NORMAN Meeting on Passive Sampling of Emerging Substances

Normation of passive sampling technology

Why Do We Need a Standard?

- Provide guidance for end users
- Aid good practice
- Avoid errors that can lead to inaccurate results
- Widen the availability of passive sampling
- Protect the reputation of passive sampling

Normation Process

- Long process (2 to 3 years)
- Involves
  - national, European, international normation bodies
  - Large scale consultation
  - A number of opportunities for experts to make comments as standard is developed
  - Voting process to check that proposed standard has general support (is considered a useful development)

What should be the scope of the standard?

- Difficult to cover all aspects of passive sampling in detail that covers all available technologies
- It should not be a user manual for all of the various types of sampler
- Cover practical aspects that apply generically, and provide sufficient background to make the standard easy to understand and use

Diversity Amongst Passive Samplers

- Structure
- Classes of chemicals involved
- Methods of calibration
- Availability of PRC approach
- Modes of operation (integrative, equilibrium)

Stages in Passive Sampling

- Preparation
- Storage
- Transport
- Deployment
- Retrieval
- Transport
- Storage
- Extraction
- Analysis
- Calculation (based on calibration data and measurements)
- Report

Common Themes

- Handling precautions
- Selection of site
- Analysis by appropriate method
- QA/QC procedures
- Use of appropriate controls
- Interpretation of results

Normation of Passive Sampling

- BSI PAS 61
  - A privately sponsored standard
  - Written with financial support of EU
    - Standardised Aquatic Monitoring of Priority Pollutants by Passive Sampling (STAMPS) project (Feb 2003 – June 2006) - EVK1-CT-2002-00119
    - University of Portsmouth, UK; British Standards Institute, UK; Aquateam, Norway; Central Finland Regional Environment Centre, Finland; Alcontrol, Sweden; Chalmers University of Technology, Sweden; Instituto de Investigaciones Quimicas Y Ambiantaled de Barcelona, Spain; Universidad Complutense de Madrid, Spain; Netherlands Institute for Fisheries Research, The Netherlands; Vysoka Skola Chemicko-technologiicka v Praze, Czech Republic

ISO/CEN

- Request came from DIN to develop a CEN or an ISO standard
- BSI put forward the proposal that received sufficient support to warrant moving to a first draft for consultation.
- The first draft received a lot of constructive comments, and sufficient support to proceed to the next stage of development

ISO/CEN

- A revised draft was circulated for further comment and voting
- Water quality -- Sampling -- Part 23: Determination of priority pollutants in surface water using passive sampling
  - ISO/DIS 5667-23
  - CEN WI 00230242 - CEN/TC 230
- Parallel voting
  - began on 02 April, 2009
  - will close on 02 September, 2009

ISO/CEN

- If the revised draft receives sufficient support then it will be developed into an ISO and in parallel into a CEN standard

Scope of ISO/CEN

- The standard describes procedures for the determination of time-weighted average concentrations of the free dissolved fraction of pollutants in surface water by passive sampling, followed by analysis

Passive Sampling

- Passive sampling involves
  - – the deployment of a passive sampling device that uses a diffusion gradient to collect pollutants over a period of days to weeks
  - – extraction and analysis of the accumulated pollutants in a laboratory

Passive Sampling

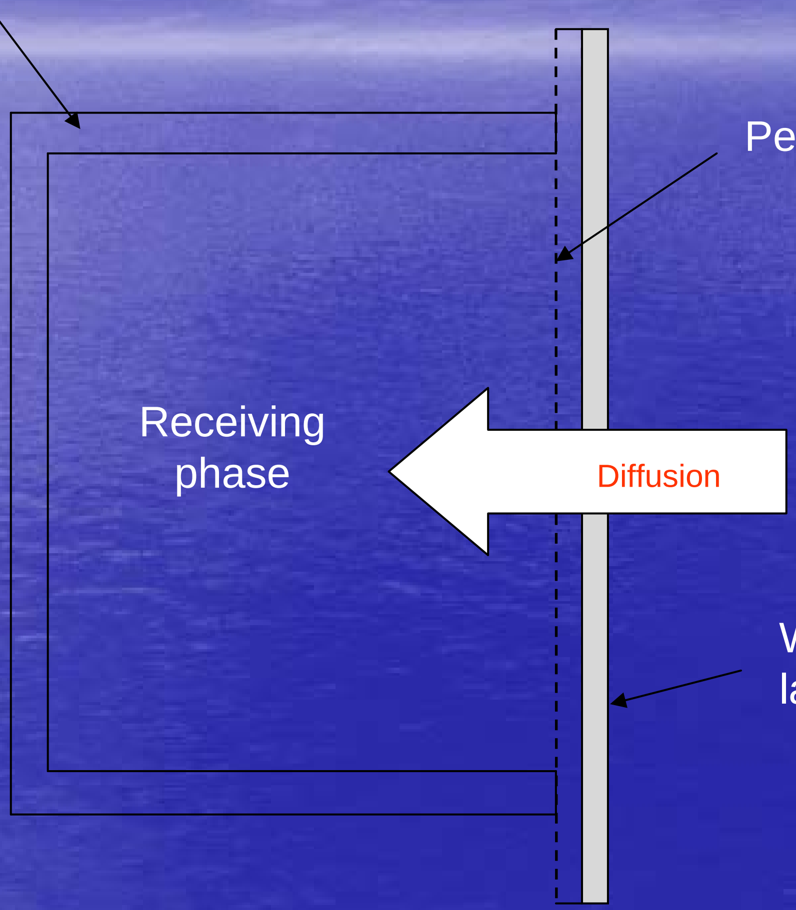
- Passive sampling devices can be used in kinetic or equilibrium modes
  - in equilibrium mode provide a measure of the concentration at the time of retrieval from the environment
  - in kinetic mode sample in an integrative way, and provides a measure of the time weighted average concentration of a pollutant in the water over the exposure period
  - operate as integrative samplers between the time of deployment and an exposure time of up to the time to half maximum accumulation in the receiving phase.

Passive Sampling

- Diffusion into the receiving phase driven by the freely dissolved fraction of pollutant, and not that bound to particulate matter and to large molecular mass organic compounds
- Provides a measure of the time-weighted average concentration of the freely dissolved fraction of pollutant to which the passive sampling device was exposed
- For some passive sampling devices for metals the concentration of analyte measured includes both freely dissolved material and that bound to large molecular mass organic compounds that can dissociate in the permeation layer

Background to a Diverse Range of Passive Samplers

- The general features of a passive sampling device are illustrated in a figure
- The structures of the types of passive sampling device for the different classes of pollutants (polar organic, non-polar organic, and inorganic (including metals)) are summarised in a table
- The commonly used procedures used to calibrate the various designs of passive sampling device are summarised in a table



Housing

Permeation membrane

Receiving
phase

Diffusion

Bulk water phase

Water boundary
layer

General Description

- The permeation membrane and water boundary layer constitute the permeation layer
- In some passive sampling device designs, the housing is replaced by a membrane that completely encloses the receiving phase
- In some passive sampling devices (for instance polyethylene strips or silicone rubber sheet) the receiving phase is not held in a housing
  - deployed naked on a holding frame
  - no permeation membrane, but the water boundary layer acts as a permeation layer

Kinetics

- A brief explanation of the kinetics of passive sampling was added to the draft CEN/ISO standard following comments from experts
- Provides the background to calibration procedures and basis of calculations

Handling passive sampling devices

- **General**
  - Keep isolated from potential sources of contamination at all times except when being exposed at the sampling site.
  - Ensure that the passive sampling devices are stored and transported in *gas-tight containers,* of inert materials relevant to the pollutants of interest.
  - Avoid physical contact with the receiving phase or membrane (use powder free vinyl or latex gloves).
  - For some passive sampling devices it may be necessary to minimize exposure to airborne contaminants.
  - Passive sampling devices and resultant extracts should not be stored in proximity to other chemicals, particularly volatile chemicals.
- **Organics passive sampling devices**
  - Minimize contact of organics passive sampling devices with plastic materials.
  - Wash, using an organic solvent, all equipment that comes into contact with passive sampling devices during preparation prior to deployment, storage, transport, and preparation for analysis.
- **Metals passive sampling devices**
  - Acid wash all equipment that comes in contact with the extract obtained from the passive sampling device after deployment, other than the passive sampling devices.
  - Use suprapure grade acid for addition to samples or for digestion.

Deployment Time

- Prior to deployment of the passive sampling device, estimate the exposure time for the class of passive sampling device
- The maximum possible deployment time will depend on the
  - expected concentration of pollutant
  - uptake rate and capacity of the receiving phase for the analytes of interest

Preparation and Assembly

- **Passive sampling device preparation**
  - Where appropriate, prepare PRC solutions for each class of passive sampling device.
  - Spike the receiving phase prior to assembly.
- **Passive sampling device assembly**
  - Passive sampling devices that need to be assembled by the user should be assembled in an environmentally controlled room
  - Label each passive sampling device in accordance with EN ISO 5667-3:2003, Clause 5.
- **Passive sampling device storage**
  - Keep isolated from potential sources of contamination during storage.
  - Store prepared devices in vapour-tight containers at controlled temperatures.
  - Avoid storing passive sampling devices in proximity to chemicals.

Quality Assurance

- Prepare multiple passive sampling devices (a minimum of 2 per sampling site) for each class (polar organics, non-polar organics and inorganics including metals) of passive sampling device to be used
- Use control samplers - number and type of controls depends on the required level of confidence, but a minimum of two per sampling site should be used
- Compare results of analysis of replicate passive sampling devices and with controls in order to calculate uncertainty of the sampling

Quality Assurance

- For monitoring the time-weighted average concentration of pollutant near the limit of detection, it is possible to combine extracts from a number of passive sampling devices. Under these circumstances it is necessary to increase the number of control passive sampling devices *pro rata.*
- The average mass of the PRC spike and the associated precision are estimated using all of the field control passive sampling devices from each batch of passive sampling devices used within a field campaign.

BSI PAS 61 - Sampling device control requirements

Control type	**Number per sampling device set**
Fabrication control	At least 3 per sampling device class
Field control	At least 1 per sampling site (2 per sampling site are recommended for quality control purposes)
Shipping control (optional)	At least 1 per sampling device class (2 per sampling site are recommended for quality control purposes)
Reagent control	At last 1 per sampling device set of analysed sampling devices
Recovery spike	At least 3 per sampling device set of analysed sampling devices

ISO/CEN - Passive sampling device control requirements

Control type	Number required	Treatment of controls
Field control	At least 2 per sampling site	Select field controls from passive sampling devices manufactured and/or delivered together. Handle in the same way as the set of passive sampling devices up to/from the moment when the sampling starts/ends. Process and analyse field controls concurrently with and identically to the passive sampling device set.
Recovery spike	At least 3 per batch of passive samplers or for each field campaign if a single batch of samplers is used	Prior to processing of a passive sampling device, fortify recovery spike passive sampling devices with a target compound mixture. Process and analyse recovery spike controls concurrently with and identically to passive sampling devices of the same class in the passive sampling device set.

Selection of Sampling sites

- Avoid
  - sources of vapour-phase contaminants, including engine fumes, oils, tars, gasoline, diesel fuel, paints, solvents, cigarette smoke and asphalt pavement, if organics passive sampling devices are to be used
  - sources of metallic contamination, if metals passive sampling devices are to be used;
  - oily films or biofilms on the surface of the water;
  - Drying out - deploy at a depth below which water levels do not drop

Passive sampling device deployment and retrieval

- Transport
- Materials and apparatus
- Deployment procedure
- Retrieval

Preparation for Analysis and Analysis

- Extraction using methods appropriate for type of sampler, and avoiding contamination
- No analytical methods specified since these depend on specific requirements, and a lot odf standard methods are available

Calculations

- A very general formulation of the calculation
  - Assumes unidirectional, linear, integrative uptake of the analyte during the whole deployment period
  - In the linear phase of uptake the apparent volume of water cleared of pollutant per unit time is independent of the concentration of the pollutant in the water.

Calculations

- The value of the overall mass transfer coefficient for any analyte is
  - in general a device- and site-specific calibration parameter
  - obtained in a variety of ways, depending on the specific passive sampling device and deployment conditions
  - a substance specific value depending on the physicochemical properties of the analytes and environmental variables such as water temperature and hydrodynamic conditions.
- Overall mass transfer coefficient obtained in a number of ways
  - empirical calibration data
  - theoretical considerations where the parameters are provided by the manufacturer
- Calibration data typically cover a range of temperatures and turbulence conditions
- Some devices can use performance reference compounds (PRCs) to correct the overall mass transfer coefficient for fluctuations in environmental conditions

Conclusions

- Development of a standard has been supported by international experts
- If the project reaches fruition, then the standard should support the application of passive sampling, and help in the capturing of fit for purpose information