QA Approaches for Water Passive Sampling Methods

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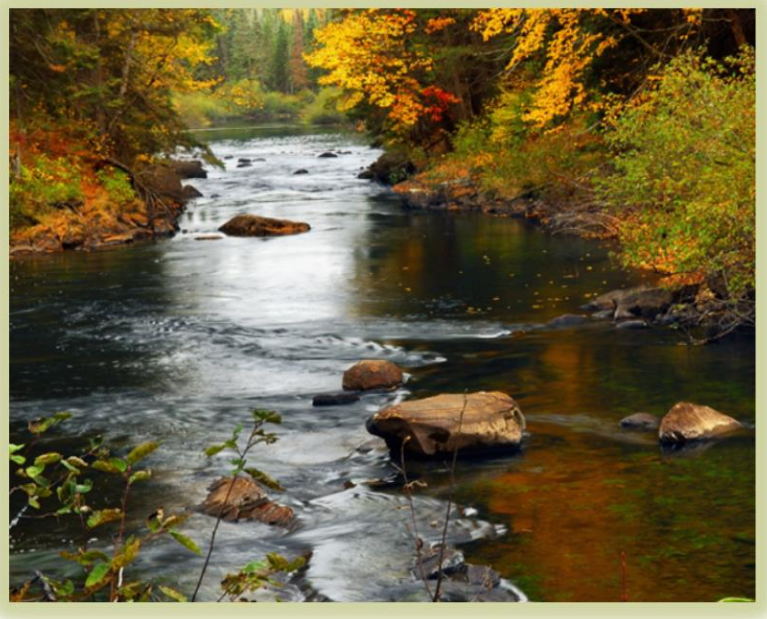
A Bureau Veritas Group Company

Outline

- Introduction to passive sampling for water analysis
- Passive sampling devices for:
  - Volatiles
  - Metals
  - Semi-volatiles
  - Polars
- QA/QC overview
- Maxxam's recommendations



Example Passive Samplers

DGT – Diffusive Gradient Thin Film

LDPE – Low Density Polyethylene

SPME – Solid Phase Microextraction

POCIS – Polar Organic Chemical Integrative Sampler

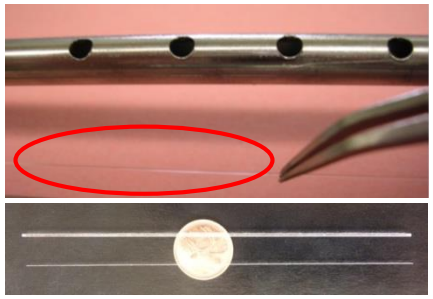
SPMD – Semi-permeable Membrane Device

PDB – Passive Diffusion Bag

Example Passive Samplers

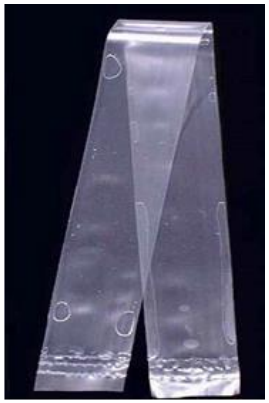
DGT – Surface Water

LDPE films - Surface Water and Groundwater



SPME - Sediment

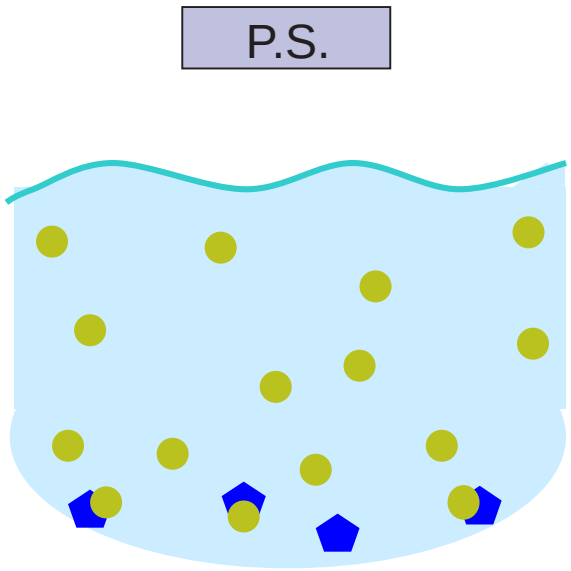
POCIS – Surface Water



SPMD – Surface Water

PDB - Groundwater

How They Work



1. Place the passive sampler into the water
2. Target compounds move into the passive sampler
3. Remove the sampler
4. Measure concentrations in the sampler
5. Estimate concentrations in the water from **analytical**, **kinetic** and **thermodynamic** terms.

$$C_W = \frac{C_{PS}}{K_{SW}}$$

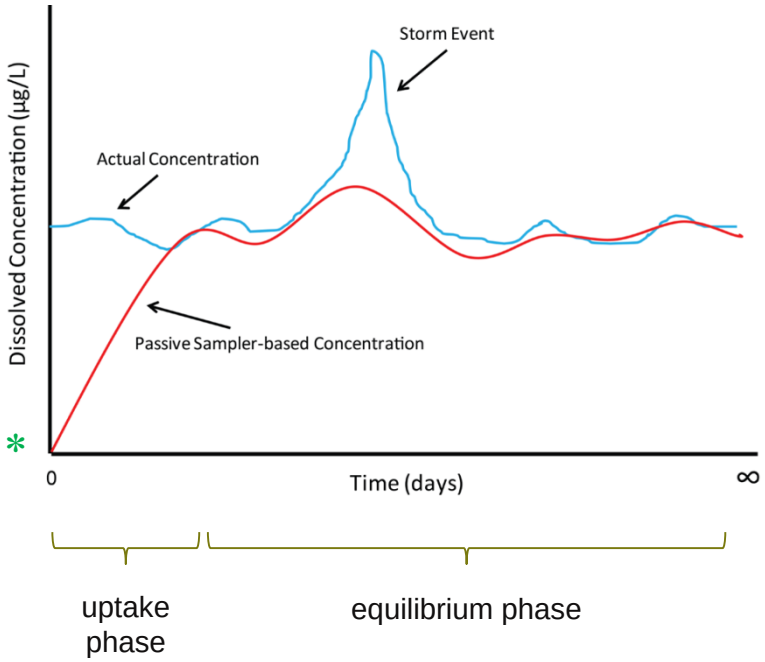
Goal: A Representative Picture of Water Quality

Passive sampling addresses the following:

- Provide average water concentrations over time
- Reports the freely dissolved concentration
- Detection limits are usually lower than with grab samples.
- Passive sampler shipment is easier, cheaper and extracted compounds are (usually) stabilized

How do we use the sampler concentration?

Red line is the passive sampler concentration



1. After equilibrium, changes in C_{PS} reflect a moving average of past water concentrations

$$C_W = \frac{C_{PS}}{K_{SW}}$$

C_W = concentration in the water
C_{PS} = concentration in the passive sampler
K_{SW} = partition coefficient

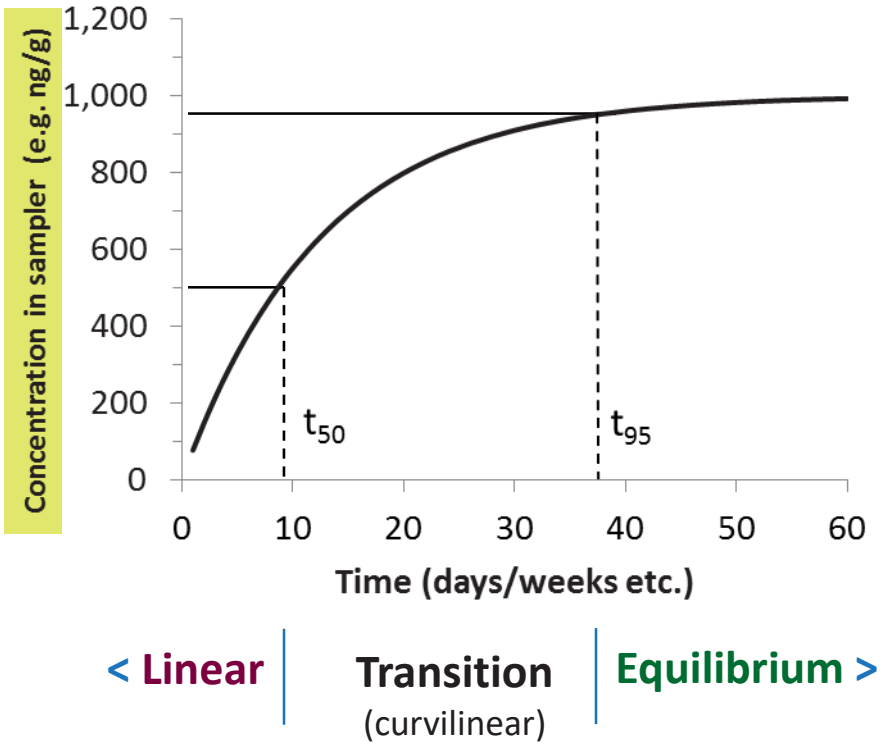
2. Before equilibrium, sampling rate must also be measured and included

If only concentration in the sampler is being reported, QA approach is the same as any other submitted solid sample.

*Reference: EPA - Office of Research and Development, and Office of Superfund Remediation &Technology Innovation, OSWER Directive 9200.1-110 FS

Typical Passive Sampler Uptake Profile

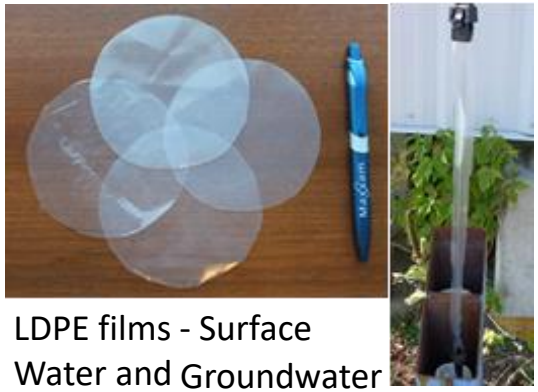
- At ~95% capacity equilibrium is reached
  - **thermodynamic**
- Initially uptake is linear
  - to ~50% capacity
  - **kinetic**
- Both kinetics and thermodynamics influence the transition region
- Different devices work in different regimes



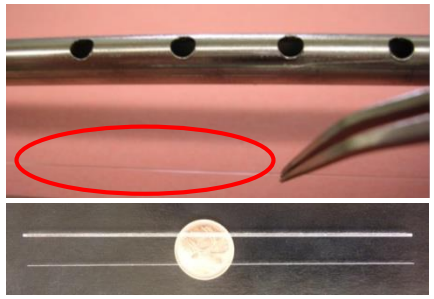
Quality assurance needs derive from the uncertainties in the calculation of C_W

Passive Sampling Regimes

DGT – Surface Water



LDPE films - Surface Water and Groundwater

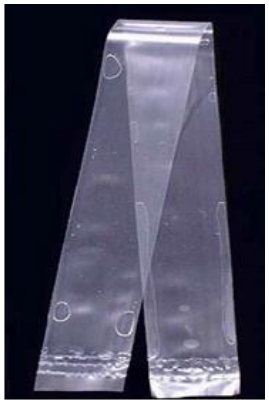


SPME - Sediment

Full Uptake Curve

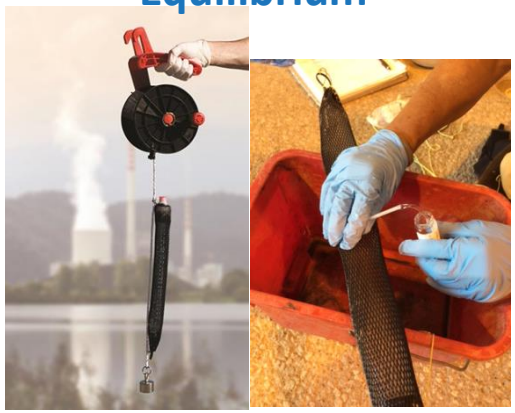
POCIS – Surface Water

Linear Uptake



SPMD – Surface Water

Equilibrium



PDB - Groundwater

All Passive Sampler Calculations

Analytical

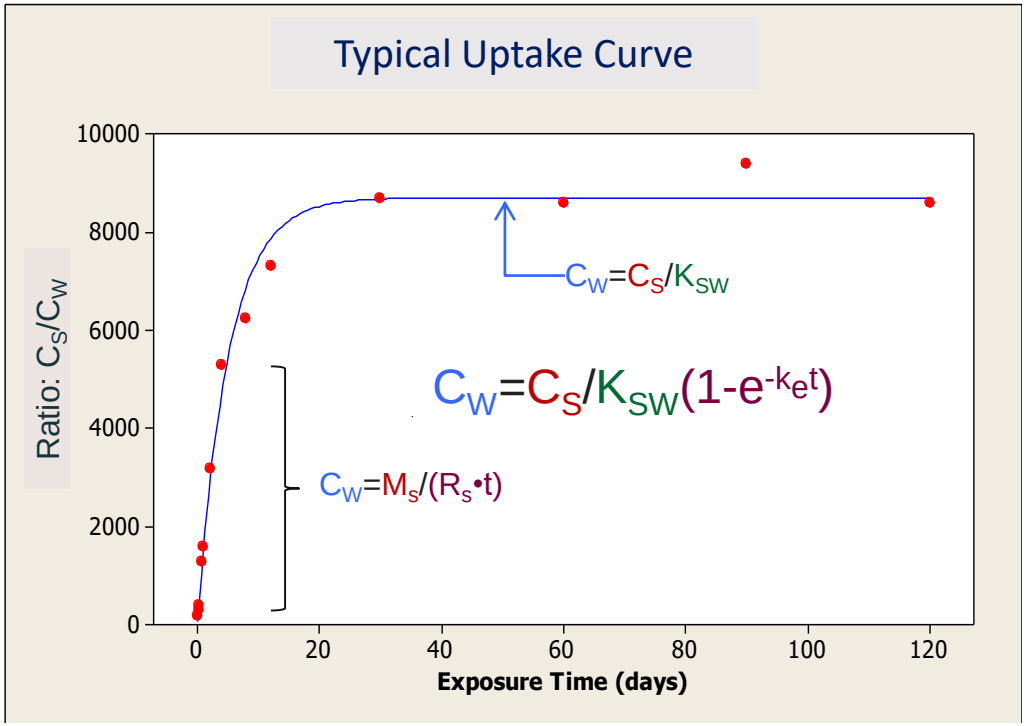
- *Cs*: conc. of chemical in sampler
- M_S: mass of chemical in sampler

Thermodynamics

- K_{SW}: partition coefficient

Kinetics

- k_e: exchange constant
- *t*: deployment time
- R_s: sampling rate (kinetics)



Uncertainties in calculated water concentrations derive from the uncertainties in these components

Method Uncertainty Overview

Two approaches are commonly used:

1: Top Down:

Statistical analysis of (typically) matrix or blank spikes from multiple samples (e.g. control chart data):

- Largely inappropriate for passive sampling data:
  - Impractical or difficult to monitor blank/matrix spikes

Method Uncertainty for Passive Samplers

2: Bottom Up:

Propagation of errors method:

- Identify the main contributors to the uncertainty for each step in the determination of the measurand.
- Overall method uncertainty is the square root of the sum of squares of all component uncertainties.

$$C_W = C_S / K_{SW} (1-e^{-k_e t})$$

$$u(C_W)^2 = u(\text{analytical components})^2 + u(\text{thermodynamic components})^2 + u(\text{kinetic components})^2$$

Jimenez, O.P. et al. 2014, Anal. Methods, 6, 5527-5536
Saari, E. et al. 2008, Chemometrics Intel. Lab. Sys., 92: 3-12

SPME and PDB – Equilibrium Sampling

PDB – decant water from sampler and analyse

- K_{SW} = 1 (zero uncertainty)
- Exchange is from water to water so concentration inside PDB = concentration outside

Equilibrium SPME – extract fiber in solvent

- Calculate C_W from established K_{SW} values

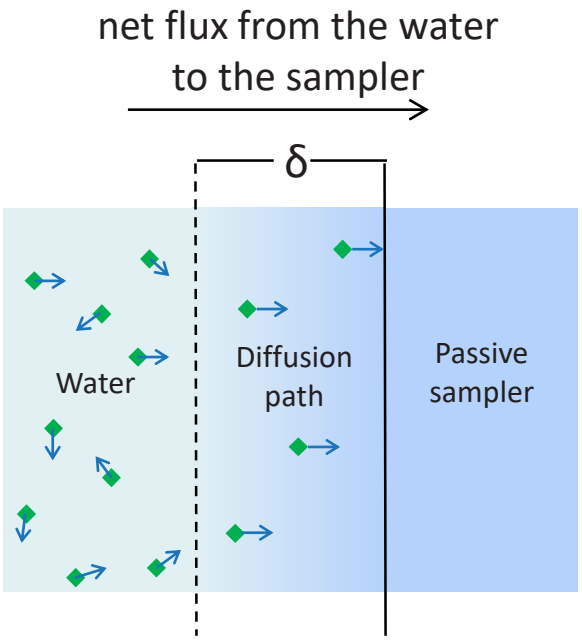
$$C_W = \frac{C_{PS}}{K_{SW}}$$

Uncertainties:

C_{PS}: standard lab uncertainty

K_{SW}: 0.2 log uncertainty

What About Other Samplers?



Need to Understand Kinetics

- Width of the diffusion path (δ) controls uptake
- Diffusion path may be either fixed or determined by the water boundary layer (WBL)

Example Passive Samplers

DGT – Metals

LDPE films - Hydrophobic Organics

SPME - Hydrophobic Organics

POCIS – Polar Organics

SPMD – Hydrophobic Organics

Linear Uptake Samplers

PDB - Volatiles

POCIS / SPMD – linear uptake

Water Concentration Calculation:

- M_S: mass of contaminant in sampler
- t: deployment time
- R_S: sampling rate
  - SPMD: Determine from Performance Reference Compounds.
  - POCIS: Determine experimentally.
  - Both: Use a literature value.

$$C_W = \frac{M_S}{R_S t}$$

Top Down Approach for determining uncertainty

Lit reference needs to include uncertainty

DGT – linear uptake

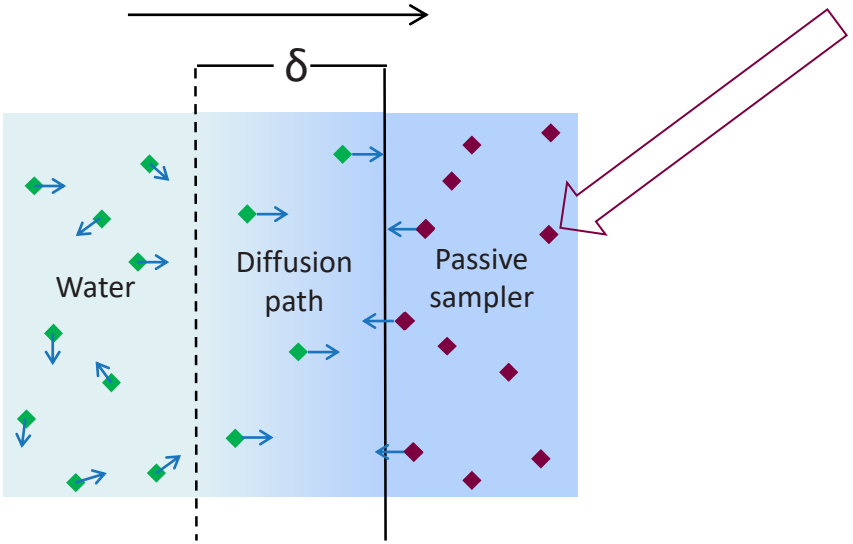
Water Concentration Calculation:

- M_S: mass of metal in sampler
- Δg: thickness of diffusion path
- A: area of sampler face
- t: deployment time
- D: diffusion coefficient of metal in diffusion path

$$C_W = \frac{M_S \Delta g}{DAt}$$

Rs

PRCs For Determining Sampling Rate

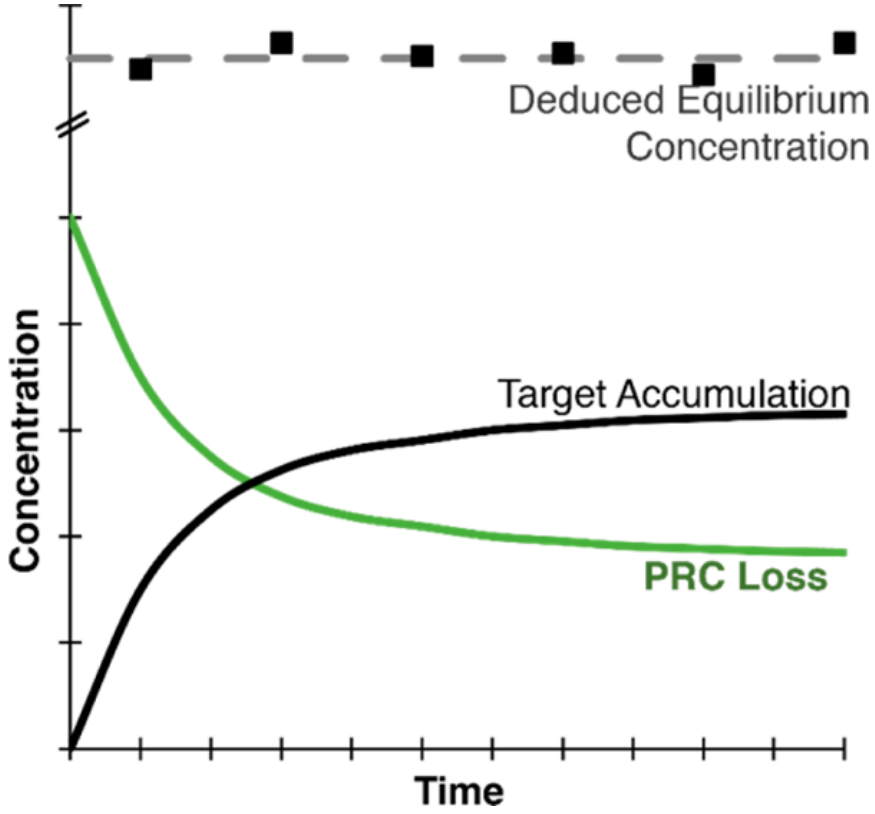


PRC: Performance Reference Compound

- Labeled analog of target chemical
- Pre-loaded into film prior to deployment
- Rate of loss is calculated and equates to rate of uptake

Determination of Uptake Kinetics from PRC Loss

- Use the shape of the PRC loss isotherm to approximate.
- As long as rate of PRC loss is symmetrical with rate of uptake the approach works.



Appel & Gschwend, 2014, ES&T, 48, 10301

Components of PRC Uptake Kinetics Calculations

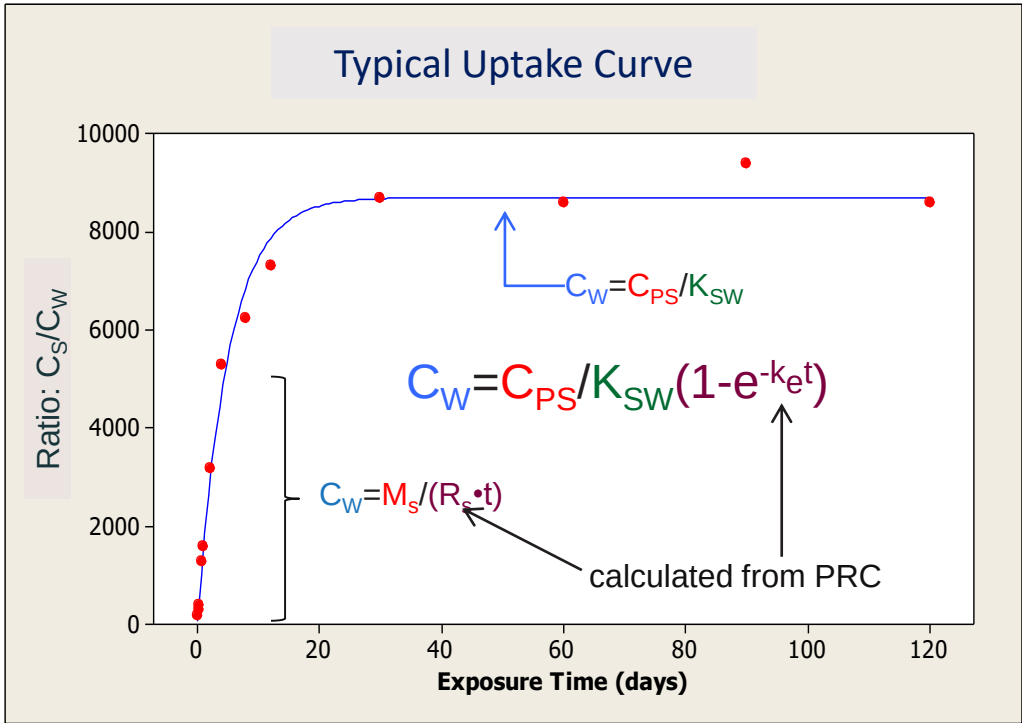
from PRC

$$k_e = ln\left(\frac{m_0}{m_t}\right)/t$$

- k_e: exchange rate coefficient
- t: deployment time
- m_0: mass PRC in sampler at t=0
- m_t: mass PRC in sampler at retrieval

$$R_S = k_e K_{SW} V_S$$

- R_s: sampling rate (L/d)
- K_{SW}: *partition coefficient*
- V_S: *volume of sorbent*



Uncertainties Measured From Field Data

C_s: Analytical uncertainty ± 10%

K_{SW}: Thermodynamic uncertainty ± 43% for all PAH

$(1-e^{(-ket)})$: Kinetic uncertainty, wide range observed

- Higher fractional uptakes (f) = lower uncertainties.
- At fractional uptakes <20%, kinetic uncertainty dominated
- Thermodynamic uncertainty dominated otherwise.

Summary:

f > 75%:	ca. 45% uncertainty
f 25% –75%:	ca. 60% uncertainty
f < 20%:	ca. 150% uncertainty

Passive sampling data includes sampling uncertainty!

Literature & Industry QA/QC Recommendations

EL-V1M4-2016 – TNI Standard

Volume 1, Module 4 – Quality Systems for Chemical Testing,

- MDL/LOQ
- Precision and Bias
- Quality Control
  - Negative and Positive controls
  - Surrogates
  - Matrix Spike / Matrix Spike Duplicate / Sample Duplicate
- Data Acceptance/Rejection Criteria
- Sample Handling

ISO Guidance on Passive Sampling in Surface Waters

Checks to address potential issues of:

- Analyte recovery: surrogate spiking — Analytical Uncertainty
- Laboratory processing: solvent blanks, spikes, calibration controls
- Purity of materials used to construct devices: fabrication control
- Well defined LDPE partition coefficients — Thermodynamics
- Variable uptake kinetics: PRCs — Kinetics
- Potential inadvertent contamination during preparation, shipping, deployment, storage, retrieval: trip blank, field control — Field QC

ISO (2011) Water quality, sampling, part 23: Guidance on passive sampling in surface waters, 5667-23:2100 (E).

LDPE Literature Recommendations

Lohmann R. et al., Env Sci Pollut Res. 2012, 19, 1885.

- Proficiency Testing
- Detection Limits
- Matrix spikes
- Solvent blanks
- Reject exposed sampler data <10x field controls
- Fabrication controls

Analytical Uncertainty

Thermodynamic Uncertainty

- Accuracy of K_{SW} / Estimating K_{SW}
- Temperature and Salinity

- Accuracy of R_S model

Kinetic Uncertainty

- Field controls
- Quantity of highly hydrophobic PRC, show insignificant dissipation in all films

Field QC

Lab, Field and Analytical Procedures for Passive Samplers

EPA/600/R-16/357, February 2017

- Standard lab QC — Analytical Uncertainty
- Surrogates / Internal Standards
- Reliability of sorbent quality, dimensions, blank levels
- PRC loading reproducibility

- Deployment and Retrieval - Field/Trip blanks
- Solvent Blanks — Field QC

- Reliability of partition coefficients — Thermodynamics

- DGT external WBL assessment — Kinetics

Maxxam's Approach

Perform Analytical and Field QA as is standard for environmental chemical analysis.

Additional QA to address uncertainties that are specific for passive sampler water concentration calculations.

Analytical Uncertainty

- Reliability of sorbent type and amount/dimensions
- Confirm diffusion path for DGT
- Sorbent blanks and spikes with each analytical batch
- Laboratory control spike duplicate into sorbent in place of sample duplicate and matrix spike
- Give spikes time to sorb into sorbent prior to extraction
- DGT and POCIS: Confirm sorbent is not over ~20% saturated
  - Establish zero-sink assumption is valid

Sampler Specific QA

For Water Concentration Calculations

- Equilibrium samplers
  - Focus on sources of thermodynamic uncertainty
    - Anything to do with K_{SW}: partition coefficient
  - Confirm equilibrium has been achieved: 80% - 95%

- Linear uptake samplers
  - Focus on sources of kinetic uncertainty
    - Anything to do with the WBL: water boundary layer

Thermodynamics

- Well-established partition coefficients
  - Or state what they are
  - 0.2 log K_{SW} = 43% uncertainty

- Partition coefficient corrections?
  - Temperature
  - Salinity

Kinetics

- Triplicate fabrication control sampler analysis to establish time = zero amount with associated uncertainty
  - Minimum PRC amount = 10x LOQ
- Get client confirmation of deployment time
- Clearly state PRC - R_s correlation equation
- State R_s for reported parameters along with concentration
- Well-established diffusion coefficients for DGT
  - Or state what was used

For fractional uptakes <20%, error associated with the kinetic term dominates overall measurement uncertainty

Field QC

Temperature

- Typically minimal impact between 4 °C and 15 °C

Salinity

- Typically minimal impact between fresh water and salt water

pH

- Generally little or no impact pH 5-8 unless target compound is acid/base dissociable

Sunlight

- Can impact photosensitive compounds (e.g. PAHs)
- Remedies: sufficient water depth, sufficient shading, UV filters in sorbent, photodegradation marker in sorbent

Field QC (cont.)

Biofouling

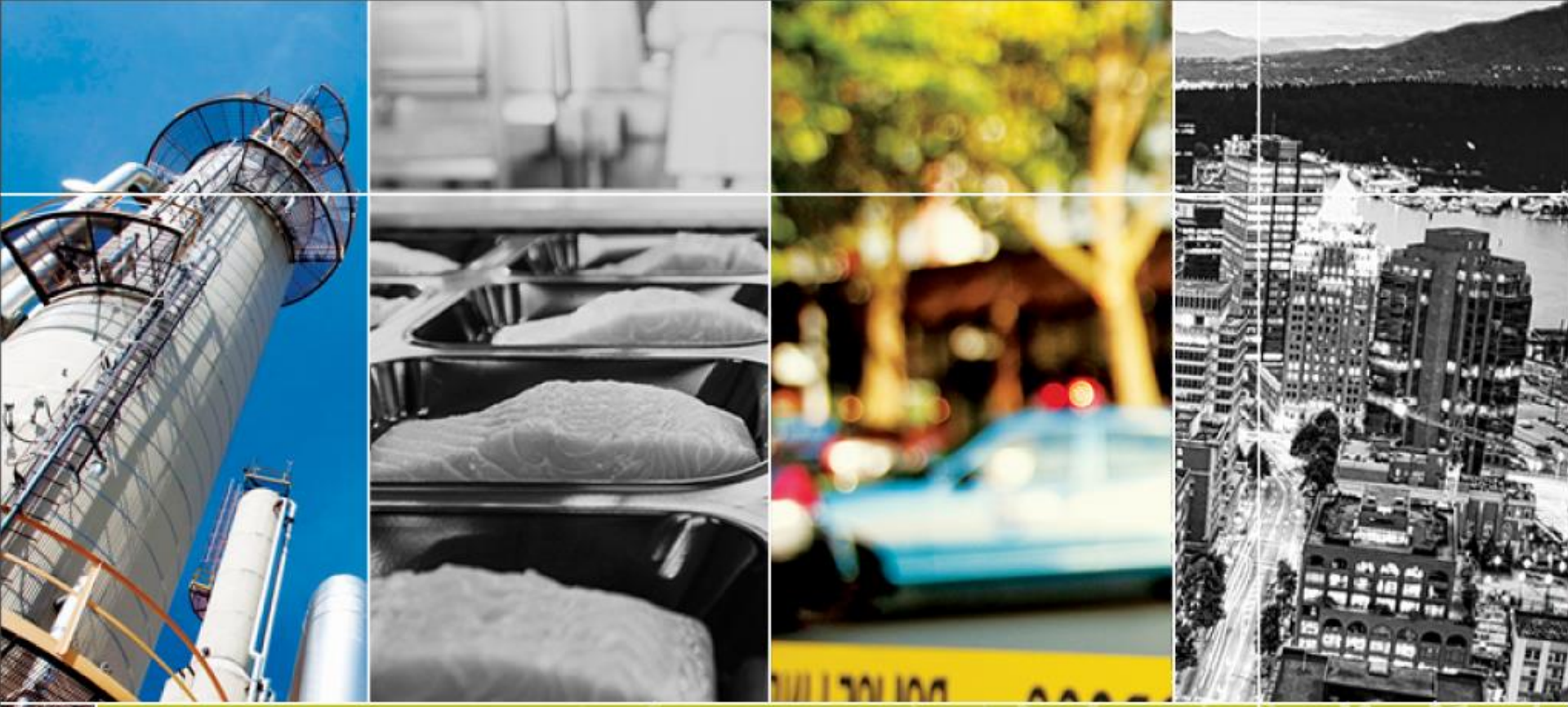
- Can cause measurable changes in sampling rate
- Typically controlled by including PRCs
  - not possible with DGT/POCIS

Turbulence

- Can cause significant changes in sampling rate where water boundary layer (WBL) controls uptake

Sediment accumulation

- Can cause significant changes in sampling rate, and alter the data interpretation
- Remedy: try to avoid if possible



Questions?

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