Harmonisation of Analytical methods for Sediment-quality Information, Monitoring and Assessment System

Péter Fodor
Szent István University
Fodor.Peter@etk.szie.hu

Wienna, 2019

SZENT ISTVÁN EGYETEM

Self introduction:
Diploma at Technical University of Leningrad.
PhD at Technical University of Budapest (Dept. of General and Analytical Chemistry)
Post doc at Univ. of Massachusetts (Amherst)
From 1988-2008. Head of Dept. Applied Chemistry of Food Science Faculty
From 1992 Doctor of Hung.Sci. Ac.
From 1995 Head of the Accreditation board of Hungary and member of Codex Alimentarius.

SZENT ISTVÁN
EGYETEM

SZENT ISTVÁN
EGYETEM

SZENT ISTVÁN EGYETEM

Our Task: Develop Protocols for:

1.Analytical methods for measuring pesticides

2.Analytical methods for measuring organic industrial pollutions

3.Analytical methods for measuring inorganic compounds as heavy metals

SZENT ISTVÁN EGYETEM

Which component to measure?

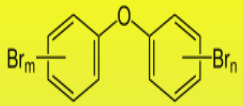
COMMON IMPLEMENTATION STRATEGY
FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC)
Guidance Document No. 25

As a rule of thumb, compounds with a log Kow>5 (octanol-water) should *preferably* be measured in **sediments,** or in suspended particulate matter (SPM), while compounds with a log Kow<3 should preferably be measured in water.

SZENT ISTVÁN EGYETEM

Anthracene (PAH)

Brominated diphenyl ethers



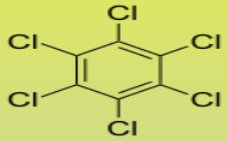
C10-13-chloroalkanes $C_{10}H_{18}Cl_4$ and $C_{13}H_{21}Cl_7$

Chlorpyrifos (-ethyl, -methyl)

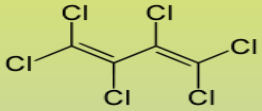
Di(2-ethylhexyl)phthalate (DEHP) (PVC)

Fluoranthene (PAH)

Hexachlorobenzene



Hexachlorobutadiene



Hexachlorocyclohexane -Lindane

Nonylphenols (detergent)

Pentachlorobenzene (PAH-pesticide)

Polyaromatic Hydrocarbons: **Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)-pyrene**

Trifluralin

DDT (including DDE, DDD)

Aldrin

Endrin

Dieldrin

SZENT ISTVÁN EGYETEM

Priority Substances relevant to the European Comission's 2012 proposal under the Water Framework Directive:

Pesticides (herbicides, insecticides): Aclonifen, Bifenox, Cypermethrin, Dicofol, Heptachlor, Heplataclorepoxide, Quinoxyfen, Cybutrine, Dichlorvos, Tetrabutryn
Industrial chemicals: Perflourooctane sulfonic acid(PFOS), Hexabromocyclo-dodecane (HBCDD)
Combustion by products: Dioxins and dioxin-like PCB-s
Pharmaceutical substances (steroids-hormons): 17-alpha-ethinylestradiol, 17-beta-estradiol, Diclofenac

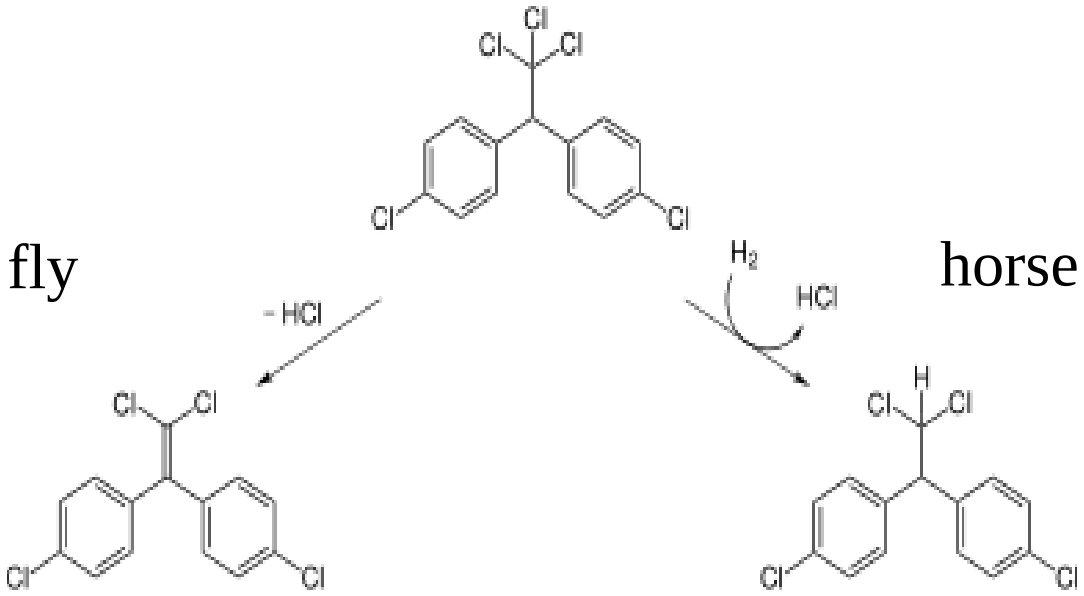
SZENT ISTVÁN EGYETEM

16 Pesticides (herbicides, insecticides): Aclonifen, *Aldrin,*Bifenox, Cypermethrin, *Chlorpyrifos (-ethyl, -methyl), DDT (including DDE, DDD),* Dicofol, *Dieldrin, Endrin,* Heptachlor, Heplataclorepoxide, Quinoxyfen, Cybutrine, Dichlorvos, Tetrabutryn, *Trifluralin*

+ Hexachlorobenzene , Hexachlorocyclohexane

EPA 8270

green fly



horse fly

Degradation of DDT to form DDE (by elimination of HCl, left) and DDD (by reductive dechlorination, right)

SZENT ISTVÁN EGYETEM

Polyaromatic Hydrocarbons: Anthracene, **Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)-pyrene, *Fluoranthene,***

EN 16181:2018

SZENT ISTVÁN EGYETEM

Semivolatile organic compounds:

Brominated diphenyl ethers EPA 1614A

C10-13-chloroalkanes EN ISO 12010

Hexachlorobutadiene EPA 8260C

SZENT ISTVÁN EGYETEM

Industrial chemicals:

Perflourooctane sulfonic acid(PFOS) **CEN/TS 15968**

Nonylphenols ***EN ISO 18857-2***

Hexabromocyclo-dodecane (HBCDD)
No standardized method
Chemosphere 82 (2011) p. 698-707 :
„Determination of HBCD isomers by isotopic dilution LC-MS/MS”

SZENT ISTVÁN EGYETEM

Pharmaceutical substances:
steroids

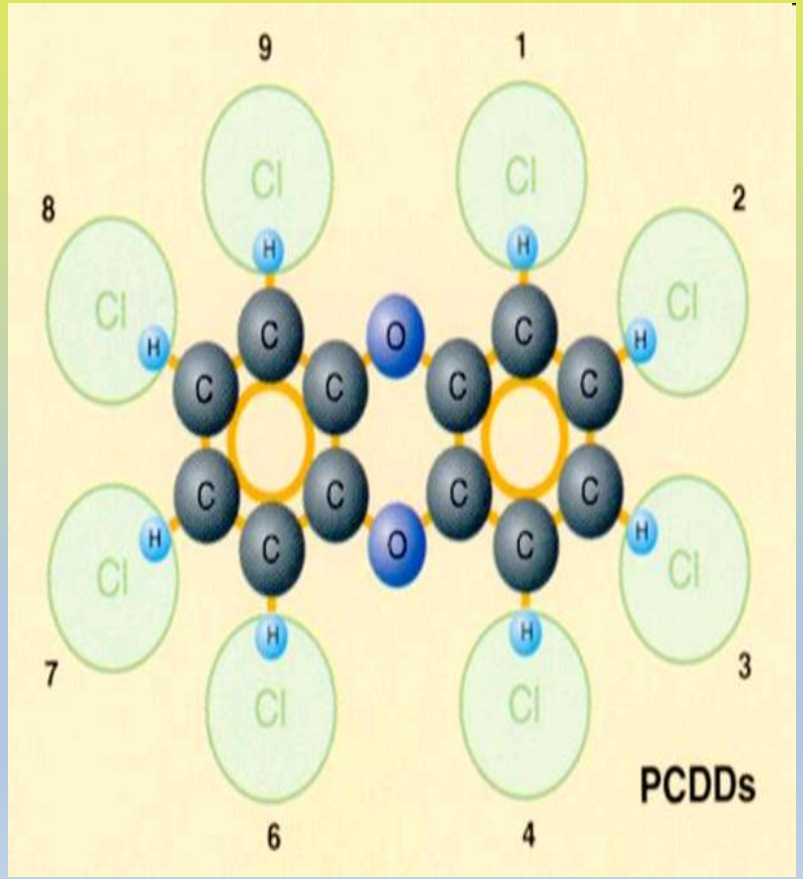
17-alpha-ethinylestradiol, 17-beta-estradiol EPA 1698

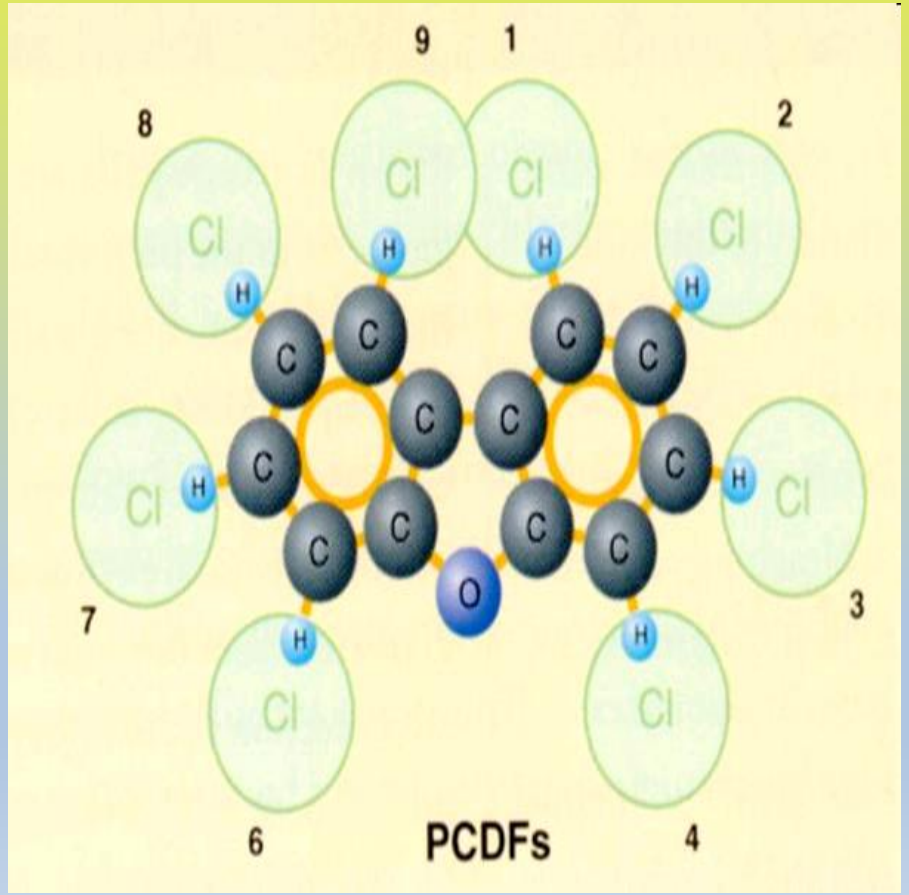
Hormon
Diclofenac EPA 542

SZENT ISTVÁN EGYETEM

Combustion by products: Dioxins and dioxin-like PCB-s

EPA 8280B





Congener	TEF value	Congener	TEF value
Dibenzo-p-dioxins (PCDDs)		**Dioxin-like PCBs: Non-ortho PCBs + Mono-ortho PCBs**	
2,3,7,8-TCDD	1		
1,2,3,7,8-PeCDD	1	*Non-ortho PCBs*	
1,2,3,4,7,8-HxCDD	0,1	PCB 77	0,0001
1,2,3,6,7,8-HxCDD	0,1	PCB 81	0,0001
1,2,3,7,8,9-HxCDD	0,1	PCB 126	0,1
1,2,3,4,6,7,8-HpCDD	0,01	PCB 169	0,01
OCDD	0,0001		
Dibenzofurans (PCDFs)		*Mono-ortho PCBs*	
2,3,7,8-TCDF	0,1	PCB 105	0,0001
1,2,3,7,8-PeCDF	0,05	PCB 114	0,0005
2,3,4,7,8-PeCDF	0,5	PCB 118	0,0001
1,2,3,4,7,8-HxCDF	0,1	PCB 123	0,0001
1,2,3,6,7,8-HxCDF	0,1	PCB 156	0,0005
1,2,3,7,8,9-HxCDF	0,1	PCB 157	0,0005
2,3,4,6,7,8-HxCDF	0,1	PCB 167	0,00001
1,2,3,4,6,7,8-HpCDF	0,01	PCB 189	0,0001
1,2,3,4,7,8,9-HpCDF	0,01		
OCDF	0,0001		

Abbreviations used: 'T' = tetra; 'Pe' = penta; 'Hx' = hexa; 'Hp' = hepta; 'O' = octa; 'CDD' = chlorodibenzodioxin; 'CDF' = chlorodibenzofuran; 'CB' = chlorobiphenyl.

SZENT ISTVÁN EGYETEM

<u>Inorganic components</u>: Elements of the periodical system-mainly not contaminats but geochemical (like soil) characterisation.
Suggested method: EN 21470-50:2006

2 g soil + 5 ml cc.HNO_3 +2 ml H_2O_2 ⟶ 50ml

Any detection method can be used, but please report:
-traceability
-validation
-proficiency testing

SZENT ISTVÁN EGYETEM

What I dont plan:

1.Harmonize home made analytical methods-when we have internationally accepted method.

2.Analyses samples in a lab., which has not real possibility to get positive data.

SZENT ISTVÁN EGYETEM

Tasks I.

1.Please obtain the recommended methods.

2.Read carefully and make decision, are you able to fulfil all requirements, or you have to give the task to an accreditated lab. in the future.

3.Please let to know to…… until……., who will do the analysis at home, who will give to accreditated lab.

4.Those who will do at home, let to know to……., until……..what kind of Proficiency Test the lab past, or do the lab needs to participate in the future.

SZENT ISTVÁN EGYETEM

Tasks II: (As Analytical methods are in the middle beetwen Sampling and Evaluation)

Task for sampling:

On the basis of recomended Analytical method.

II.1. Pls calculate the amount of samples (how many grams from one sampling place)

II.2.Plan the physical condition of sampling and the shipment

Task for evaluation:

How many data is needed for evaluation.

SZENT ISTVÁN EGYETEM

Thank you for attention! Questions Please!

Participants	Suggested method for pesticide analysis
AITB-GBA	non
Bulgaria	VIM 1014/2010, EN ISO12918
Croatia	non
Hungary	WBSE-125:2016 GC-MS, WBSE-123:2016 LC-MS
Moldova	EPA 1699, EN ISO12918
Montenegro	non
Republika Srpska	EPA 508.1:1994
Romania	ISO 10382:2002
Slovakia	US EPA 8010 US EPA 8015
BH-Federation	EPA-508.1:1994
Slovenia, Ukraina	non