How to select substances for screening: Challenges in sampling and analyses

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Challenges

- Study design
- Sampling location
- Sample matrix
- Sampling method
- Contamination
- Analyte stability
- Behaviour & fate
- Method development
- Validation
- Data interpretation

Assessing an environmental system

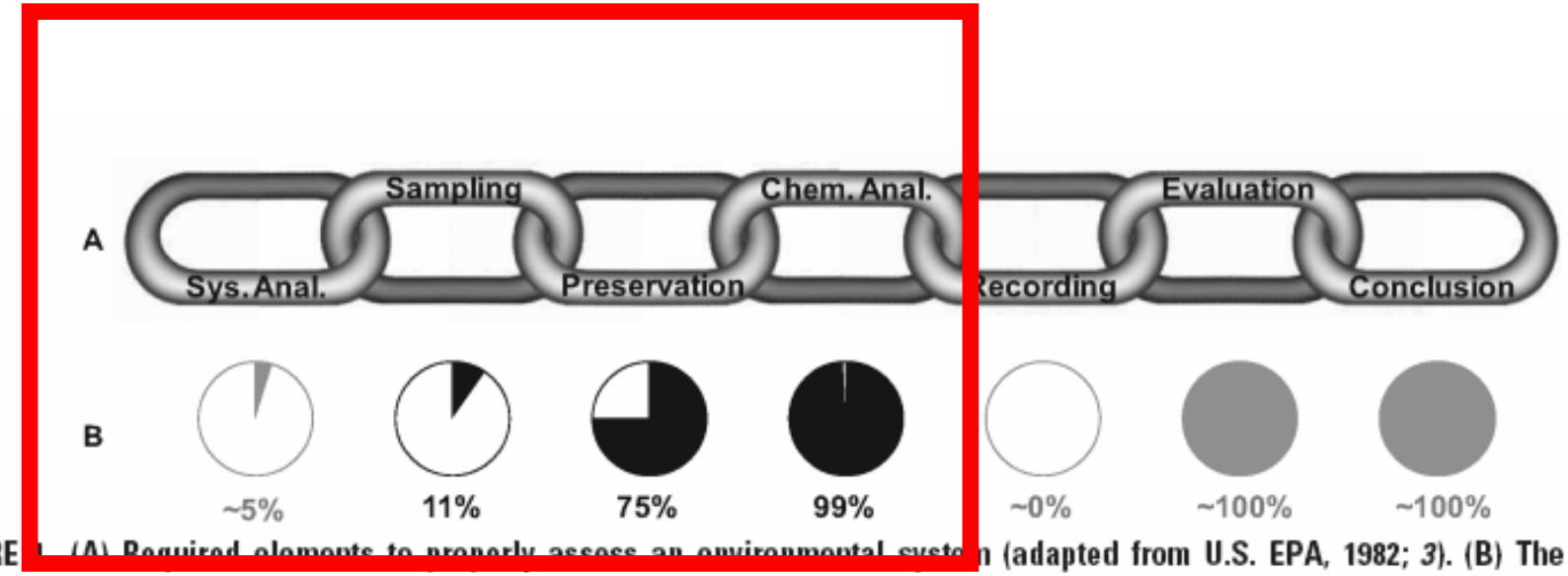


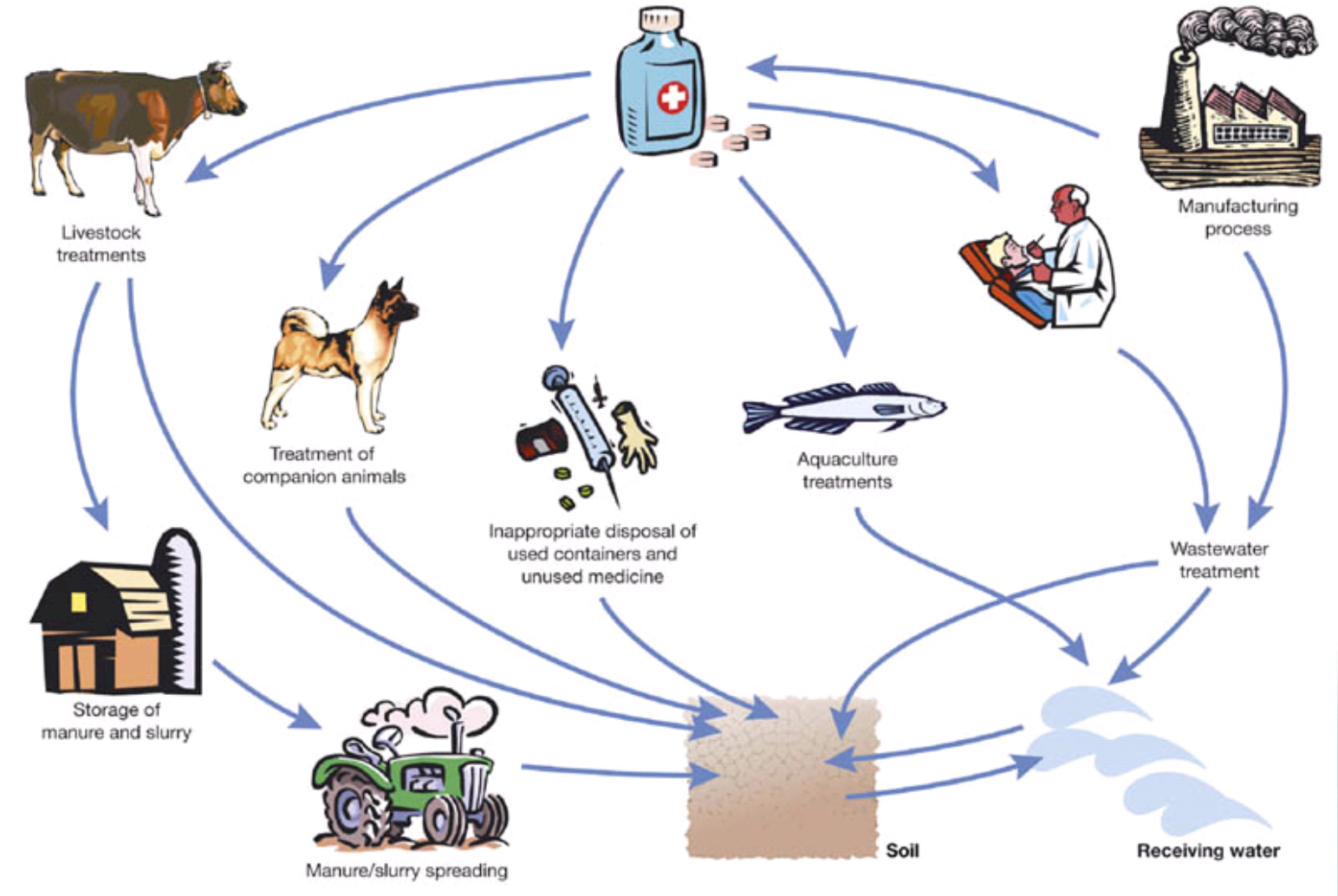
FIGURE 1. (A) Required elements to properly assess an environmental system (adapted from U.S. EPA, 1982; *3*). (B) The percentage indicates the fraction of papers addressing the corresponding element. Eighty-seven journal articles (*4–90*) investigating the fate of pharmaceuticals and personal care products at 267 different sewer sites (including sewage treatment plant influents) were analyzed. (black: objective evaluation according to the scheme presented in Figure 2; gray: subjective judgment).

Ort et al. ES&T 2010

Sampling locations

- Need to use 'intelligent' sampling strategies.
- Assessment of point and diffuse sources.
- Develop relevant scenarios.
- Example: Antifouling biocides (Irgarol 1051)

Sources & inputs of pharmaceuticals



Sample matrix

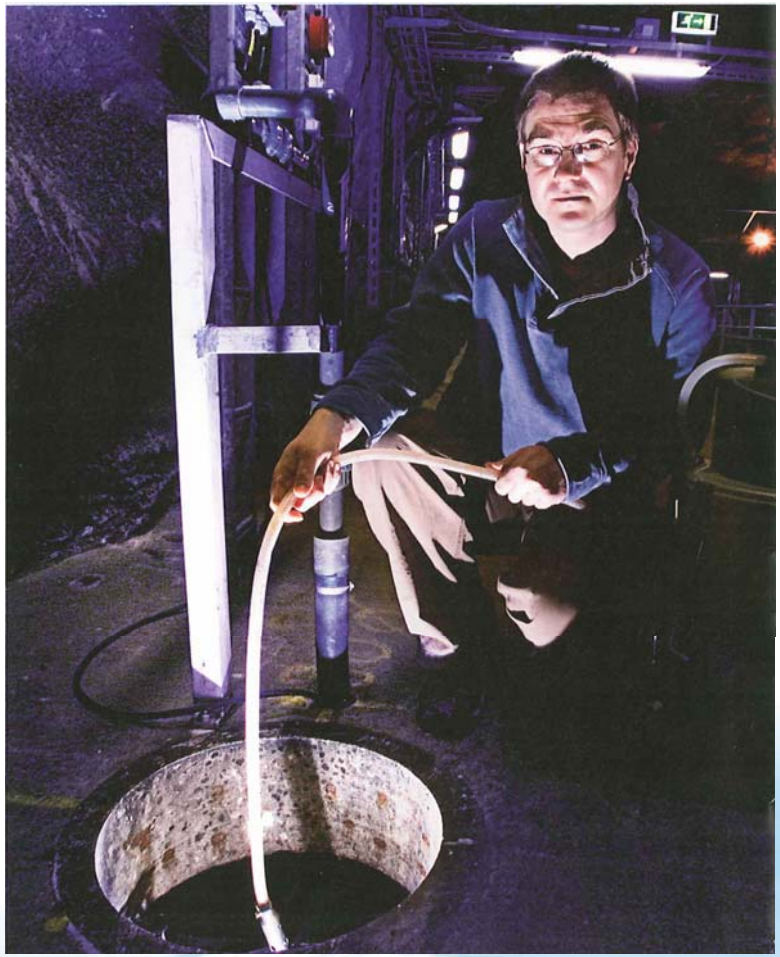
- Assessment of physico-chemical properties.
- Use of models (e.g. EPI-Win) to plug data gaps and predict fate.
- Not always an easy task!

Effluent/sludge/sediment?

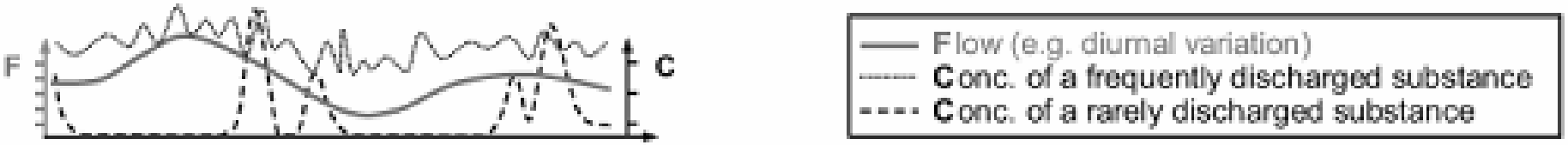
- Solid-specific equilibrium sorption constant (Kd)? Normalised to OC (K_{OC})
- Other factors influencing sorption:
  - temperature, pH and ionic strength, cation bridging, cation exchange and hydrogen bonding.
- Compounds with Kd/K_{OC} predicted from K_{OW} data, may NOT necessary partition onto sludge if other sorption mechanisms predominate, but may partition onto sediments where there may be an array of different active sorption sites.

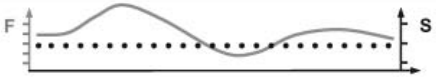
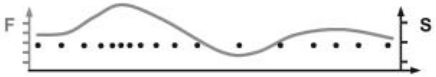
Sampling method

- Grab vs. composite
- Conventional vs. passive techniques
- Sufficient and representative sample
- Follow monitoring guidelines?
- Other guidelines (USEPA)?



Different sampling modes



Sampling mode		Short description (see *Sampling Guide* to find out which sampling mode is suitable in which situation).	Illustration (F=Flow in sewer, S=Sampling volume)	Specific equipment [1]	Flow meter [2]
Continuous	flow-proportional	Divert a side stream, proportional to the flow in the sewer		Pump with speed control (proportional to external flow signal)[3]	Yes
	constant	Divert a constant side stream from the sewer		Pump	No
Discrete	time-proportional	Take a constant sample volume at constant time intervals		Standard auto-sampler	No
	flow-proportional	Make sample volume proportional to the flow in the sewer taking them at constant time intervals		Auto-sampler with adjustable sampling volume [4] (proportional to external flow signal)	Yes
	volume-proportional	Take a constant sample volume at variable time intervals, after a certain volume of wastewater has passed the sampling point		Auto-sampler totaling an external flow signal up to a predefined volume and then triggering a sample [5]	Yes
	grab sample	Take one (or a number of) grab sample		Scoop, no power supply.	No

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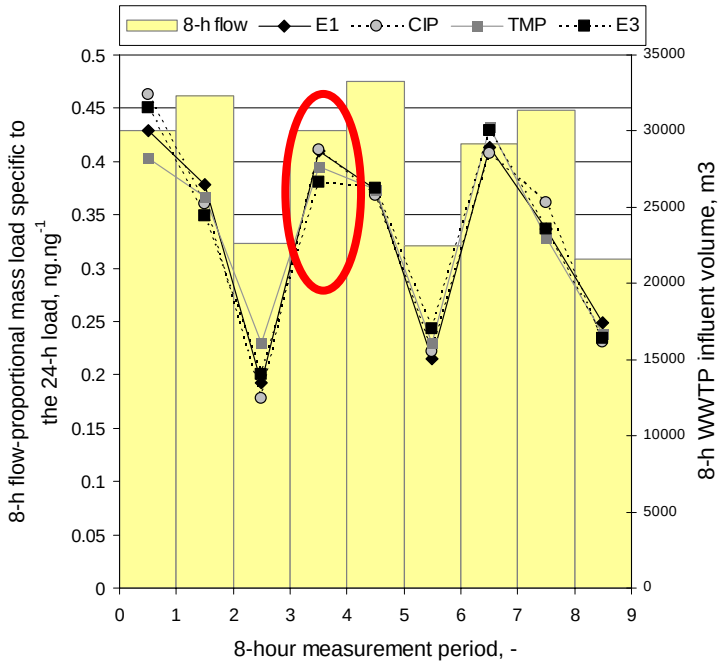
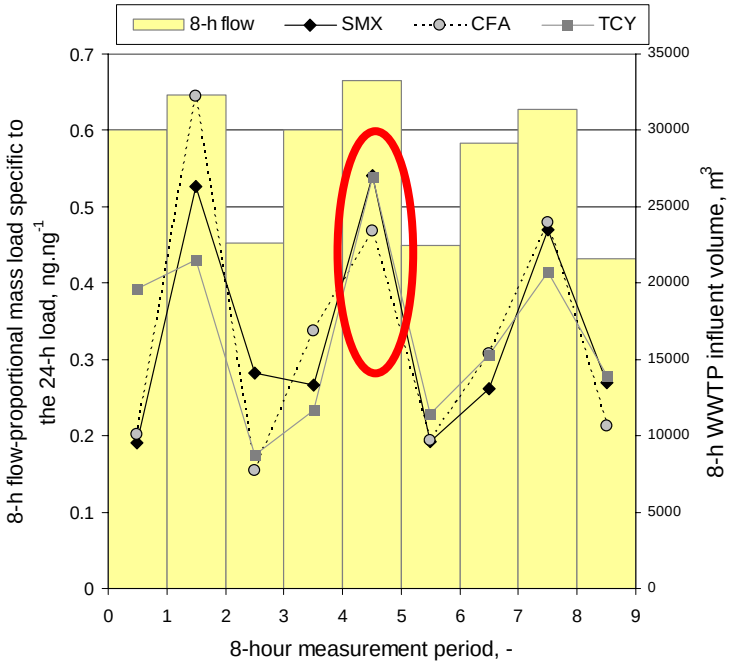
Dynamics in influent mass loads

- Drugs administered **<u>every 12 hour</u>**



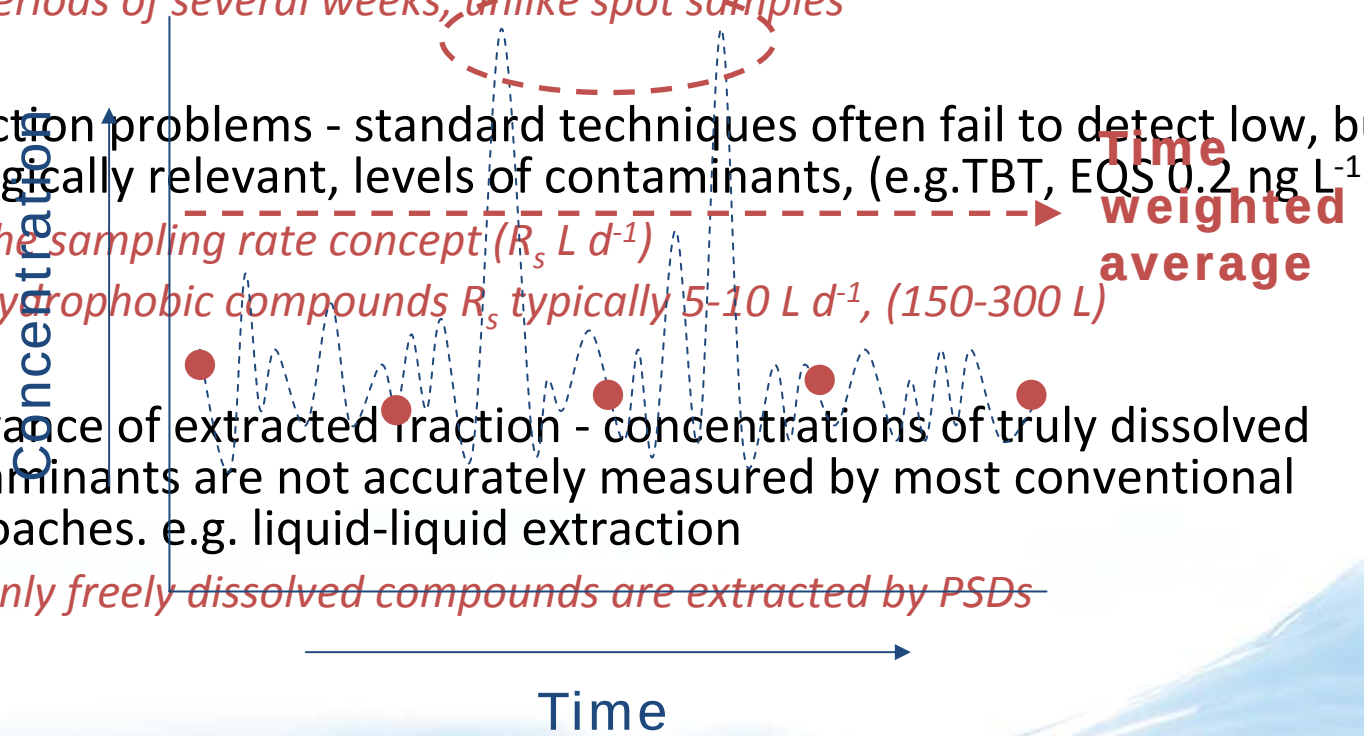
- Drugs administered **<u>every 8 hours</u>**



Plosz et al. ES&T 2010

Passive sampling for screening?

- Representativeness - spot water samples reflect residue composition only at the moment of sampling and may fail to detect or overestimate episodic contamination
  - *Passive samplers (PSDs) are typically left to accumulate contaminants for periods of several weeks, unlike spot samples*
- Detection problems - standard techniques often fail to detect low, but ecologically relevant, levels of contaminants, (e.g.TBT, EQS 0.2 ng L^{-1}).
  - *The sampling rate concept (R_s L d^{-1})*
  - *Hydrophobic compounds R_s typically 5-10 L d^{-1}, (150-300 L)*
- Relevance of extracted fraction - concentrations of truly dissolved contaminants are not accurately measured by most conventional approaches. e.g. liquid-liquid extraction
  - *Only freely dissolved compounds are extracted by PSDs*



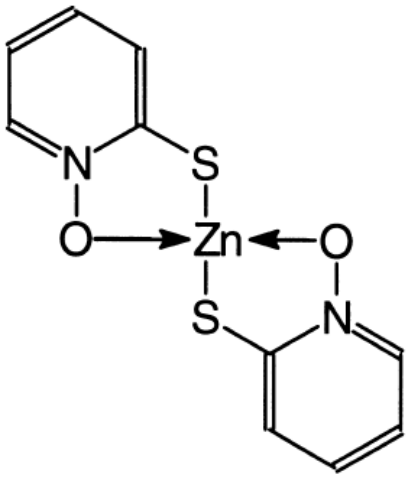
SED 2

Analyte stability/preservation

- Stability of screening compounds often unknown.
- Important consideration even if samples are extracted within 24h of collection.
- How to store your samples?

Photodegradation

- Zinc pyrithione (ZnPT)
  - Anti-dandruff and antifouling compound.



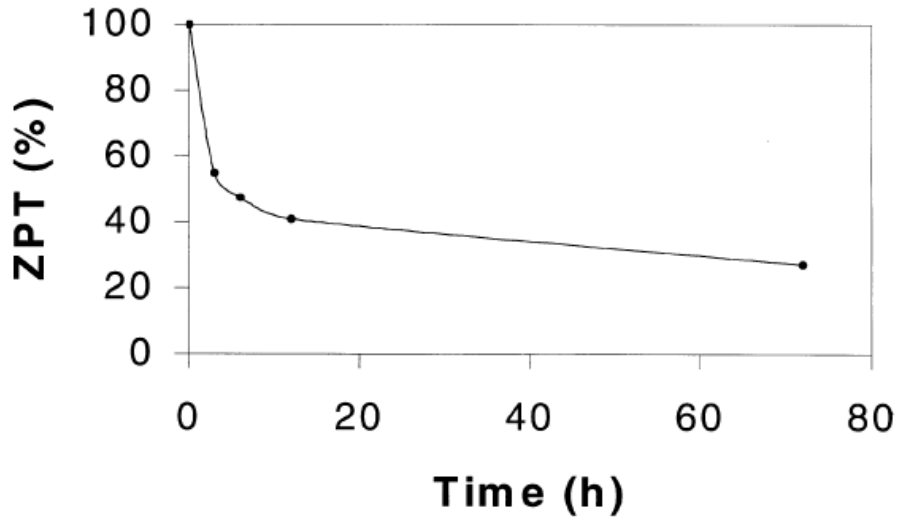
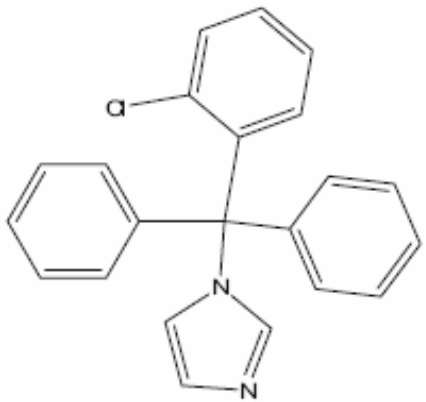


Fig. 3. Degradation of ZPT in filtered sea water under laboratory conditions.

Partitioning to glassware or particulates.

- Clotrimazole:
  - Persistent topical antifungal.
  - Widespread occurrence at low ng/L concentrations



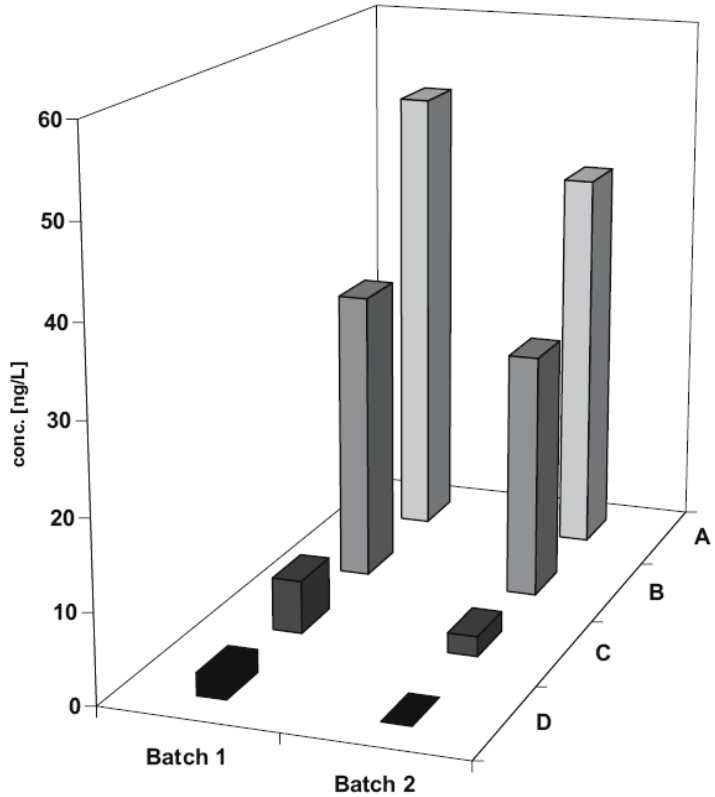


Fig. 5 Analyte loss due to a longer storage time (*A–D* concentrations spiked by the Centre for Environment, Fisheries and Aquaculture Science—see Table 4); batch 1 was analysed 2 days after spiking; batch 2 was analysed 4 days after spiking

Sample contamination

- Contamination during sample collection and analysis.
- Issue when dealing with chemicals from consumer products.
- Examples:
  - Siloxanes & musks from PCPs.
  - Perfluorinated compounds from materials.

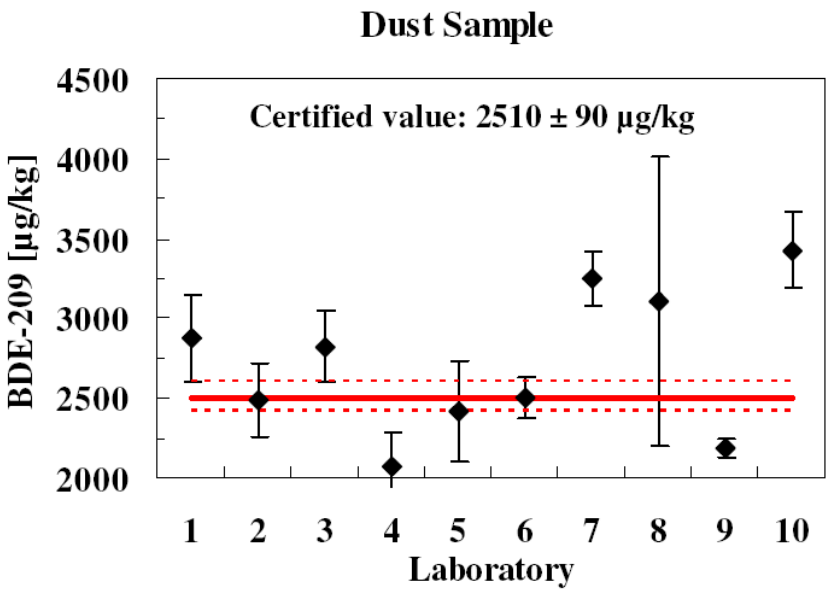
Analysis challenges

- Typically use GC or LC coupled to MS.
  - Specific & accurate
  - High equipment cost
  - High level of expertise
- Very few 'off-the-shelf' methods.
- Many analytes difficult to analyse and present in complex matrices.
- Certain chemicals offer their own unique challenge (e.g. nanoparticles)

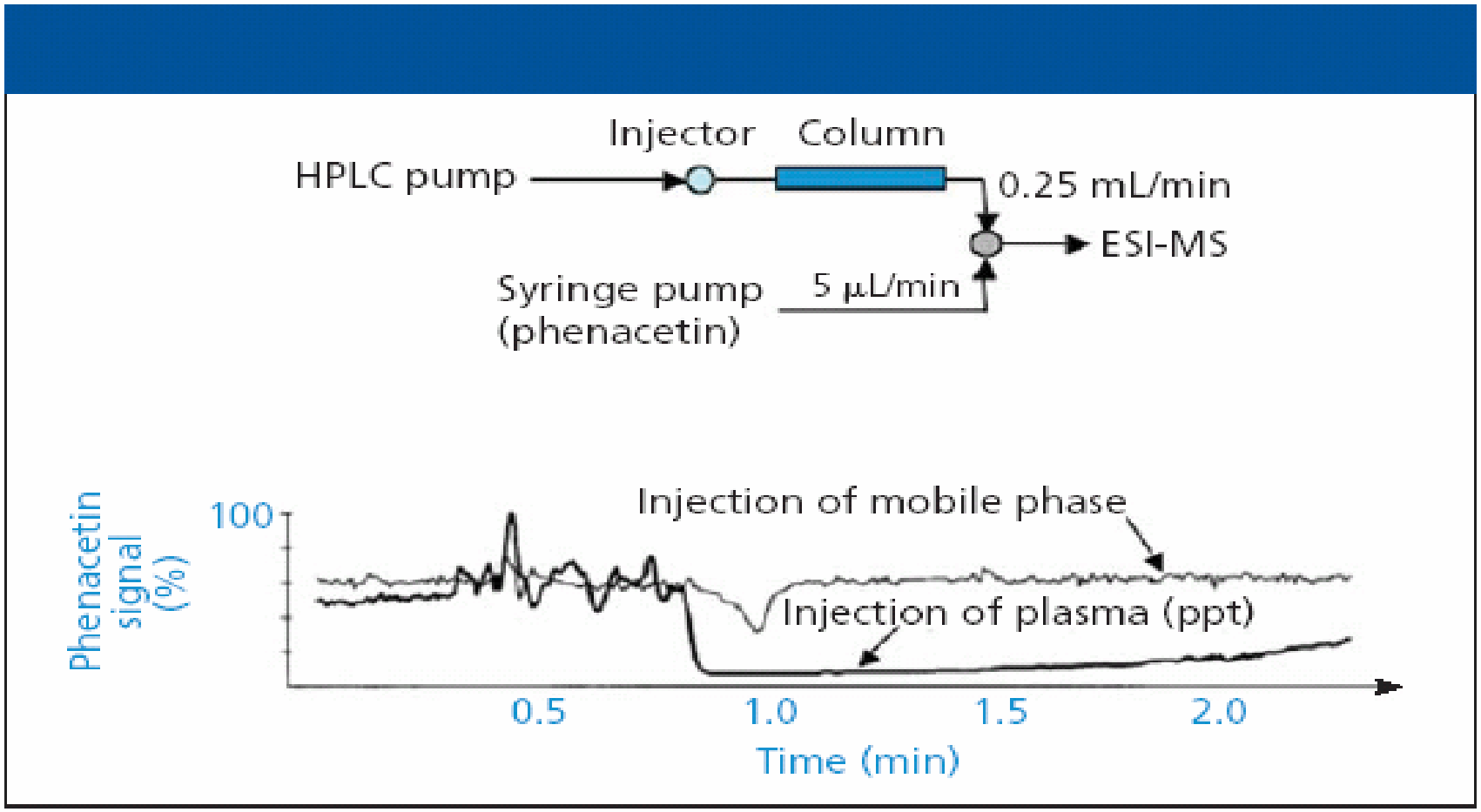
- Frequent problems:
  - Availability of appropriate standards
  - Lack of reference spectra
  - No intercomparison
  - No CRM

Validation

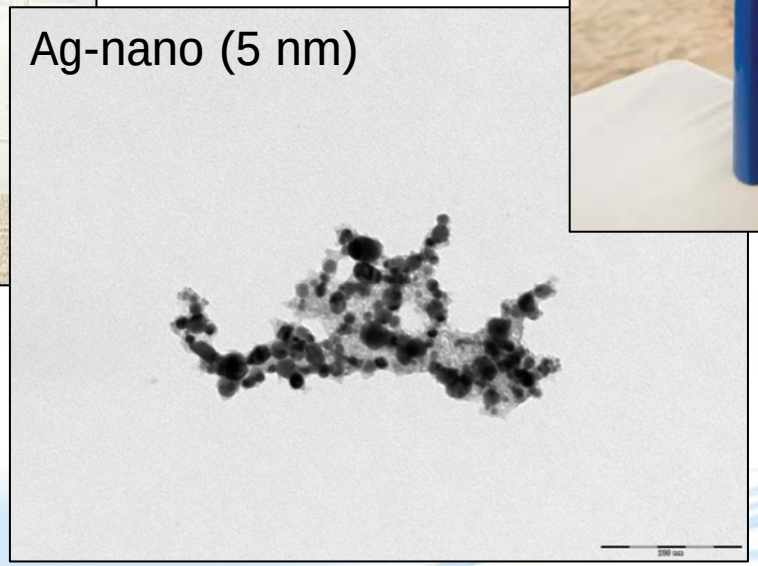
- Defined validation data required.
  - E.g. Norman guidelines
- Essential for assessing data reliability.
- Challenges:
  - Clean material for spiking



Ion supression



Nanoparticles

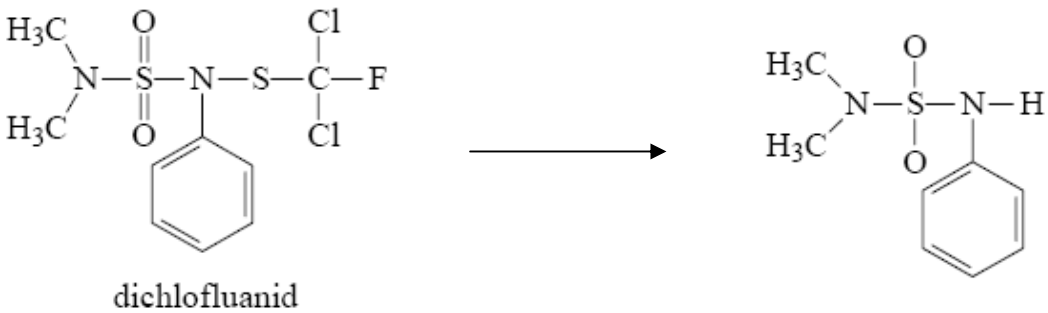


Data interpretation

- Poor data interpretation can (and has) led to the incorrect reporting of occurrence.
- Example: dichlofluanid

  Biocide used in paints

Dichlofluanid

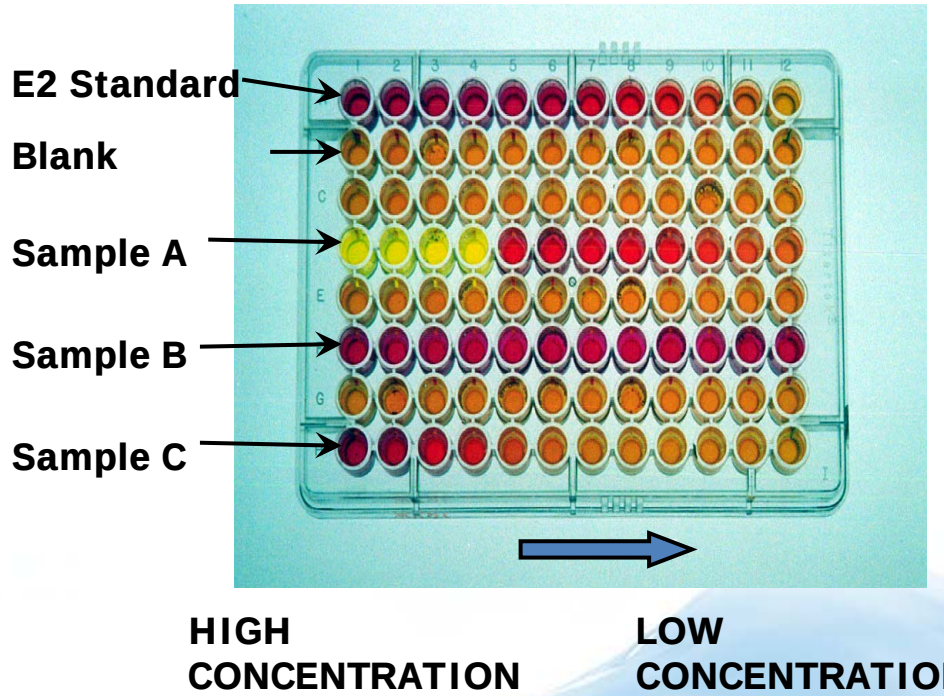


- Reported occurrence in Greek, Spanish and UK sediments (Sakkas *et al.* 2002; Martinez *et al.* 2001; Voulvoulis *et al.* 2000).
- T½= < 0.5 days

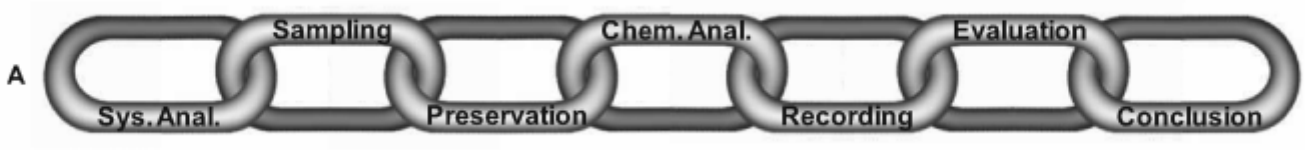
- Metabolite: DMSA
  - 'False positives' arising from the use of non-specific detectors or inappropriate confirmation ions (Hamwijk *et al.* 2005; Schouten *et al.* 2005).

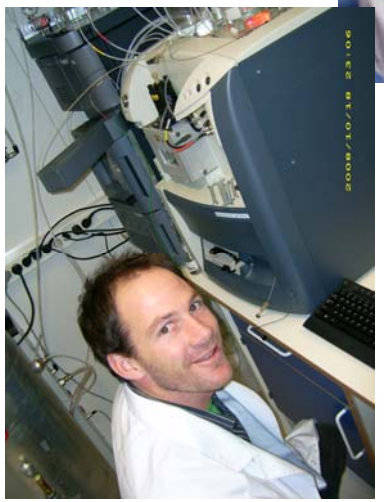
Why not bio-analytical approaches

- *In vitro* cell bioassays: sensitive, specific, and rapid bio-analytical tools that are useful in characterising responses in complex environmental mixtures.
- Advantage: Response & not compound specific
- Examples:
  - Estrogens (anti-)
  - Androgens (anti-)
  - Dioxin-like
  - glucocorticoid-like
  - Progesterone-like
  - Thyroid-hormone
  - ++++++



Recommendations



- Evaluate the system to be investigated.
- Evaluate the physico-chem properties of the chemicals selected for screening.
  - Stability, behaviour….
  - Modelling
- Optimise the sampling design so that it provides the data that you need.
- Carefully consider preservation/stability….
- Chain of sample custody.
- Analysis method
  - Use fully validated methods
  - Report method performance data
  - Report QC data
  - Robust interpretation of the data
- Consider an integrated approach using targeted analysis and effects techniques.

Thank you for your attention!