OUT TO SEA: ANTARCTIC RESEARCH STATION EFFLUENTS AS A SOURCE OF ORGANIC MICROPOLLUTANTS IN COASTAL WATERS

Phil Emnet, Sally Gaw, Grant Northcott, Bryan Storey, Lisa Graham
Pharmaceuticals and Personal Care Products (PPCPs)

- Pharmaceuticals includes prescription and over the counter medications

- Personal care products include sunscreens, moisturizers, toothpastes, make up....

- Personal care products contain wide range of chemicals
  - Preservatives (e.g. parabens)
  - Antimicrobials (e.g. triclosan)
  - UV-filters (e.g. benzophenones)
  - Plastics (e.g. BPA)

- Widely used, including Antarctica

mParaben  Triclosan  Benzophenone-3  Bisphenol-A

http://chemistscorner.com/the-10-different-types-of-cosmetic-formulas-you-must-know/
Pharmaceuticals and Personal Care Products (PPCPs)

• Wastewater effluent is a major source of PPCPs

• Found in surface waters worldwide
  • Low-mid parts per trillion
  • Continuous release causes pseudo-persistence

• Concern due to
  • endocrine disrupting effects
  • impacts on microorganisms
  • behavioural effects
Relevance to Antarctica

- Permanent stations
- Summer stations

http://www.ecophotoexplorers.com/AntarcticaStations.asp
Relevance to Antarctica

- 37% of permanent and 69% of summer stations do not have sewage treatment

- Treatment plants can malfunction
  - Fluctuating water volumes
  - Low temperatures can freeze pipes
  - Complete treatment failure possible

- Environmental conditions may enhance persistence of organic micropollutants
  - Cold temperatures
  - Variable light conditions
  - Presence of sea-ice
Research Questions

• Are PPCPs present in sewage effluents and the ocean waters in the proximity of research stations?

• Are PPCPs present in marine biota in the proximity of research stations?
Study area
Study outline

• 09/10 Field season
  • Sewage effluents from McMurdo and Scott Base
  • Coastal seawater
  • Clams (*Laternula elliptica*), fish (*Trematomus bernachii*) and sea urchins (*Sterichinus neumayeri*)

• 12/13 Field season
  • Sewage effluents from Scott Base
    • Monthly sampling for 6 months plus 7 day study
  • Coastal seawater
  • Sea ice
Methodology

• Water collected through sea ice drill holes
• Sewage effluent discharge before released into ocean
• Solid Phase Extraction
  • Ocean water (4 L)
  • Sewage effluent (1 L)
  • Reference site (10 L)
  • $C_{13}$ surrogates
• Florosil clean-up
• Kept at -80 °C until analysis
• BSTFA/TMSI derivatization (NZ)
• GC-MS SIM analysis (NZ)
Target analytes

- Preservatives & antimicrobial compounds
  - 4 parabens, triclosan and methyl triclosan

- Uv-filters
  - BP-1, BP-3, 4-MBC, OMC

- Natural and synthetic steroid hormones
  - E1, E2, E3 and EE2

- Surfactants
  - Octyl-phenol and nonyl phenol

- Plastic monomer
  - BPA
## 09/10 Season results: Sewage effluents

<table>
<thead>
<tr>
<th>Analyte (ng L⁻¹)</th>
<th>Use</th>
<th>Scott Base</th>
<th>McMuro</th>
<th>Literature Range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octylphenol</td>
<td>Surfactant</td>
<td>39 – 118</td>
<td>–</td>
<td>37 – 470</td>
<td>[1,4,5]</td>
</tr>
<tr>
<td>4-MBC</td>
<td>UV-filter</td>
<td>173 - 234</td>
<td>–</td>
<td>42 – 2,300</td>
<td>[8,9]</td>
</tr>
<tr>
<td>BP-3</td>
<td>UV-filter</td>
<td>70 – 105</td>
<td>110 – 130</td>
<td>3 – 300</td>
<td>[8,9,12]</td>
</tr>
<tr>
<td>BP-1</td>
<td>UV-filter</td>
<td>143 – 358</td>
<td>7</td>
<td>&lt;2 – 41</td>
<td>[14-16]</td>
</tr>
<tr>
<td>Bisphenol A (BPA)</td>
<td>Plastics</td>
<td>23 – 87</td>
<td>28</td>
<td>6 – 3642</td>
<td>[17]</td>
</tr>
<tr>
<td>E1</td>
<td>Natural steroid</td>
<td>40 – 60</td>
<td>–</td>
<td>&lt;1 – 110</td>
<td>[4,5]</td>
</tr>
</tbody>
</table>
09/10 Season: Coastal waters

<table>
<thead>
<tr>
<th>Analyte (ng L(^{-1}))</th>
<th>Use</th>
<th>Range</th>
<th>Literature Range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>mParaben</td>
<td>Preservative</td>
<td>1.9 – 33.3</td>
<td>2.1 – 51</td>
<td>[1]</td>
</tr>
<tr>
<td>pParaben</td>
<td>Preservative</td>
<td>&lt;LOQ – 3.0</td>
<td>&lt;0.5 – 7.9</td>
<td>[1]</td>
</tr>
<tr>
<td>bParaben</td>
<td>Preservative</td>
<td>&lt;LOQ – 2.3</td>
<td>&lt;0.2 – 0.7</td>
<td>[1]</td>
</tr>
<tr>
<td>Octylphenol</td>
<td>Surfactant</td>
<td>0.3 – 1.7</td>
<td>&lt;1.2 - 81</td>
<td>[1-3]</td>
</tr>
<tr>
<td>4-MBC</td>
<td>UV-filter</td>
<td>45.1</td>
<td>13.1 – 798.7</td>
<td>[6-7]</td>
</tr>
<tr>
<td>BP-3</td>
<td>UV-filter</td>
<td>12.0 – 88.4</td>
<td>1.8 – 3,300</td>
<td>[6,10,11]</td>
</tr>
<tr>
<td>BP-1</td>
<td>UV-filter</td>
<td>&lt;LOQ – 10.3</td>
<td>280</td>
<td>[11]</td>
</tr>
<tr>
<td>OMC</td>
<td>UV-filter</td>
<td>&lt;LOQ – 32.3</td>
<td>7.4 – 389.9</td>
<td>[6,7]</td>
</tr>
<tr>
<td>mTric</td>
<td>Triclosan metabolite</td>
<td>0.2</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Triclosan</td>
<td>Antimicrobial</td>
<td>0.2 – 1.8</td>
<td>0.008 – 28.9</td>
<td>[13]</td>
</tr>
<tr>
<td>Bisphenol A (BPA)</td>
<td>Plastics</td>
<td>2.2 – 29.5</td>
<td>&lt;0.04 - 330</td>
<td>[17]</td>
</tr>
</tbody>
</table>

Target analytes were detected at the Cape Evans reference site
09/10 Season: Biota

• Clams
  • BP-3, E2, EE2, mParaben and pParaben

• Fish
  • BP-3 and pParaben
  • Detected in fish from Cape Evans, the reference site

• Sea urchin composite
  • BP-3, mParaben and octylphenol

• Concentrations comparable to those reported internationally

• Issues with the extraction method – other analytes may be present
12/13 Season: sewage effluent

- Nine most commonly detected analytes were uv-filters (4-MBC, BP-1, BP-3), BPA, E1, triclosan and its degradation product methyl triclosan

- No correlation between PPCP concentrations and WWTP operating temperature or the number of people at Scott Base

- Higher concentrations were measured during the 7 day study than in the monthly samples

- EE2 was detected during the 7 day study
12/13 Season: Seven day effluent study

The diagrams show the concentration (ng/L) of BP-3, mTric, and EE2 on different days of the week. The concentration levels are indicated by bars, with days of the week labeled as Monday (Mon), Tuesday (Tue), Wednesday (Wed), Thursday (Thr), Friday (Fri), Saturday (Sat), and Sunday (Sun). The concentration ranges vary across the substances, with BP-3 showing the highest concentration levels compared to mTric and EE2.
12/13 Season: Coastal waters and sea ice

- 24 sampling sites for coastal waters
- Fewer analytes detected in coastal waters than in 09/10
- Concentrations generally lower than in 09/10
- Target analytes still detected 25 km from the research bases
- Sea ice concentrations of PPCPs were comparable to those in coastal waters
Tide cracking

- Tide cracking
  - NZ field parties
  - Ice Runway
  - Overall can discharge 1000+ L of wastewater each season
Conclusions

• First report of PPCPs in Antarctic coastal waters and sewage effluent

• PPCP concentrations were comparable to studies in temperate climates

• WWTPs are ineffective at removing PPCPs
  • Stations with no treatment likely to release higher concentrations

• WWTPs are potentially not the only sources of PPCPs into Erebus Bay

• Larger geographic areas than initially suspected may be impacted
Implications

• Further assessment of organic micropollutants in Antarctic ecosystems is required

• Protocols for use of PPCPs in Antarctica need to be developed

• Upgraded or new waste water treatment plants should be designed to remove organic micropollutants including PPCPs
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