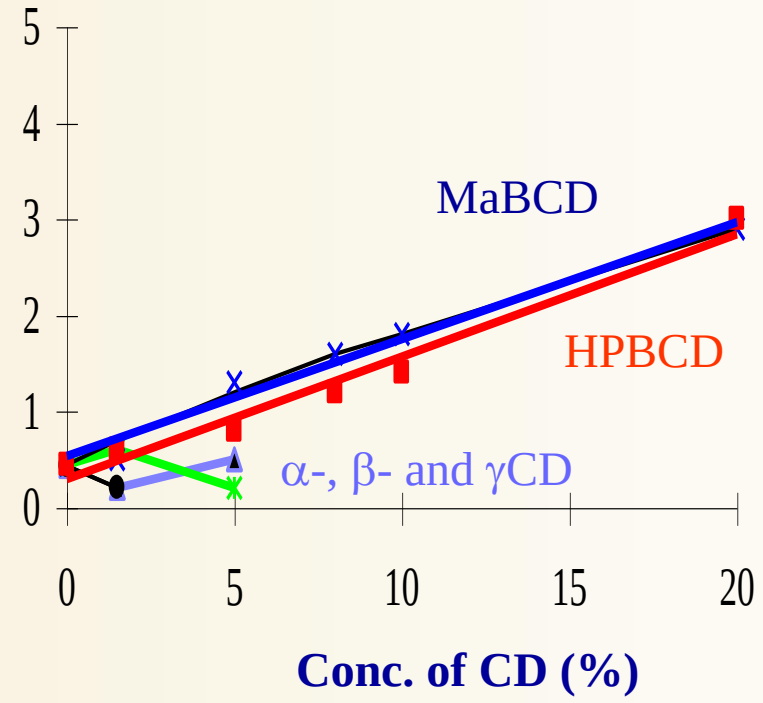


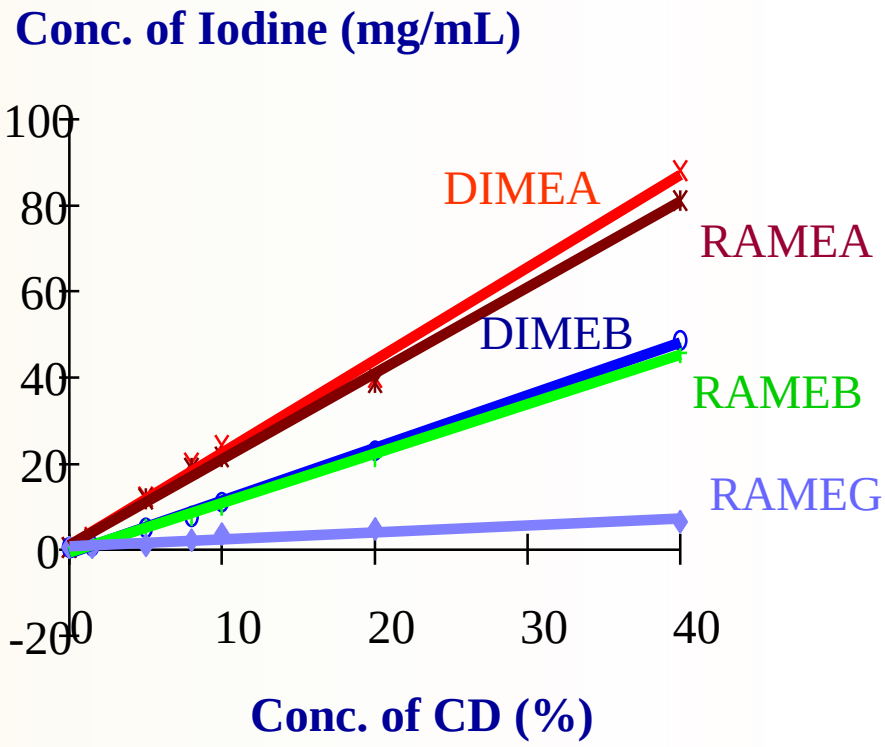
Air Filtration

Binding solvent vapor with CD solution applied in counter current
Binding dioxin from the flue gas of waste incinerator
Filters for cigarette smoke
Capture of radioactive iodine discharged by nuclear power plants

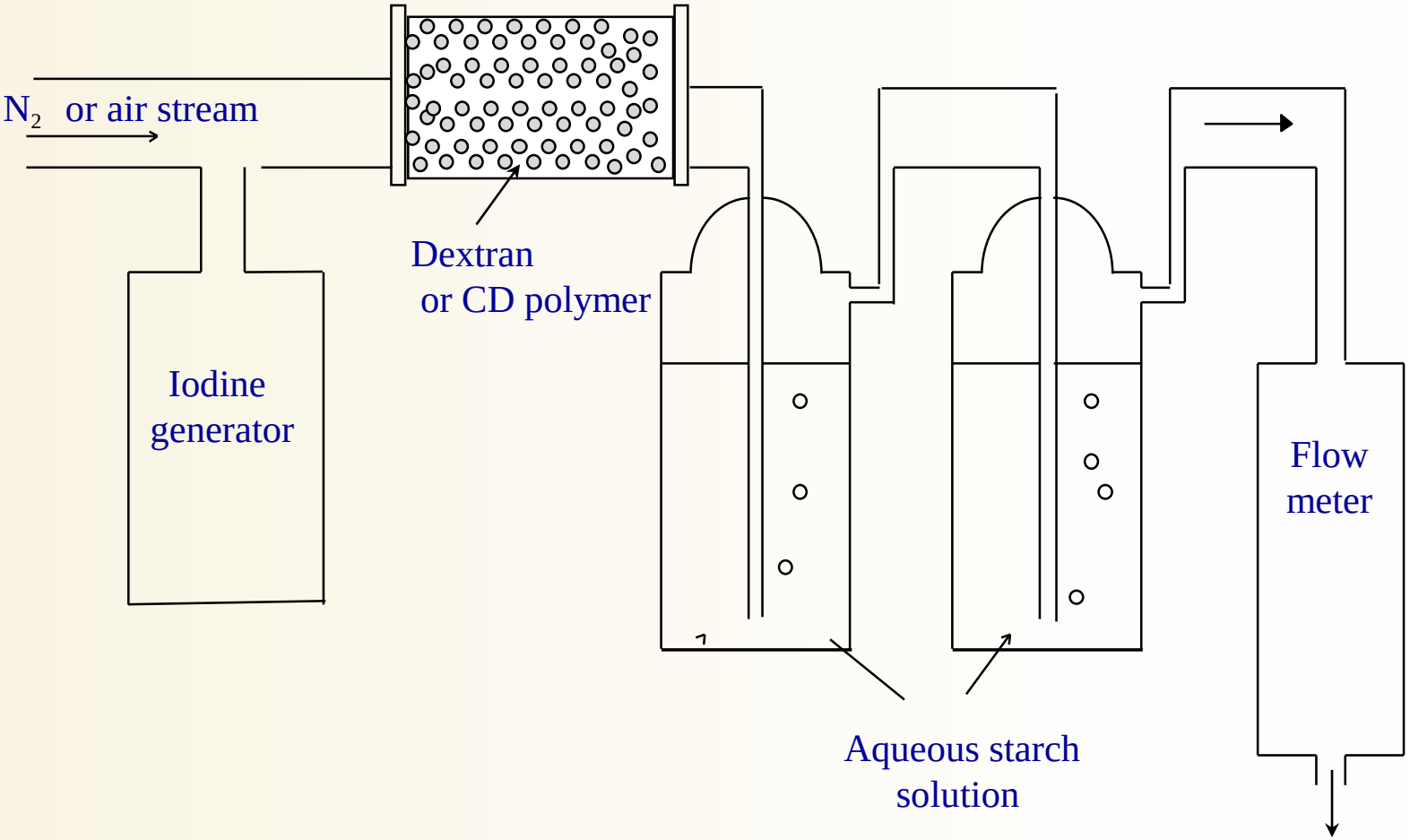
Solubilization of iodine with aqueous CD solutions



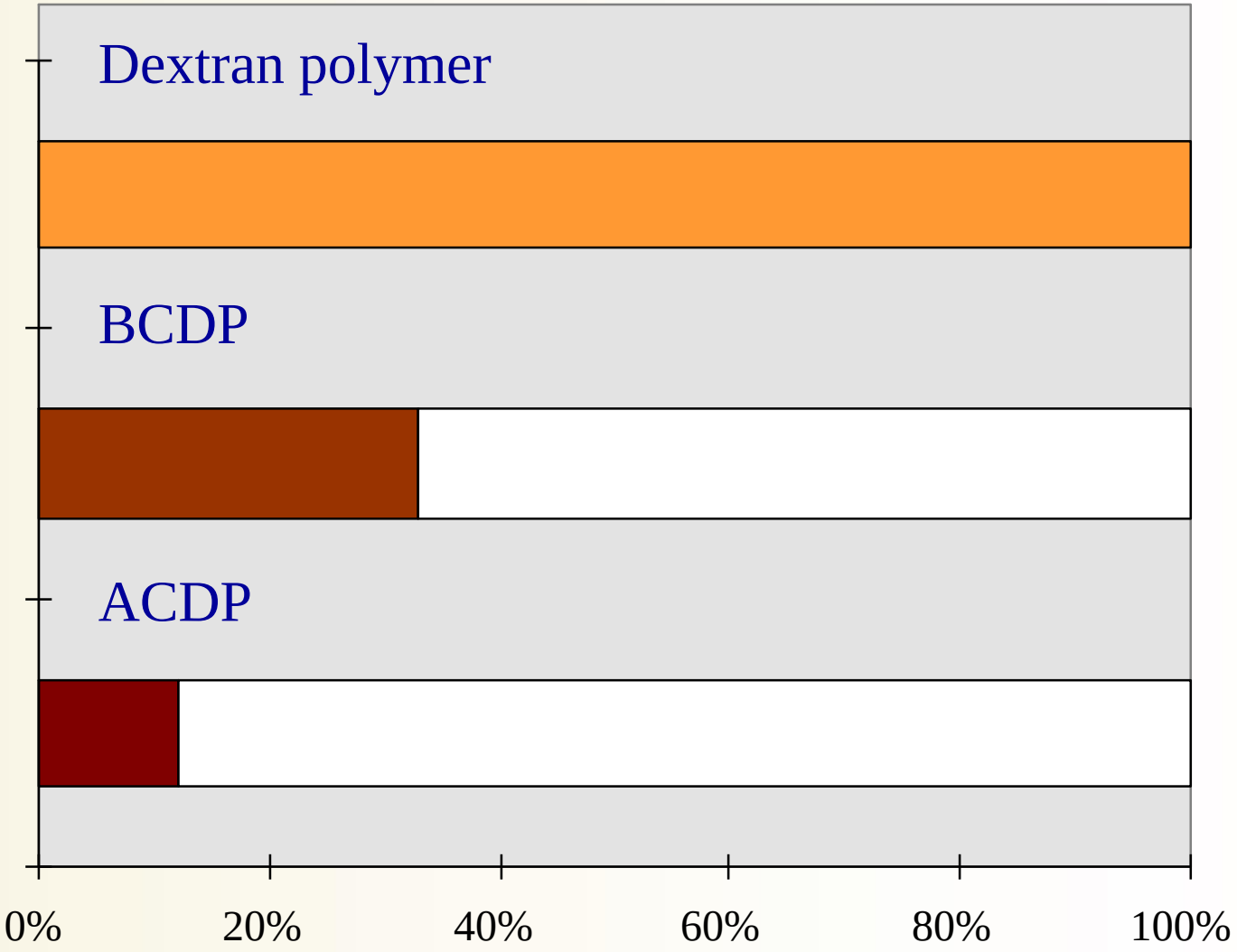




Experimental set-up for measurement of iodine binding



Iodine binding by various sorbents after 1 h



March 11, 2011 Fukushima

cesium-137 and **iodine-*131*** escaped in the air

Personal protective equipments and clothing

Summary

- CDs enhance the efficiency of various environmental technologies
- Highly water-soluble derivatives are useful for soil remediation
- CD-epichlorohydrin bead polymer proved to be efficient in the removal of emerging pollutants from purified waste water.
- The bead polymer can capture iodine from the air
- The technologies were demonstrated in pilot scale