Active and Passive Sampling for Pollutants of Emerging Concern

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Emerging contaminants in waters and soils, practical considerations: Sampling, analysis and consequences
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Pollutants of emerging concern

• "Emerging contaminants" can be broadly defined as any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and(or) human health effects.

• In some cases, release of emerging chemical or microbial contaminants to the environment has likely occurred for a long time, but may not have been recognized until new detection methods were developed.

• In other cases, synthesis of new chemicals or changes in use and disposal of existing chemicals can create new sources of emerging contaminants.
Chemicals of emerging concern

Chemicals of emerging concern arise from a plethora of product types and cover a wide range of chemical classes.

- Naturally produced compounds such as toxins produced by fungi, bacteria and plants
- Bio-terrorism/sabotage agents
- Human personal care products such as essential oils, herbal medicines, anti-bacterials and fragrances
- Emerging persistent organic pollutants such as flame retardants and dioxin-like compounds
- Veterinary medicines such as antibiotics and anti-parasitic agents
- Hormones such as synthetic and natural estrogens and androgens
- Nanomaterials
- Human medicines
- Metabolites and transformation products of man-made chemicals that are produced from biological, chemical and physical breakdown reactions – e.g. waste water treatment plants
- Example substances is available on the EU NORMAN network website (www.norman-etwork.net)
Take one three times a day. Or you can just drink the local water...

Doctor of Medicine

Is it boy or a girl?

Both, actually, thanks to all the chemicals in the water these days.

Birch
Overview

• Introduction to Water Framework Directive/water monitoring
• Use of passive samplers for monitoring pollutants
• Types of passive sampling devices (briefly)
• Passive samplers for monitoring emerging pollutants
  - Advantages and disadvantages (issues in use)
• Application of passive samplers for emerging pollutants
• Conclusions
Three modes of monitoring are specified:

- **Surveillance** - to establish baseline quality status and assess long term changes
- **Operational** - to provide extra data on water bodies at risk or failing to meet the environmental objectives of the WFD
- **Investigative** - to determine the causes of such failure where they are unknown

Each mode represents a different challenge to monitoring – potential to use different monitoring tools?
Environmental Quality Standards (EQS)

• Issues with analytical methods for the new proposed Priority Substances of the European Water Framework Directive
• Methods limits of quantification (LoQs) are compared with one third of the EQS, mandatory for WFD compliance monitoring
• Example EQS in the recent revision (2013) of WFD:
  – Cypermethrin 80 pg/L (8 pg/L for coastal salt waters)
  – Dichlorvos 60 pg/L in coastal waters
  – Dicofol 32 pg/L in coastal waters
  – 17-alpha-ethinylestradiol 35 pg/L (7 pg/L in coastal waters)
  – 17-beta-estradiol 80 pg/L in coastal waters
  – Heptachlor/epoxide 0.2 pg/L (10 fg/L in coastal waters)
  – BDEs 49 fg/L (2.4 fg/L in coastal waters)

red = polar substances
Current monitoring practice

Currently the most widely used method used for measuring concentrations of chemical pollutants for all three modes of WFD monitoring is spot (bottle/grab) sampling followed by laboratory chemical analysis.

This has a number of disadvantages:

• Cost (manpower/transport).
• Provides only a ‘snapshot’ of the pollution situation at the instant of sampling.
• May not be representative of conditions where concentrations of pollutants fluctuate or are not homogeneous.
• Issues of detection limits (EQS) when low volume samples (1-5 L) are only collected.
Chemically what do we measure in the spot sample – water is complex!? 

• Total concentration of a pollutant?
• Concentration in filtrate (freely dissolved and bound to dissolved organic matter)?
• Material bound to suspended matter
• Changes to speciation of metals
• Issues of transport, storage, pre-treatments
• Often little attention given to sampling process – only the subsequent laboratory analytical step
• Often poor guidance from regulators
Diuron concentration (µg/ L) continuously monitored in the Meuse River - RIZA’s Eijsden station (2001-2005)
Variation in pollution over time

Concentrations
In individual
Spot samples

TWA = time-weighted average
Spatial variation

Flow of river

Discharge point

Secondary river flow
Passive samplers

• Provide time-weighted-average (TWA) and equilibrium concentrations over the deployment time, rather than a snap shot at one moment

• Typically measure the freely dissolved (some times called biologically available fraction)

• Are non-mechanical; are easy to deploy and require no maintenance

• Can be deployed in a range of environments; at sites that have limited security; are remote with little/no infrastructure

• Are not dependent on a power or other energy supply

• Used for short (days) or long term (months) monitoring

• Can effectively concentrate pollutants compared to spot sampling
Principles of passive sampling: uptake process from water

Diffusional path $\delta$

Bulk water | Water boundary layer (WBL) | Membrane | Sorbent (Receiving phase)

In some designs of sampler the membrane is omitted and only a received phased is used.
Example of transport barriers in a sampler used for polar compounds
Some passive sampling devices

**Monitoring non-polar organic contaminants - partition/absorption**
- Semi-Permeable Membrane Devices (SPMD)
- Low-density polyethylene membrane and silicone rubber strips/sheets
- Membrane Enclosed Sorptive Sampler (MESCO)
- SPME fibres – using various phases (like air monitoring)
- Chemcatcher® (Non-polar version)
- Naked chromatographic disks (e.g. C$_{18}$, C$_8$)

**Monitoring polar organic contaminants - adsorption**
- Polar Organic Compound Integrative Sampler (POCIS)
- Chemcatcher® (Polar version)
- Naked chromatographic disks (e.g. SDB- and Oasis-based phases)
- Ion-exchange resins (anionic and cationic)

**Monitoring metals – chelating any other mechanisms**
- Diffusive Gradient in Thin films Device (DGT)
- Chemcatcher® (Metals/organo-metals version)
- Ecoscope (ALcontrol AB)
- Various permeation devices
Types of passive sampling devices

- DGT
- Chemcatcher
- MESCO
- LDPE sheet
- POCIS
- SPMD
Uptake of a chemical by a passive sampler

\[ M_S(t) = M_0 + C_w R_S t \]

**RS** = substance specific sampling rate [L d\(^{-1}\)]

Sampling rate \(R_S\) [L d\(^{-1}\)] - equivalent volume of water cleared of the target analyte per unit of time
Calibration of a passive sampler in a typical flow-through system

- **Peristaltic pump**
  - 100 µL/min
- **Chemicals in MeOH**
- **Analytes in MeOH**
- **Exposure tank**
- **Overhead stirrer**
- **Waste water**
- **Water reservoir**
- **Samplers**
- **Water**
- **Peristaltic pump**
  - 30 ml/min

The diagram illustrates the setup with labeled components and flow directions.
A flow-through calibration system

- No standard methods unlike with air samplers:
  - Static
  - Semi-static
  - Flow-through designs all been used.
- Aware of lag-phase in uptake (monitoring short-term events).
- Type of water used for calibration purposes (e.g. DOC level, saline).
- Transfer of lab-based calibrations to field conditions.
In-field calibration

Alternative to calibration in laboratory

Locations where the concentration of a substance is relatively stable

Examples include deployment in effluent of waste water treatment plants

Useful where chemical standards for calibration are expensive or not available commercially.

Example metabolites of specific pharmaceutical

Flow and water turbulence as site also need to be considered in the calibration procedures
Types of adsorbent passive sampler

- Samplers differed in surface area, type and mass of adsorbent material applied.
- The same type of membrane and similar sampler geometry - similar mass transfer is expected.
- Chemcatcher uses adsorbent/exchange phase bound into a supporting matrix.
- Two sided version of Chemcatcher has been trialed.

**Chemcatcher**

- Sorbent: Empore SDB-XC; ion-exchange; OASIS - HLB
- Membrane: PES
- Surface area: 17.5 cm² (one sided)
- Geometry: flat disk

**POCIS**

- Sorbent: OASIS - HLB
- Membrane: PES
- Surface area: 46 cm² (two sided)
- Geometry: flat disk

<table>
<thead>
<tr>
<th></th>
<th>Chemcatcher</th>
<th>POCIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbent</td>
<td>Empore SDB-XC</td>
<td>OASIS - HLB</td>
</tr>
<tr>
<td>Membrane</td>
<td>PES</td>
<td>PES</td>
</tr>
<tr>
<td>Surface area</td>
<td>17.5 cm² (one sided)</td>
<td>46 cm² (two sided)</td>
</tr>
<tr>
<td>Geometry</td>
<td>flat disk</td>
<td>flat disk</td>
</tr>
</tbody>
</table>
Multiple binding sites
Example: Oasis HLB

Solute – sorbent interactions:
• van der Waals
• Coulomb
• π–π interaction
• hydrogen bonding

HLB = Hydrophilic-lipophilic-balanced reversed-phase sorbent
Effect of flow velocity on uptake

Effect of pH and salinity on POCIS performance
Sampler calibration in a flow-through system:

- Peristaltic pump for water
- Peristaltic pump for methanolic solution
- Stirrers
- Exposure tank
- Artificial seawater tank

- pH7; 0 PSU
- pH7; 15 PSU
- pH5; 0 PSU
- pH7; 35 PSU
- pH10; 0 PSU

- Waste

36 pesticides; 17 pharmaceuticals
Effect of pH on analyte uptake

Example: Dissociating acidic compounds

\[ \text{HA} \rightarrow \text{H}^+ + A^- \]

\[ pK_a = 4.91 \quad 4.15 \quad - \quad 4.45 \quad 4.15 \]

\[ pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) \]
Biofouling
Recent applications of passive sampling

• Water Framework Directive Investigative Monitoring

• Identify chemical pressure on watercourses with poor ecology

• GCMS and HRAM LCMS Screening with libraries for targeted identification of pharmaceuticals & personal care products (PPCPs) in effluents & rivers

• Metaldehyde – use of Chemcatcher for targeted monitoring
PPCPs—Why look for them?

- Widespread detection in environmental samples
- Many have significant EDC effects such as the Hormones
- Anti-biotic resistance
- “Pseudo-persistent”
- European Union’s Water Framework Directive – Watch list of pharmaceuticals added
<table>
<thead>
<tr>
<th>Tgt Name</th>
<th>Tgt Score</th>
<th>RT Diff</th>
<th>Mass Error (ppm)</th>
<th>Tgt Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cpd 1: Sotalol</td>
<td>98.19</td>
<td>-0.015</td>
<td>-0.78</td>
<td>C12 H20 N2 O3 S</td>
</tr>
<tr>
<td>Cpd 2: Atenolol</td>
<td>98.16</td>
<td>0.031</td>
<td>2.33</td>
<td>C14 H22 N2 O3</td>
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<td>Cpd 3: Ranitidine</td>
<td>92.48</td>
<td>0.068</td>
<td>0.32</td>
<td>C13 H22 N4 O3 S</td>
</tr>
<tr>
<td>Cpd 4: Trimethoprim</td>
<td>99.59</td>
<td>-0.003</td>
<td>0.17</td>
<td>C14 H18 N4 O3</td>
</tr>
<tr>
<td>Cpd 5: Amisulpride</td>
<td>97.4</td>
<td>0.019</td>
<td>1.08</td>
<td>C17 H27 N3 O4 S</td>
</tr>
<tr>
<td>Cpd 6: Lidocaine</td>
<td>99.71</td>
<td>0.188</td>
<td>-0.58</td>
<td>C14 H22 N2 O</td>
</tr>
<tr>
<td>Cpd 7: Metoclopramide</td>
<td>75.91</td>
<td>0.046</td>
<td>0.51</td>
<td>C14 H22 Cl N3 O2</td>
</tr>
<tr>
<td>Cpd 9: Tramadol</td>
<td>99.87</td>
<td>-0.494</td>
<td>0.36</td>
<td>C16 H25 N O2</td>
</tr>
<tr>
<td>Cpd 10: Lamotrigine</td>
<td>98.86</td>
<td>-0.03</td>
<td>-0.21</td>
<td>C9 H7 Cl2 N5</td>
</tr>
<tr>
<td>Cpd 11: Mirtazapine</td>
<td>91.14</td>
<td>0.207</td>
<td>0.96</td>
<td>C17 H19 N3</td>
</tr>
<tr>
<td>Cpd 12: Celiprolol</td>
<td>98.63</td>
<td>-0.081</td>
<td>-0.99</td>
<td>C20 H33 N3 O4</td>
</tr>
<tr>
<td>Cpd 13: Quinine</td>
<td>98.76</td>
<td>0.069</td>
<td>0.39</td>
<td>C20 H24 N2 O2</td>
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<tr>
<td>Cpd 14: Labetalol</td>
<td>78.41</td>
<td>-0.17</td>
<td>-1.6</td>
<td>C19 H24 N2 O3</td>
</tr>
<tr>
<td>Cpd 15: Venlafaxine</td>
<td>98.75</td>
<td>0.035</td>
<td>0.08</td>
<td>C17 H27 N O2</td>
</tr>
<tr>
<td>Cpd 16: Bisoprolol</td>
<td>95.33</td>
<td>0.056</td>
<td>-2.64</td>
<td>C18 H31 N O4</td>
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<tr>
<td>Cpd 17: Propranolol</td>
<td>89.72</td>
<td>0.046</td>
<td>0.19</td>
<td>C16 H21 N O2</td>
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<tr>
<td>Cpd 18: Citalopram</td>
<td>99.89</td>
<td>-0.01</td>
<td>0.1</td>
<td>C20 H21 F N2 O</td>
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<tr>
<td>Cpd 19: Flecaínide</td>
<td>99.39</td>
<td>-0.013</td>
<td>-0.42</td>
<td>C17 H20 F6 N2 O3</td>
</tr>
<tr>
<td>Cpd 20: Mebeverine</td>
<td>97.31</td>
<td>0.01</td>
<td>0.25</td>
<td>C25 H35 N O5</td>
</tr>
</tbody>
</table>

**PPCPs found in final effluent (i)**

- **Beta blocker**
- **Anti-depressant**
### PPCPs found in final effluent (ii)

<table>
<thead>
<tr>
<th>Tgt Name</th>
<th>Tgt Score</th>
<th>RT Diff</th>
<th>Mass Error (ppm)</th>
<th>Tgt Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cpd 21: Diltiazem-Cis</td>
<td>98.99</td>
<td>0.024</td>
<td>-0.19</td>
<td>C22 H26 N2 O4 S</td>
</tr>
<tr>
<td>Cpd 22: Carbamazepine</td>
<td>99.75</td>
<td>0.003</td>
<td>0.12</td>
<td>C15 H12 N2 O</td>
</tr>
<tr>
<td>Cpd 23: Fexofenadine</td>
<td>98.91</td>
<td>-0.039</td>
<td>0.61</td>
<td>C32 H39 N O4</td>
</tr>
<tr>
<td>Cpd 24: Amitriptyline</td>
<td>97.31</td>
<td>0.104</td>
<td>0.65</td>
<td>C20 H23 N</td>
</tr>
<tr>
<td>Cpd 25: Erythromycin</td>
<td>99.73</td>
<td>0.103</td>
<td>-0.1</td>
<td>C37 H67 N O13</td>
</tr>
<tr>
<td>Cpd 26: Losartan</td>
<td>88.33</td>
<td>-0.037</td>
<td>0.79</td>
<td>C22 H23 Cl N6 O</td>
</tr>
<tr>
<td>Cpd 27: Cetirizine</td>
<td>97.46</td>
<td>0.011</td>
<td>0.15</td>
<td>C21 H25 Cl N2 O3</td>
</tr>
<tr>
<td>Cpd 28: Naproxen</td>
<td>99.42</td>
<td>-0.091</td>
<td>-0.2</td>
<td>C14 H14 O3</td>
</tr>
<tr>
<td>Cpd 29: Bezafibrate</td>
<td>95.39</td>
<td>-0.113</td>
<td>0.66</td>
<td>C19 H20 Cl N O4</td>
</tr>
<tr>
<td>Cpd 30: Clarithromycin</td>
<td>97.82</td>
<td>0.077</td>
<td>-0.45</td>
<td>C38 H69 N O13</td>
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<tr>
<td>Cpd 32: Valsartan</td>
<td>95.74</td>
<td>-0.064</td>
<td>0.05</td>
<td>C24 H29 N5 O3</td>
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<tr>
<td>Cpd 31: Dipyridamole</td>
<td>99.15</td>
<td>0.432</td>
<td>-0.33</td>
<td>C24 H40 N8 O4</td>
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<tr>
<td>Cpd 33: Irbesartan</td>
<td>98.93</td>
<td>0.019</td>
<td>-0.61</td>
<td>C25 H28 N6 O</td>
</tr>
<tr>
<td>Cpd 34: Ketoconazole</td>
<td>78.76</td>
<td>0.419</td>
<td>0.29</td>
<td>C26 H28 Cl2 N4 O4</td>
</tr>
<tr>
<td>Cpd 35: Atorvastatin</td>
<td>85</td>
<td>0.013</td>
<td>-1.63</td>
<td>C33 H35 F N2 O5</td>
</tr>
<tr>
<td>Cpd 36: Telmisartan</td>
<td>97.87</td>
<td>0.09</td>
<td>-0.56</td>
<td>C33 H30 N4 O2</td>
</tr>
<tr>
<td>Cpd 37: Clopidogrel</td>
<td>96.52</td>
<td>0.089</td>
<td>0.4</td>
<td>C16 H16 Cl N O2 S</td>
</tr>
<tr>
<td>Cpd 38: Dioctyl sulfosuccinate</td>
<td>98.88</td>
<td>0.023</td>
<td>0.24</td>
<td>C20 H38 O7 S</td>
</tr>
<tr>
<td>Cpd 39: Orlistat</td>
<td>98.45</td>
<td>0.055</td>
<td>0.1</td>
<td>C29 H53 N O5</td>
</tr>
</tbody>
</table>
PPCPs found in surface water

plus a lot more!
Confirmation of Propranolol by MS/MS

Average mass error = -2.67 ppm
Metaldehyde – Troublesome ‘Slug Slayer’

- Molluscicide widely used on cereals and OSR
- Very stable, high solubility and mobile in the environment
- Hard to remove from water even using advanced treatment processes
- Has frequently exceeded 0.1µg/L PCV in treated water since monitoring began in mid-2000s.
Metaldehyde Receiving Phase

• Existing SWW lab method for analysing metaldehyde in spot samples based on solid phase extraction using a poly(divinylbenzene-vinylpyrrolidone) phase (TELOS ENV™)
• Atlantic™ HLB-L is a type of receiving disk based on the same chemistry
• Filtration studies using river water spiked with metaldehyde at 1µg/L indicated virtually quantitative recovery
• Metaldehyde can readily be recovered from loaded disks by elution with ethyl acetate
Metaldehyde Uptake Profile

Mass of metaldehyde accumulated (µg) vs. Time (h)
Field Trial Design

- Trial carried out over a 15 day period in late March 2014
- Chemcatchers deployed in triplicate at nine different sites (four in the Pitsford catchment & five at Grafham)
- Accompanying spot samples collected at each site on six occasions throughout the trial. Analysed for metaldehyde and DOC at AWS laboratory in Huntingdon
- On-site temperature, pH and flow velocity measured
- Chemcatchers returned to SWW laboratory in Exeter and analysed for metaldehyde to allow TWA values to be calculated
- Results of all analyses collated by SWW
Field Trial Results Summary

<table>
<thead>
<tr>
<th>Location</th>
<th>Mass on Chemcatchers (ng)</th>
<th>Calculated TWA Concentration (ng/l)</th>
<th>Average Spot Sample Result (ng/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Disk 1</td>
<td>Disk 2</td>
<td>Disk 3</td>
</tr>
<tr>
<td>Holcot Feeder Stream (Pitsford)</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Pitsford Compensation Stream</td>
<td>69</td>
<td>71</td>
<td>71</td>
</tr>
<tr>
<td>Walgrave Feeder Stream (Pitsford)</td>
<td>6</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>Scaldwell Brook Feeder Stream (Pitsford)</td>
<td>6</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Grafham Intake - River Great Ouse</td>
<td>12</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>Offord Stream - Grafham Pumphouse</td>
<td>18</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>Offord Stream - Grafham Intake Access Road</td>
<td>18</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>Grafham Reservoir Draw-Off Tower</td>
<td>60</td>
<td>65</td>
<td>63</td>
</tr>
<tr>
<td>Diddington Feeder Stream (Grafham)</td>
<td>4</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

- Rank ordering of mean masses on Chemcatcher correlates well with that of the average spot sample results (one exception).

- Reproducibility of masses of metaldehyde captured on Chemcatchers excellent at all sites.

- Calculated TWA values generally ~50% of the corresponding mean spot sample results.
Conclusions

- A lot of calibration data is available in the literature – but how robust are the measurements?
- Most work has concentrated on making measurements rather than trying to understand the uptake mechanisms involved.
- Little is known about the link between the sampling rate, uptake capacity and a compound’s physico-chemical properties.
- More research is needed into in-situ calibration and conversion to concentrations in the water phase.
- Although environmental variables affect uptake into samplers, sampling rates are not significantly affected by environmental variables (flow, salinity, pH) over the range of conditions typically found in the aquatic environment.
- Time integrative sampling offers many advantages over discontinuous spot samples in terms of the uncertainty of overall measurements.
Thank you for your attention!