

ThermoFisher
SCIENTIFIC

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A deeper look into the world of POPs

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Historical aspects

- ▶ Pesticides; Chemical industry



Picture: www.heinze-photography.com

- ▶ Accidents and/or intentional use

Historical aspects

**Klärschlammverordnung
(AbfKlärV)¹⁾**
Vom 15. April 1992

§ 1
Anwendungsbereich
(1) Diese Verordnung hat zu beachten, wer
1. Abwasserbehandlungsanlagen betreibt und Klärschlamm zum Aufbringen auf landwirtschaftlich oder gärtnerisch genutzte Böden abgibt oder abgeben will,
2. Klärschlamm auf landwirtschaftlich oder gärtnerisch genutzte Böden aufbringt oder aufbringen will.
(2) Unter Verwendung von Klärschlamm hergestellte Gemische mit Kohlenstoffäugen, Kalk- oder Gesteinsmehlzusätzen oder anderen Stoffen, die auf landwirtschaftlich oder gärtnerisch genutzte Böden aufgebracht werden sollen, unterliegen dieser Verordnung, sofern diese Gemische nicht nach § 1 des Düngemittelgesetzes den Bestimmungen des Düngemittelrechts unterliegen.
(3) Die betroffenen Stellen wirken darauf hin, daß die in dieser Verordnung genannten Grenzwerte soweit wie möglich unterschritten werden. Die in der Verordnung genannten Bodengrenzwerte werden für die spezifischen Bedingungen der landwirtschaftlichen Klärschlammverwertung festgelegt. Generelle Anbauerschänkungen oder Beschränkungen anderer Art lassen sich aus dem Erreichen oder Überschreiten der Werte nicht ableiten.

§ 2
Begriffsbestimmungen
(1) Abwasserbehandlungsanlagen sind Anlagen zur Behandlung von Abwasser, ungeschichtet deren Ausbaugröße und Behandlungszug. Kleinkläranlagen sind Anlagen mit mehreren Kammern zur Behandlung häuslichen Abwassers mit einem Schmutzwasserzufluß von weniger als 8 Kubikmetern je Tag. Abwassersammelgruben ohne Abfluß sind keine Abwasserbehandlungsanlagen im Sinne der Verordnung.
(2) Klärschlamm ist der bei der Behandlung von Abwasser in Abwasserbehandlungsanlagen einschließlich zugehöriger Anlagen zu weitergehenden Abwasserreinigung anfallende Schlamm, auch entwässert oder getrocknet oder in sonstiger Form behandelt. Rohschlamm ist Schlamm, der Abwasserbehandlungsanlagen unbehandelt entnommen wird. Die Entwässerung von Rohschlamm gilt nicht als Behandlung von Klärschlamm. In Kleinkläranlagen anfallender Schlamm gilt als Klärschlamm im Sinne dieser Verordnung.
(3) Feldfrüchte im Sinne dieser Verordnung sind Pflanzenarten, die auf Ackerflächen angebaut werden und deren vegetative Teile für eine Verfüttung an Tiere vorgesehen sind. Der Anbau von Mais zählt nicht zum Feldfrüchtebau im Sinne dieser Verordnung.

§ 3
Voraussetzungen für das Aufbringen
(1) Klärschlamm darf auf landwirtschaftlich oder gärtnerisch genutzten Böden nur so aufgebracht werden, daß das Wort der Allgemeinheit nicht beeinträchtigt wird und die Aufbringung nach Art, Menge und Zeit auf den Nährstoffbedarf der Pflanzen unter Berücksichtigung der im Boden verfügbaren Nährstoffe und organischen Substanz sowie der Standort- und Anbaubedingungen ausgerichtet wird. Im übrigen gelten für das Aufbringen von Klärschlamm die Bestimmungen des Düngemittelrechts entsprechende.

¹⁾ Diese Verordnung dient der Umsetzung der Richtlinie 86/273/EWG des Rates vom 12. Juni 1986 über den Schutz der Umwelt und insbesondere der Böden bei der Verwendung von Klärschlamm in der Landwirtschaft (Abk. EG N. L 181 S. 6).

▶ National regulations

STATE OF CALIFORNIA
ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENVIRONMENTAL HEALTH HAZARD ASSESSMENT
SAFE DRINKING WATER AND TOXIC ENFORCEMENT ACT OF 1986

CHEMICALS KNOWN TO THE STATE TO CAUSE CANCER OR REPRODUCTIVE TOXICITY
October 27, 2017

The Safe Drinking Water and Toxic Enforcement Act of 1986 requires that the Governor revise and republish at least once per year the list of chemicals known to the State to cause cancer or reproductive toxicity. The identification number indicated in the following list is the Chemical Abstracts Service (CAS) Registry Number. No CAS number is given when several substances are presented as a single listing. The date refers to the initial appearance of the chemical on the list. For easy reference, chemicals which are shown underlined are newly added. Chemicals or endpoints shown in ~~strikeout~~ were placed on the Proposition 65 list on the date noted, and have subsequently been removed.

▶ International discussion





- ▶ Requirements to become one of the POP:
 - ▶ remain intact for exceptionally long periods of time (many years);
 - ▶ become widely distributed throughout the environment as a result of natural processes involving soil, water and, most notably, air;
 - ▶ accumulate in the fatty tissue of living organisms including humans, and are found at higher concentrations at higher levels in the food chain; and
 - ▶ are toxic to both humans and wildlife.

► Characterisation by source

- 1. Pesticide
- 2. Industrial Chemical
- 3. Unintentional Product



Pictures: chm.pops.int

► Listed in different Annexes of Stockholm Convention

- A: Elimination
- B: Restriction
- C: Unintentional Production



► Initially →

The Dirty Dozen



Stockholm Convention on
Persistent Organic Pollutants (POPs)

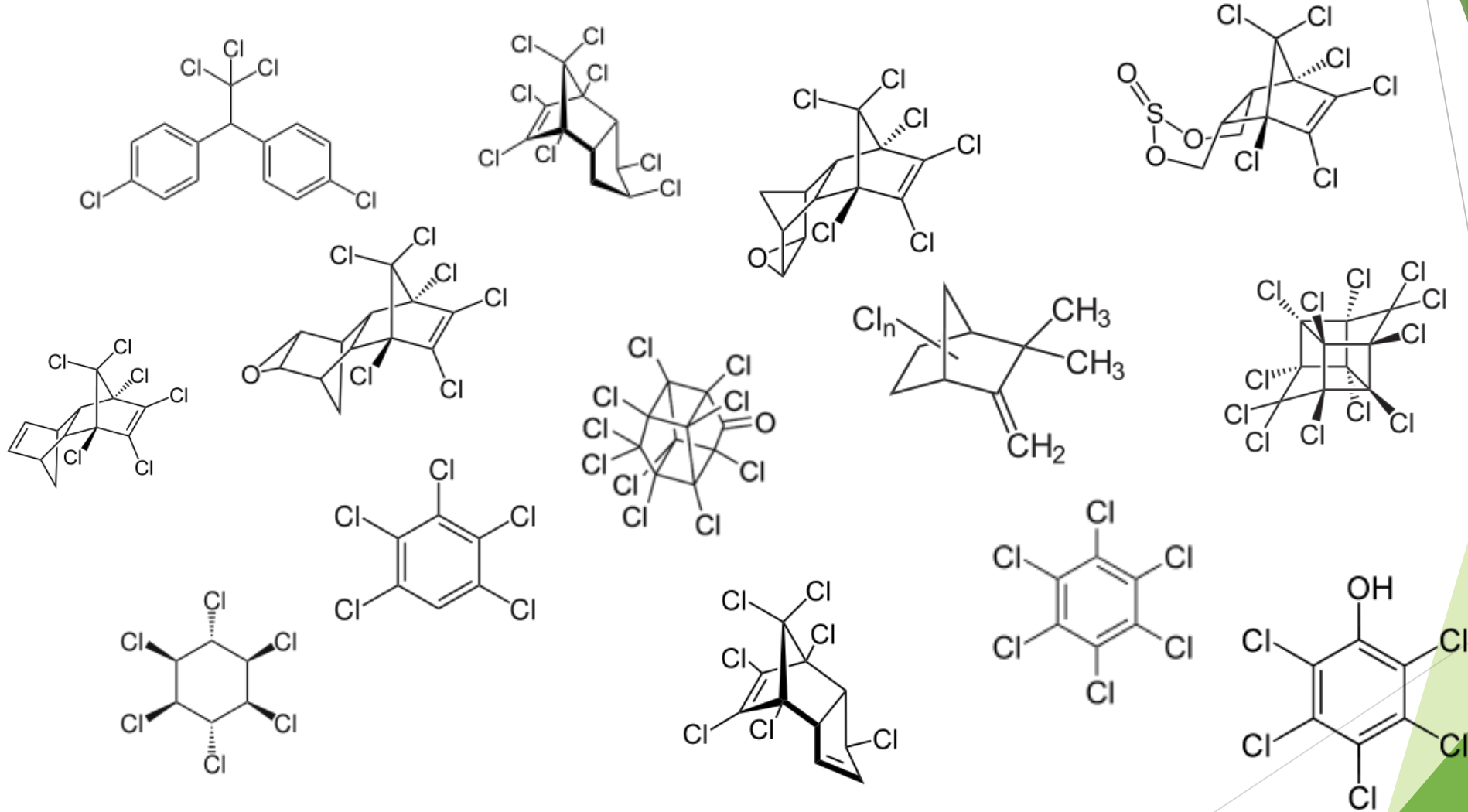
► Amendments ongoing →

The 16 New POPs

*An introduction to the chemicals added to the Stockholm Convention
as Persistent Organic Pollutants by the Conference of the Parties*

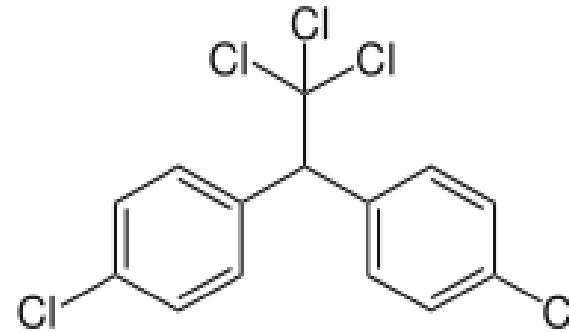
June 2017

Introduction → The Pesticides

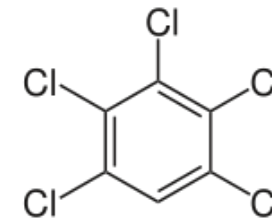
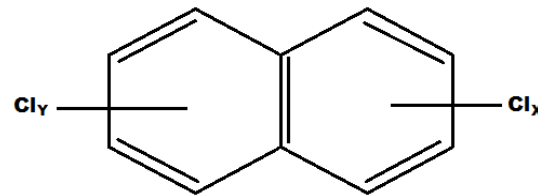
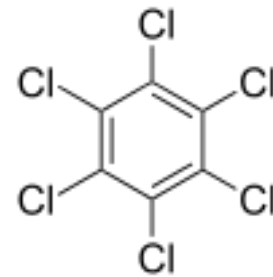
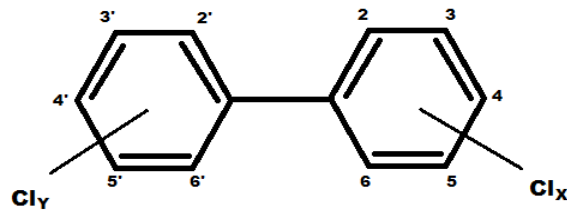
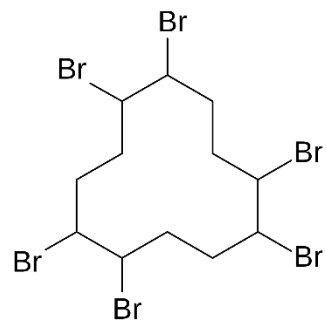
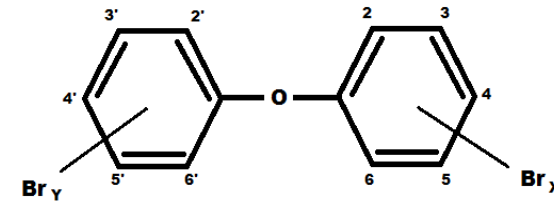
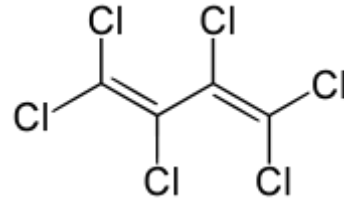
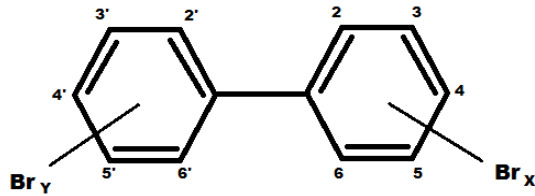


Dichlorodiphenyltrichloroethane DDT

- ▶ In use since 1940th
- ▶ Very effective, e.g. Malaria control
- ▶ Isomeres and transformation products
(p,p'-DDT/-DDD/-DDE, o,p'-DDT /-DDD/-DDE)
- ▶ Banned in the US in 1973, produced in US until 1985, under restrictions still in use → listed in Annex B of Stockholm Convention

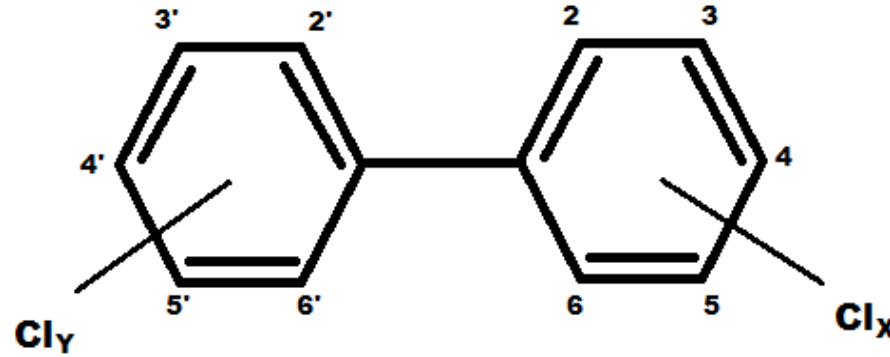


Introduction → Industrial Chemicals

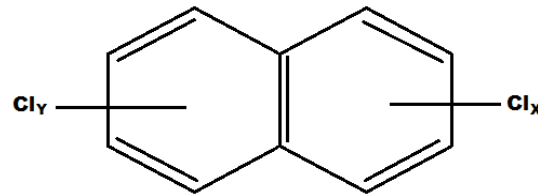
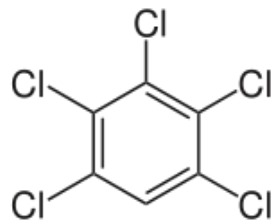
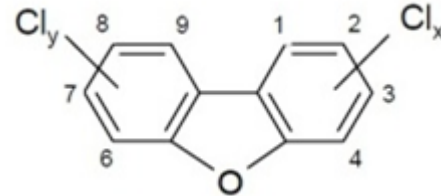
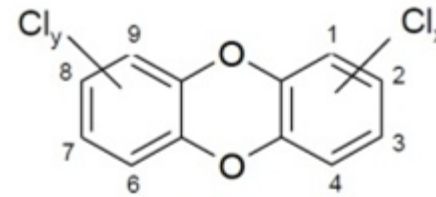
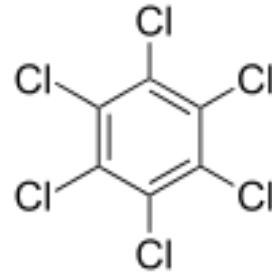
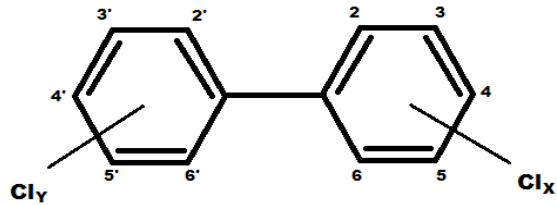


Polychlorinated biphenyls (PCB)

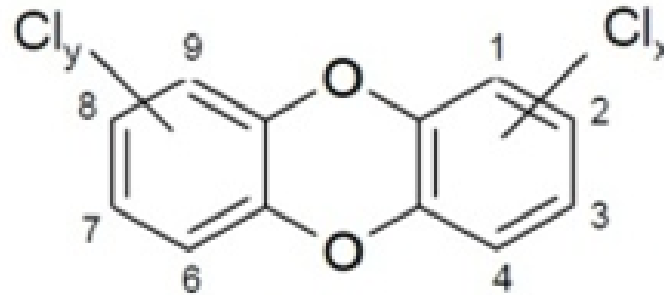
- ▶ In use since 1930th
- ▶ Thermal and chemical stable
- ▶ 209 possible congeners, different methods for summation (sum of 6, sum of 7, sum 12 and sum of 209)
- ▶ Banned in the US in 1979, world wide production: at least 1 million tons and a certain amount is remains in use → listed in Annex A



Introduction → Unintentional Production



Polychlorinated dibenzo-p-dioxins (PCDD)



- ▶ In use just for analytical reasons
- ▶ Most toxic POP;
created during combustions processes or as impurity of other chemicals
- ▶ 75 possible congeners (210 together with the PCDF) → seven are 2,3,7,8-substituted (17 together with the PCDF)
- ▶ Just unintentionally production → listed in Annex C

In the beginning there was the sampling ...

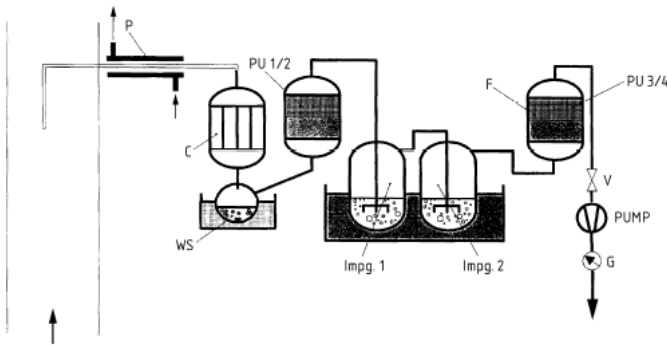


Picture: Kay Kelterer

- ▶ Generate a representative part of whatever needs to be analysed!



- ▶ Preserve the sample to have it also representative when it arrives in the lab!



Picture: EN 1948

- ▶ Different techniques in dependency on matrices and analytes

Homogenisation and storage

- ▶ Important step in the lab, especially if many parameters need to be analysed



Picture: Kay Kelterer

- ▶ Sometimes special storage conditions are necessary



Picture: Kay Kelterer

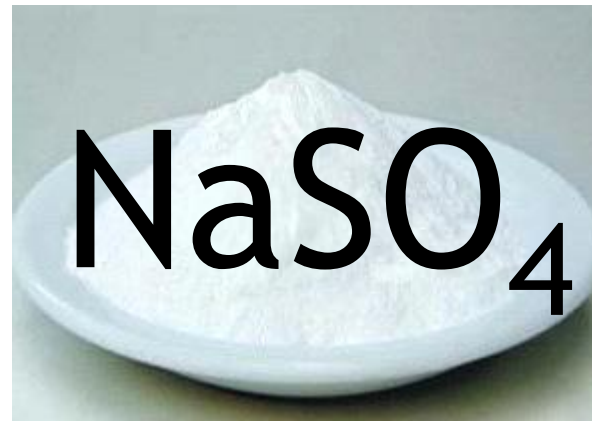
Preparation for extraction

- ▶ Not needed for all kind of samples, e.g. oil samples
- ▶ Example for preparation step → removing or binding of water

Remove



Bind



Free the analytes

- ▶ The analytes need to be extracted from the sample matrix.
- ▶ Several techniques depending on the specific analytes
 - ▶ Liquid/liquid
 - ▶ SPE
 - ▶ Ultrasonic
 - ▶ Hot solvent extraction



Picture: Kay Kelterer

Hot solvent extraction

- ▶ Classical (e.g. Soxhlet)



Picture: Kay Kelterer

- ▶ Automated (ASE)



Extract clean-up and separation of the analytes

- ▶ A mixture of several substances has been extracted. To prepare the sample extract for measurement interferences have to be removed.



Picture: Kay Kelterer

- ▶ Different ad- and absorbents can be used
- ▶ Examples are:
 - ▶ Silica gel
 - ▶ Alumina
 - ▶ Carbon
 - ▶ Bio beads

Automated systems (e.g. PCDD/F)



Picture: www.lctech.de



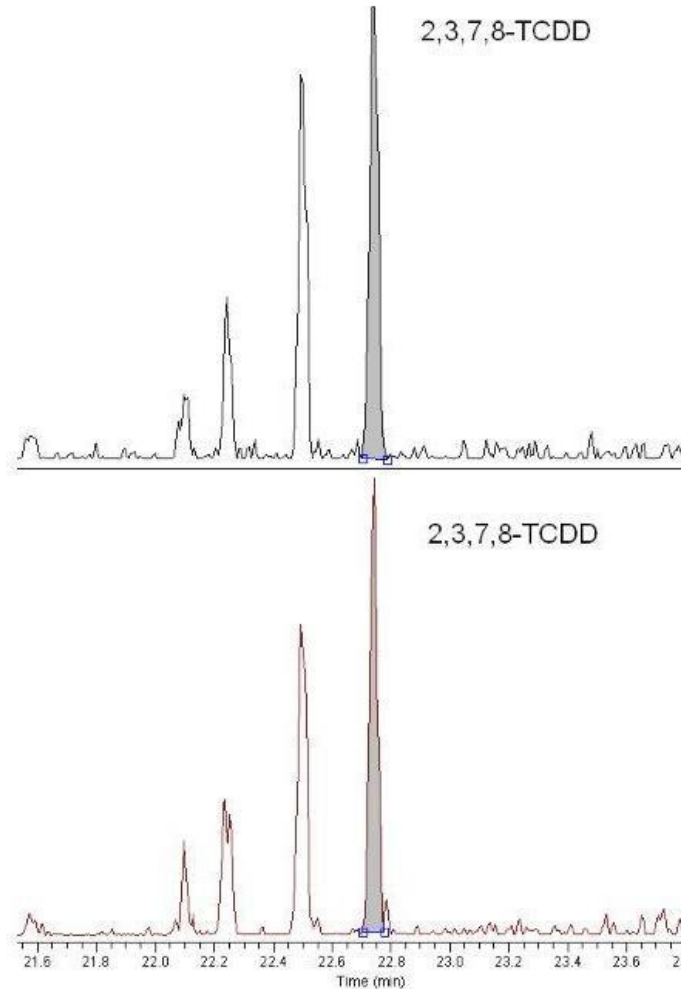
Picture: www.dpssystems.eu



Picture: www.fms-inc.com

Unmask the analytes

- ▶ Looking for the best combination of injection system, chromatographic column and detection system, to get the best signals



Mass spectrometer

- ▶ Most flexible detector usable for all POPs
- ▶ In combination with

Liquid Chromatograph



or

Gas Chromatograph



Isotope dilution for mass spectrometer

- Use of the ^{13}C marked carbon for quantification

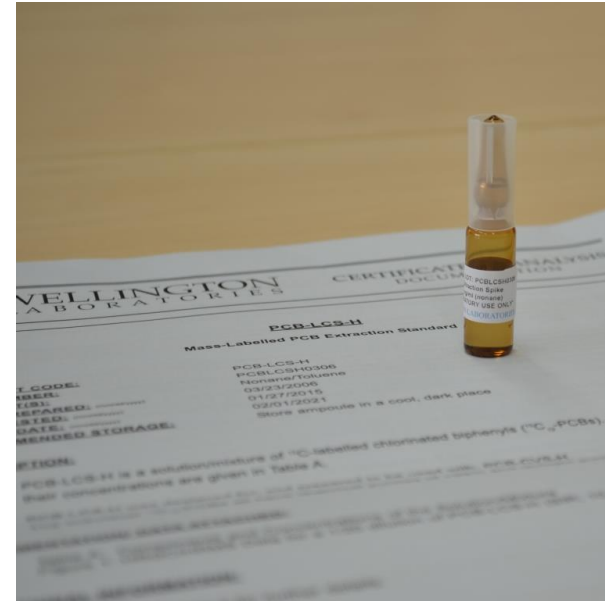
Isotope	Atomic number	Nuclear number	Neutron number	Isotope mass	Half-life	Ratio
^{12}C	6	12	6	12.000000000	stable	~99 %
^{13}C	6	13	7	13.003354835	stable	~1 %

Isotope	Atomic number	Nuclear number	Neutron number	Isotope mass	Half-life	Ratio
^{35}Cl	17	35	18	34.9688527	stable	~76 %
^{37}Cl	17	37	20	36.9659026	stable	~24 %
^{79}Br	35	79	44	78.918338	stable	~51 %
^{81}Br	35	81	46	80.91690	stable	~49 %

- Most POPs are chlorinated or brominated
→ use of ratio for identification

QA/QC

- ▶ Quality assurance and quality control comes with the analytical methods or the required quality system (e.g. ISO 17025)
- ▶ Depending on analytical request different methods are applicable; e.g. for PCDD/F:



Picture: Kay Kelterer

EN 1948: Stationary source emissions
Determination of the mass concentration of
PCDDs/PCDFs and dioxin-like PCBs

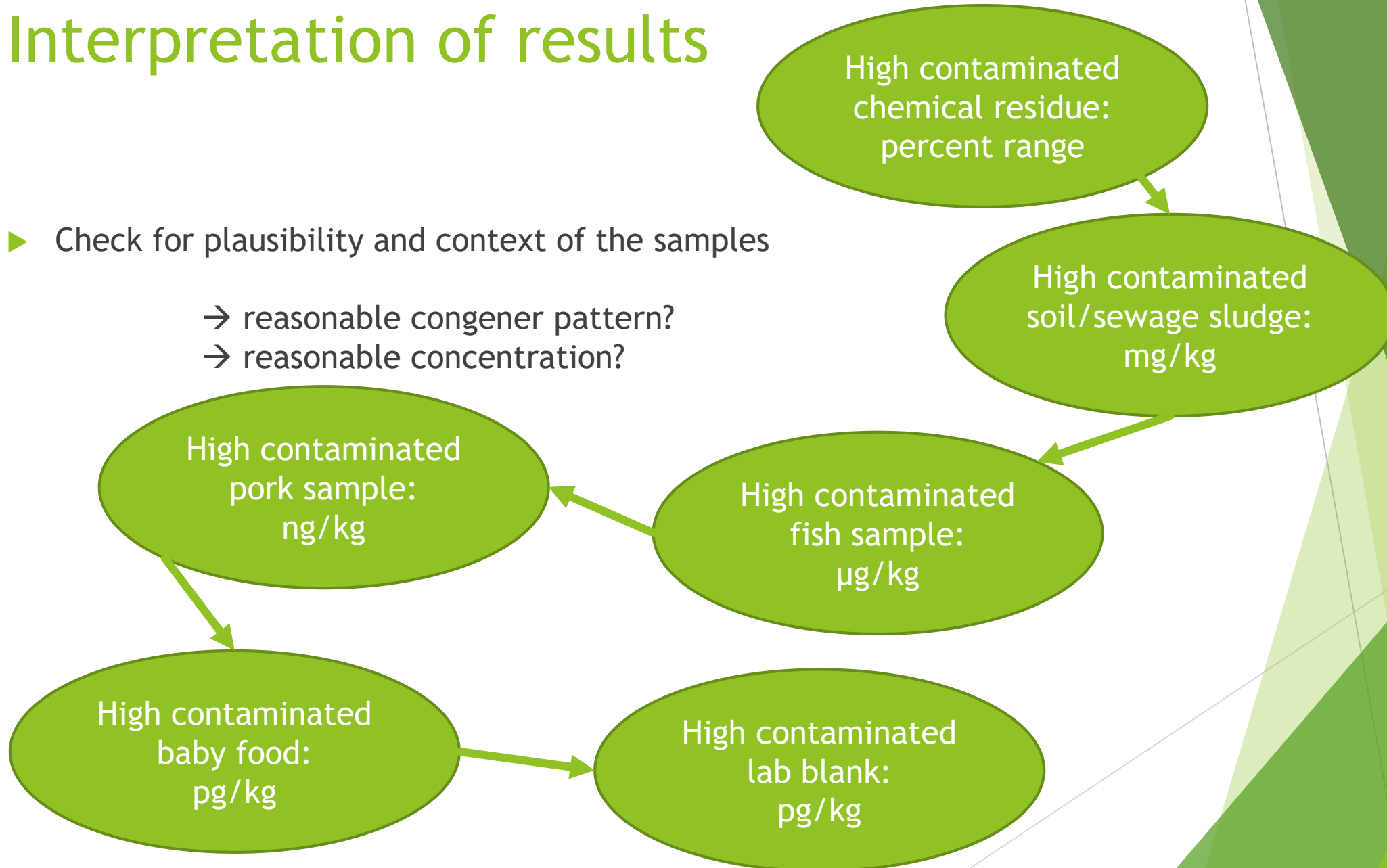
US EPA 23: Determination of PCDD and
PCDF from stationary sources

JIS K0311: Method for determination of tetra-through octachlorodibenzo-p-dioxins,
tetra-through octachlorodibenzofurans and dioxin-like polychlorinatedbiphenyls
in stationary source emission

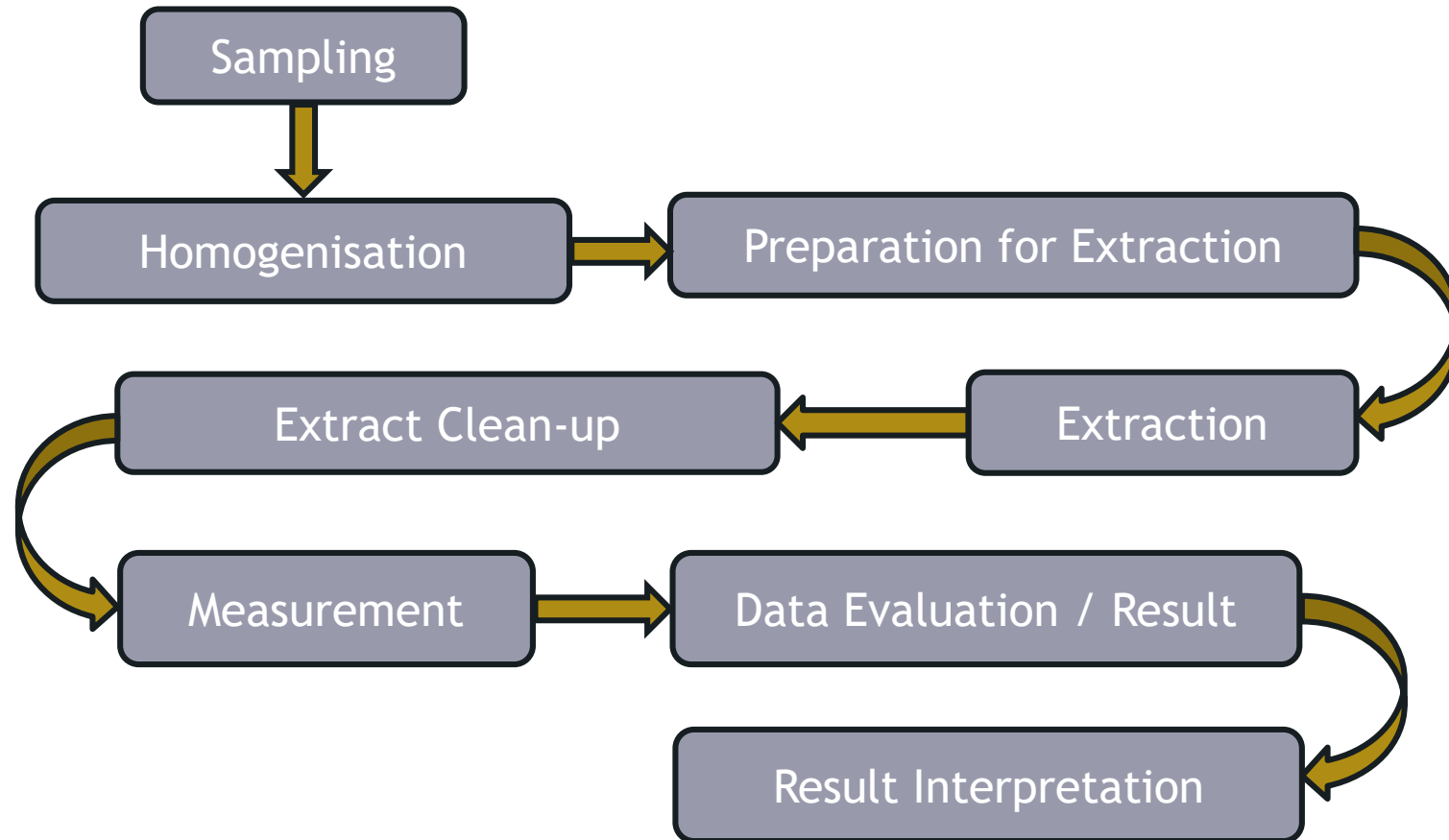
Interpretation of results

► Check for plausibility and context of the samples

- reasonable congener pattern?
- reasonable concentration?

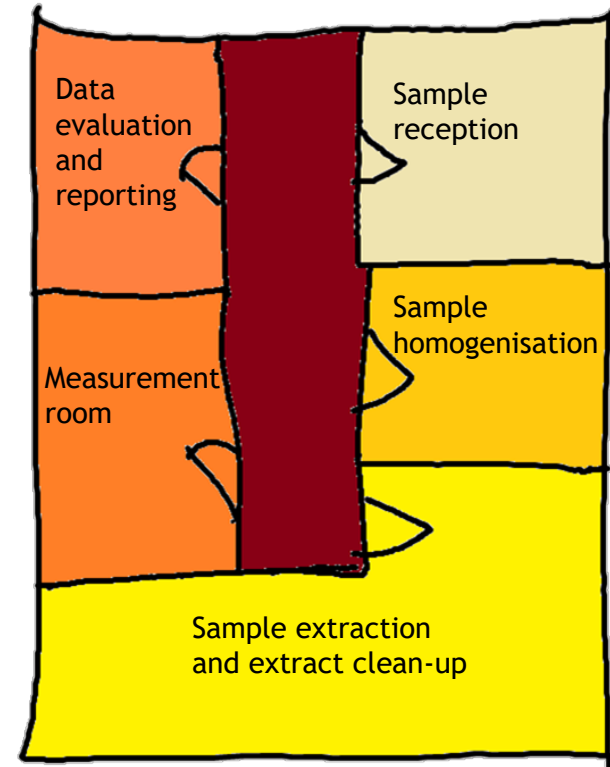


Analytical procedure



Summary

- ▶ POPs = Persistent Organic Pollutants
- ▶ Many rules / methods to control POP concentrations
- ▶ Analytical procedure may need many steps → implementing a new method needs to be planned well



Questions?