Determination of Booster Biocides in Seawater and Marine Sediments from Panamanian Coastal Areas: Method Development and Survey

Research line: Environmental Analytical Chemistry

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Co-adviser: Prof. Gilberto Fillmann PhD

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GENERAL OBJECTIVE

• To determine booster biocides (Diuron, Irgarol, TCMTB, DCOIT and dichlofluanid) in marine sediments and seawater from Panamanian coastal areas applying vortex assisted MSPD and SPE technique accompanied with LC–MS/MS.

SPECIFIC OBJECTIVES

• To develop a SPE and a MSPD environmental friendly method for determining five booster biocides in seawater and marine sediment;
• To validate these methods with SANCO parameters;
• To collect samples in Panama;
• To discuss the distribution of booster biocides in Panamanian coastal areas;
• To compare the results with other studies worldwide.
SUMMARY

1. Introduction

2. Selected analytes
   • Booster biocides

3. Materials and methods
   • Solid Phase Extraction (SPE)
   • Matrix Solid Phase Dispersion (MSPD)
   • Liquid Chromatography coupled to mass spectrometric analysis (LC MS/MS)

4. Sampling
   • Seawater
   • Sediment

5. Results
   • SPE optimization
   • MSPD optimization
   • SPE Validation
   • Distribution of booster biocides in seawater from Panamanian coastal areas

6. Next steps
1. Introduction

Old wooden vessels

Antifouling painting

Marine biofouling

### 2. Selected analytes

**Table 1: Selected booster biocides for this study**

| Compound | \[
\begin{align*}
\text{Irgarol 1051} & : & \text{2-( tert-butylamino)-4 (cyclopropylamino)-6- (methylthio) 1,3,5-triazine} \\
\text{Diuron} & : & \text{3-(3,4-dichlorophenyl)-1,1-dimethylurea}
\end{align*}
\] |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Effects</strong></td>
<td>Inhibition of photosynthesis in plants</td>
<td>Carcinogenic and deformed growth in fish larvae</td>
</tr>
<tr>
<td><strong>Log Kow</strong></td>
<td>3.95</td>
<td>2.85</td>
</tr>
<tr>
<td><strong>Molar mass</strong></td>
<td>253.4 g mol(^{-1})</td>
<td>233.1 g mol(^{-1})</td>
</tr>
<tr>
<td><strong>Vapor pressure</strong></td>
<td>(1.5 \times 10^{-5}) Pa</td>
<td>(4.1 \times 10^{-4}) Pa</td>
</tr>
<tr>
<td><strong>Boiling point</strong></td>
<td>428.0°C</td>
<td>385.2°C</td>
</tr>
<tr>
<td><strong>Water solubility</strong></td>
<td>7.0 mg L(^{-1})</td>
<td>36.4 mg L(^{-1})</td>
</tr>
</tbody>
</table>


### 2. Selected analytes

**Table 1: Selected booster biocides for this study (cont.)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>TCMTB (Busan)</th>
<th>Dichlofluanid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2-(Thiocyanomethylthio) benzothiazole</td>
<td>N-dimethyl-N-phenylsulphamide</td>
</tr>
<tr>
<td><strong>Effects</strong></td>
<td>Inhibitor of the electron transport chain at the level of mitochondria</td>
<td>Carcinogenic and mutagenic effects in unicellular microorganisms</td>
</tr>
<tr>
<td><strong>Log Kow</strong></td>
<td>3.30</td>
<td>3.70</td>
</tr>
<tr>
<td><strong>Molar mass</strong></td>
<td>238.4 g mol(^{-1})</td>
<td>333.2 g mol(^{-1})</td>
</tr>
<tr>
<td><strong>Vapor pressure</strong></td>
<td>1.0 Pa</td>
<td>1.3 x 10(^{-4}) Pa</td>
</tr>
<tr>
<td><strong>Boiling point</strong></td>
<td>NA</td>
<td>336.8°C</td>
</tr>
<tr>
<td><strong>Water solubility</strong></td>
<td>45 mg L(^{-1})</td>
<td>0.006 mg L(^{-1})</td>
</tr>
</tbody>
</table>


2. Selected analytes

| Compound          | DCOIT  
|-------------------|--------
| 4,5-dichloro-2-octyl-thiazol-3-one |

Table 1: Selected booster biocides for this study (cont.)

<table>
<thead>
<tr>
<th>Effects</th>
<th>High microbial activity, especially with bacteria, fungi and algae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log Kow</td>
<td>2.85</td>
</tr>
<tr>
<td>Molar mass</td>
<td>213.3 g mol(^{-1})</td>
</tr>
<tr>
<td>Vapor pressure</td>
<td>4.0 \times 10(^{-4}) Pa</td>
</tr>
<tr>
<td>Boiling point</td>
<td>322.6</td>
</tr>
<tr>
<td>Water solubility</td>
<td>0.0065 mg L(^{-1})</td>
</tr>
</tbody>
</table>

3. Methods

- Solid Phase Extraction (SPE)

SPE refers to the nonequilibrium, exhaustive removal of chemical constituents from a flowing liquid sample via retention on a contained solid sorbent and subsequent recovery of selected constituents by elution from the sorbent.

- Reduce organic solvent
- Reduce analysis time
- Requires less manipulation
- SPE provides higher concentrations factors
- Can be used to store analytes in a sorbed state

3. Methods

- **Solid Phase Extraction (SPE)**

*Figure 1*: Four basic steps for solid-phase-extraction

3. Methods

- Matrix Solid Phase Dispersion (MSPD)

**Figure 2:** Vortex-assisted MSPD adapted by Caldas et al, 2013

Recent modification to the original technique based on matrix solid-phase dispersion (MSPD) to determine pesticides in fish liver and crab hepatopancreas. VA-MSPD substitutes the SPE elution step with vortex agitation followed by centrifugation and further chromatographic analysis.

SOUZA CALDAS, S. et al. A vortex-assisted MSPD method for the extraction of pesticide residues from fish liver and crab hepatopancreas with determination by GC–MS. *Talanta*, v. 112, n. 0, p. 63-68, 2013
3. Methods

- **Matrix Solid Phase Dispersion (MSPD)**

  - One step for extraction and cleaning
  - High recovery %
  - Short extraction times, low cost.
  - Small amounts of sample
  - Small amounts of sorbent and solvent
  - Viability, flexibility, versatility
  - Biological tissues, soil, sludge, food and sediments

3. Methods

Figure 3: Liquid chromatograph Alliance Separations Module 2695 (Waters, EUA), Detector MS, Micromass® Quatro Micro™ API (Waters, Inglaterra) API, electrospray ionization
4. Sampling

Common shipping routes

13 000 - 14 000 vessels/year
38-40 vessels/day

http://micanaldepanama.com/nosotros/
4. Sampling

**Figure 4:** Sampling sites
## 4. Sampling

### Table 2: Sampling location information

<table>
<thead>
<tr>
<th>Identification</th>
<th>Site</th>
<th>Latitude (N)</th>
<th>Longitude (W)</th>
<th>Activities</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA01A</td>
<td>Shelter Marina 1</td>
<td>09°21'58.00&quot;</td>
<td>79°57'04.10&quot;</td>
<td>Recreational boats and shipyards (repair)</td>
</tr>
<tr>
<td>PA01B</td>
<td>Shelter Marina 2</td>
<td>09°21'55.20&quot;</td>
<td>79°57'00.25&quot;</td>
<td>Open sea (way of the boats)</td>
</tr>
<tr>
<td></td>
<td>(Sea output)</td>
<td></td>
<td></td>
<td>Container port and shipyards (repair)</td>
</tr>
<tr>
<td>PA02</td>
<td>Colon port</td>
<td>09°21'54.49&quot;</td>
<td>79°53'40.49&quot;</td>
<td>Container port and shipyards (repair)</td>
</tr>
<tr>
<td>PA03</td>
<td>Panama port</td>
<td>08°57'49.70&quot;</td>
<td>79°34'21.10&quot;</td>
<td>Container port and small fishing boats</td>
</tr>
<tr>
<td>PA04</td>
<td>The Americas Bridge</td>
<td>08°56'43.20&quot;</td>
<td>79°33'54.90&quot;</td>
<td>Entrance of Panama Canal-Pacific side (way to the vessels)</td>
</tr>
<tr>
<td>PA05</td>
<td>La Playita Marina</td>
<td>08°54'33.50&quot;</td>
<td>79°31'37.60&quot;</td>
<td>Marina, recreational boats, harbor and shipyards (repair)</td>
</tr>
<tr>
<td>PA06</td>
<td>Vacamonte port</td>
<td>08°51'44.50&quot;</td>
<td>79°40'22.60&quot;</td>
<td>Fishing port</td>
</tr>
</tbody>
</table>
## 4. Sampling

### Table 2: Sampling location information (cont.)

<table>
<thead>
<tr>
<th>Identification</th>
<th>Site</th>
<th>Latitude (N)</th>
<th>Longitude (W)</th>
<th>Activities</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA08</td>
<td>Flamenco marina</td>
<td>08°54'40.20&quot;</td>
<td>79°31'18.50&quot;</td>
<td>Marina, recreational boats, harbor and shipyards (repair)</td>
</tr>
<tr>
<td>PA09</td>
<td>Seafood Market</td>
<td>08°57'30.78&quot;</td>
<td>79°32'09.41&quot;</td>
<td>Fishing port, commercial and passengers jetty</td>
</tr>
<tr>
<td>PA10</td>
<td>Chiriqui Grande</td>
<td>10°38'29.30&quot;</td>
<td>85°39'00.30&quot;</td>
<td>Oil tanks area, commercial and passengers jetty</td>
</tr>
<tr>
<td>PA11</td>
<td>Almirante</td>
<td>09°17'24.80&quot;</td>
<td>82°24'05.60&quot;</td>
<td>Container port, commercial and passengers jetty</td>
</tr>
<tr>
<td>PA12</td>
<td>Bocas del Toro</td>
<td>09°20'12.20&quot;</td>
<td>82°14'34.70&quot;</td>
<td>Recreational boats, commercial and passengers jetty</td>
</tr>
<tr>
<td>PA13</td>
<td>Puerto Armuelles</td>
<td>08°13'34.80&quot;</td>
<td>82°52'29.60&quot;</td>
<td>Oil port and oil tanks area</td>
</tr>
</tbody>
</table>
4. **Sampling: Sediment**

**Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual**

**Designation: D4547 – 09**

**Standard Guide for Sampling Waste and Soils for Volatile Organic Compounds**

This standard is issued under the fixed designation D4547; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.


4. **Sampling:** Sediment

**Materials:**
- Van Veen/Eckman grab
- Aluminum containers previously calcined (450 °C for 4 hours)
- Aluminum foil (also calcined)
- Latex gloves
- Stainless steel spatula
- Permanent markers, tape and plastic bags
4. Sampling: Sediment

Recomendations:

• Sediment samples should preferably have a granulometry with percentages of fines (clay and silt) above 30%.

• It is desirable that these be collected in places where the granulometry is previously known.

• **These samples must be taking only the surface layer (2cm), representative of recent sediments.**

• It must also be ruled out of the sample that is in direct contact with the walls of the collection team.
4. Sampling

Figure 5: Sample preparation steps
4. Sampling

**Figure 6**: Samples ready for analysis
4. Sampling

Figure 7: Granulometry test
## 5. Results

### Chromatographic parameters

**Table 3**: MRM conditions of mass spectrometry and retention time of the booster biocides. Positive ion (PI) mode (ESI +) and dwell time: 0.2 s

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time (min)</th>
<th>Quantification transition (m/z)</th>
<th>Collision energy (eV)</th>
<th>Confirmation transition (m/z)</th>
<th>Collision energy (eV)</th>
<th>Cone voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diuron-d6*</td>
<td>4.20</td>
<td>239.33&gt;78.1</td>
<td>17</td>
<td>239.33&gt;52.1</td>
<td>15</td>
<td>29</td>
</tr>
<tr>
<td>Diuron</td>
<td>4.39</td>
<td>232.97&gt;72</td>
<td>17</td>
<td>232.97&gt;160</td>
<td>37</td>
<td>23</td>
</tr>
<tr>
<td>TCMTB</td>
<td>5.18</td>
<td>238.76&gt;180</td>
<td>15</td>
<td>238.76&gt;136</td>
<td>25</td>
<td>17</td>
</tr>
<tr>
<td>Irgarol</td>
<td>5.82</td>
<td>253.87&gt;198</td>
<td>17</td>
<td>253.87&gt;108</td>
<td>31</td>
<td>27</td>
</tr>
<tr>
<td>Dichlofluanid</td>
<td>5.98</td>
<td>332.82&gt;123</td>
<td>29</td>
<td>332.82&gt;76.9</td>
<td>57</td>
<td>23</td>
</tr>
<tr>
<td>DCOIT</td>
<td>7.84</td>
<td>281.91&gt;170</td>
<td>15</td>
<td>281.97&gt;57</td>
<td>17</td>
<td>29</td>
</tr>
</tbody>
</table>

* Surrogate standard
5. Results

Chromatographic separation

**Figure 8:** Multiple reaction monitoring (MRM) chromatograms for target analytes
5. Results

MSPD for determining booster biocides in MARINE SEDIMENTS
5. Results: MSPD optimization

Graphic 1: Effect of organic solvent on the extraction efficiency. Conditions: sample mass: 2 g; 50 ng g\(^{-1}\) of each biocide in sediment sample; volume of organic solvent: 10 mL; maceration time: 5 min; vortex time: 1 min; centrifugation time: 5 min

- MeOH
  - R: 55 – 95 %
  - RSD: < 11 %

- EtOH
  - R: 68 – 102 %
  - RSD: < 4 %

Diuron
Irgarol
TCMTB
DCOIT
Dichlofluanid
5. Results: MSPD optimization

Graphic 2: Effect of volume of ethanol on the extraction efficiency. Conditions: sample mass: 2 g; 50 ng g$^{-1}$ of each biocide in sediment sample; maceration time: 5 min; vortex time: 1 min; centrifugation time: 5 min.

R: 91 – 99 %
RSD: < 20%

R: 86 – 96 %
RSD: < 6%
5. Results: MSPD optimization

Graphic 3: Effect matrix of volume of organic solvent. Conditions: sample mass: 2 g; 50 ng g⁻¹ of each biocide in sediment sample; maceration time: 5 min; vortex time: 1 min; centrifugation time: 5 min.
4. **Results: MSPD optimization**

Optimal MSPD procedure

Sample mass: 2 g
Solid support: 0.5 g C18
Dispersion time: 5 min
Solvent volume: 5 mL EtOH
1 min vortex
5 min centrifugation
Extract ready for analysis
5. Results

SPE for determining booster biocides in SEAWATER
5. Results: SPE optimization

Graphic 4: Effect of the type of cartridge on the extraction efficiency. Conditions: sample solution: 250 mL; 10 µg L\(^{-1}\) of each biocide in water sample; volume of elution solvent: 2 mL
5. Results: SPE optimization

Graphic 4: Effect of sample pH on the extraction efficiency. Conditions: sample solution: 250 mL; 10 µg L⁻¹ of each biocide in water sample; cartridge: Strata C18-E; volume of elution solvent: 2 mL.

<table>
<thead>
<tr>
<th>pH</th>
<th>Diuron R</th>
<th>Irgarol R</th>
<th>TCMTB R</th>
<th>DCOIT R</th>
<th>Dichlofluanid R</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0</td>
<td>56 – 94%</td>
<td>69 – 94%</td>
<td>60 – 93%</td>
<td>69 – 94%</td>
<td>60 – 93%</td>
</tr>
<tr>
<td></td>
<td>RSD: &lt;6%</td>
<td>RSD: &lt;9%</td>
<td>RSD: &lt;8%</td>
<td>RSD: &lt;9%</td>
<td>RSD: &lt;8%</td>
</tr>
</tbody>
</table>

Legend:
- **Diuron**
- **Irgarol**
- **TCMTB**
- **DCOIT**
- **Dichlofluanid**
### 5. Results: SPE optimization

Table 4: pKa of compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irgarol</td>
<td>3.70</td>
</tr>
<tr>
<td>Diuron</td>
<td>4.12</td>
</tr>
<tr>
<td>TCMTB</td>
<td>-----</td>
</tr>
<tr>
<td>DCOIT</td>
<td>-----</td>
</tr>
<tr>
<td>Dichlofluanid</td>
<td>-----</td>
</tr>
</tbody>
</table>

![Chemical structure of Irgarol 1051](image)

![Chemical structure of Diuron](image)

**Graphic 5:** Species distribution of diuron as a function of pH values


5. Results: SPE optimization

Graphic 6: Effect of sample salinity on the extraction efficiency. Conditions: sample solution: 250 mL; 10 µg L⁻¹ of each biocide in water sample; cartridge: Strata C18-E; volume of elution solvent (MeOH): 2 mL

- Salinity 10: % Recovery: R: 58 – 117 %, RSD: < 4%
- Salinity 20: % Recovery: R: 59 – 112 %, RSD: < 18%
- Salinity 30: % Recovery: R: 52 – 102 %, RSD: < 19%
5. Results: SPE optimization

Optimal SPE procedure:
- Sample volume: 250 mL pH = 7-8
- Salinity: 20 - 30
- Filtration: Sartorius cellulose acetate filter 0.45 µm
- Cartridge: C18-E
- Conditioning: $6 \text{ mL MeOH} + 6 \text{ mL milli-Q water}$
- Flow rate: $10 \text{ mL min}^{-1}$
- Rinse: 1 mL milli-Q water
- Elution: 2 mL MeOH

Surrogate standard: 100 µL of 0.2 mg L$^{-1}$ diuron-d$_6$

Pre-concentration factor: 125x
5. Results: SPE validation

- Limit of detection (LOD)
- Limit of quantification (LOQ)
- Linearity
- Accuracy
- Precision
- Matrix effect

EUROPEN-COMMISSION. Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed. SANCO/12571/2013, 2013, rev. 0. 386. 2013
5. Results: SPE validation

Table 5: Method Limits of detection (LODm) and quantification (LOQm), calibration curves prepared at solvent and at the extract, with their respective correlation coefficients (r).

<table>
<thead>
<tr>
<th>Analytes</th>
<th>LODm (ng L⁻¹)</th>
<th>LOQm (ng L⁻¹)</th>
<th>Calibration curves</th>
<th>Solvent</th>
<th>r</th>
<th>Extract</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diuron</td>
<td>2.7</td>
<td>8.0</td>
<td>y=76387x+18.514</td>
<td>0.9995</td>
<td></td>
<td>y=89094x+20.253</td>
<td>0.9972</td>
</tr>
<tr>
<td>Irgarol</td>
<td>0.3</td>
<td>0.8</td>
<td>y=3×10⁶x+213.42</td>
<td>0.9912</td>
<td></td>
<td>y=2.9×10⁶x+248.33</td>
<td>0.9973</td>
</tr>
<tr>
<td>TCMTB</td>
<td>13.3</td>
<td>40</td>
<td>y=214771x+175.67</td>
<td>0.9993</td>
<td></td>
<td>y=210633x+4.362</td>
<td>0.9989</td>
</tr>
<tr>
<td>DCOIT</td>
<td>1.3</td>
<td>4.0</td>
<td>y=67582x+28.643</td>
<td>0.9968</td>
<td></td>
<td>y=83255x+2.8077</td>
<td>0.9978</td>
</tr>
<tr>
<td>Dichlofluanid</td>
<td>2.7</td>
<td>8.0</td>
<td>y=36935x+31.468</td>
<td>0.9991</td>
<td></td>
<td>y=34378x+28.054</td>
<td>0.9937</td>
</tr>
</tbody>
</table>
5. Results: SPE validation

**Table 6: Accuracy (R), precision (RSDr and RSDip), and matrix effect (ME)**

<table>
<thead>
<tr>
<th>Analytes</th>
<th>R (%)</th>
<th>RSDr (%)</th>
<th>RSDip (%)</th>
<th>ME (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LOQ</td>
<td>5LOQ</td>
<td>10LOQ</td>
<td>LOQ</td>
</tr>
<tr>
<td>Diuron</td>
<td>106</td>
<td>111</td>
<td>117</td>
<td>12</td>
</tr>
<tr>
<td>Irgarol</td>
<td>130</td>
<td>83</td>
<td>112</td>
<td>3</td>
</tr>
<tr>
<td>TCMTB</td>
<td>89</td>
<td>81</td>
<td>88</td>
<td>10</td>
</tr>
<tr>
<td>DCOIT</td>
<td>113</td>
<td>88</td>
<td>88</td>
<td>13</td>
</tr>
<tr>
<td>Dichlofluanid</td>
<td>92</td>
<td>83</td>
<td>75</td>
<td>9</td>
</tr>
</tbody>
</table>
5. Results

ANTIFOULING BOOSTER BIOCIDES IN SEAWATER FROM COASTAL AREAS OF PANAMA:
First data in one of the world’s busiest shipping zones
### 5. Results: Distribution of booster biocides in seawater

**Table 7:** Concentration of antifouling biocides found in seawater samples taken from Panamanian coastal areas

<table>
<thead>
<tr>
<th>Identification</th>
<th>Site</th>
<th>Diuron (ng L(^{-1}) ± RSD (%)</th>
<th>Irgarol (ng L(^{-1}) ± RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA01A</td>
<td>Shelter Marina 1</td>
<td>36 ± 9</td>
<td>5 ± 6</td>
</tr>
<tr>
<td>PA01B</td>
<td>Shelter Marina 2</td>
<td>&lt;LOQ</td>
<td>&lt;LOQ</td>
</tr>
<tr>
<td></td>
<td>(Sea output)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA02</td>
<td>Colon port</td>
<td>&lt;LOQ</td>
<td>&lt;LOQ</td>
</tr>
<tr>
<td>PA08</td>
<td>Flamenco marina</td>
<td>70 ± 6</td>
<td>2 ± 8</td>
</tr>
</tbody>
</table>
5. Results: Distribution of booster biocides in seawater

Graphic 7: Recoveries of Diuron-d6 in real samples from Panama. Conditions: sample solution: 250 mL; 100 µL of 0.2 mg L$^{-1}$ of diuron-d6 in seawater sample; sample pH: 7-8; salinity: 20-30; cartridge: Strata C18-E; volume of elution solvent: 2 mL

%R: 78 to 120%
RSD: < 13%
5. Results: Distribution of booster biocides in seawater

**PA01A:** Shelter Marina
36 ng L\(^{-1}\) Diuron
5 ng L\(^{-1}\) Irgarol
5. Results: Distribution of booster biocides in seawater

PA01A: Shelter Marina
36 ng L\(^{-1}\) Diuron
5 ng L\(^{-1}\) Irgarol

a) Standard Irgarol 0.005 mg L\(^{-1}\)

b) Sample PA01A

Figure 9: MRM of a) Irgarol standard in solvent at 0.005 mg L\(^{-1}\) and b) real sample PA01A
5. Results: Distribution of booster biocides in seawater

PA01B: Shelter Marina (Output sea)
<LOQ Diuron
<LOQ Irgarol
5. Results: Distribution of booster biocides in seawater

PA02: Colon
<LOQ Diuron
<LOQ Irgarol
5. Results: Distribution of booster biocides in seawater

PA08: Flamenco Marina
70 ng L\(^{-1}\) Diuron
2 ng L\(^{-1}\) Irgarol
5. Results: Distribution of booster biocides in seawater

PA08: Flamenco Marina
70 ng L\(^{-1}\) Diuron
2 ng L\(^{-1}\) Irgarol

a) Standard Diuron 0.01 mg L\(^{-1}\)

b) Sample PA08

Figure 10: MRM of a) Diuron standard in solvent at 0.005 mg L\(^{-1}\) and b) real sample PA08
5. Results: Distribution of booster biocides in seawater

Results:

**Distribution of booster biocides in seawater**

**TCMTB (Busan)**

2-(Thiocyanomethylthio) benzothiazole

Log$K_{ow}$: 3.30
Sw: 45 mg L$^{-1}$

**DCOIT**

4,5-dichloro-2-octyl-thiazol-3-one

Log$K_{ow}$: 2.85
Sw: 0.0065 mg L$^{-1}$
- It extremely stable complexes with sediments.
- Rapid degradation (less than a few days) and have a short half-life (in a few hours) in water and sediment

**DMSA**

N$^{\prime}$-dimethyl-N-phenyl-sulphamide

**Dichlofluanid**

N-dimethyl-N-phenylsulphamide

Log$K_{ow}$: 3.70
Sw: 0.006 mg L$^{-1}$
- Hydrolytic half-life in seawater (pH 8.2, 20 °C): 1.2 h
- Photolysis half-life in seawater by natural solar irradiation: 53 h


5. Results: Distribution of booster biocides in seawater

What we know about the other sampling sites?

Are they still using TBT paints?

Triphenyltin (TPT)

Penis in females

Imposex in gastropods

Picture by: Ítalo Braga Castro
5. Results: Distribution of booster biocides in seawater

Are these levels harmful to the marine ecosystem?

UK, Sweden and Denmark restricted Irgarol use on boats <25 m in length

Dutch National Institute of Public Health and the Environment: 430 ng L\(^{-1}\) for Diuron and 24 ng L\(^{-1}\) for Irgarol

Climatic factors

Consider partitioning, persistence and bioavailability

These data demonstrate the use of these compounds in antifouling paints


## 5. Results: Distribution of booster biocides in seawater

**Table 8:** Comparison of antifouling biocide concentrations (ng L⁻¹) found in water in this study with other reported studies.

<table>
<thead>
<tr>
<th>Location, year</th>
<th>Analysis</th>
<th>Irgarol (ng L⁻¹)</th>
<th>Diuron (ng L⁻¹)</th>
<th>Other biocides (ng L⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Dichlofluanid: 24 – 284</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Chlorothalonil: 63-31</td>
<td></td>
</tr>
<tr>
<td>Netherlands, 2000</td>
<td>SPE LC-MS/MS</td>
<td><strong>9 - 90</strong></td>
<td><strong>90 - 1130</strong></td>
<td>-----</td>
<td>(LAMOREE <em>et al.</em>, 2002)</td>
</tr>
<tr>
<td>Denmark, 2004</td>
<td>SPE GC-MS</td>
<td>-----</td>
<td>-----</td>
<td>DCOIT: <strong>283</strong></td>
<td>(STEEN <em>et al.</em>, 2004)</td>
</tr>
<tr>
<td>Puerto Rico and the US Virgin Islands, 2006</td>
<td>SPE GC-MS</td>
<td><strong>1 - 1300</strong></td>
<td>-----</td>
<td>-----</td>
<td>(CARBERY <em>et al.</em>, 2006)</td>
</tr>
<tr>
<td>Southern England, UK, 2008</td>
<td>SPE GC-MS</td>
<td>&lt;<strong>3.1</strong> - <strong>89</strong></td>
<td>-----</td>
<td>M1: &lt;0.5 – 30</td>
<td>(ZHOU, 2008)</td>
</tr>
<tr>
<td>Gran Canaria, Spain, 2011</td>
<td>SPE LC-MS/MS</td>
<td><strong>2.4</strong> - <strong>146</strong></td>
<td><strong>2.3</strong> - <strong>203</strong></td>
<td>TCMTB: nd</td>
<td>(SÁNCHEZ-RODRÍGUEZ <em>et al.</em>, 2011)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Dichlofluanid: nd</td>
<td></td>
</tr>
<tr>
<td>Panama, 2016</td>
<td>SPE LC-MS/MS</td>
<td>&lt;<strong>1</strong> – <strong>5</strong></td>
<td>&lt;<strong>8</strong> – <strong>70</strong></td>
<td>DCOIT: nd</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td>TCMTB: nd</td>
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<td></td>
<td>Dichlofluanid: nd</td>
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</tbody>
</table>
## 5. Results: Distribution of booster biocides in seawater

**Table 8:** Comparison of antifouling biocide concentrations (ng L\(^{-1}\)) found in water in this study with other reported studies (cont).

<table>
<thead>
<tr>
<th>Location, year</th>
<th>Analysis</th>
<th>Irgarol (ng L(^{-1}))</th>
<th>Diuron (ng L(^{-1}))</th>
<th>Other biocides (ng L(^{-1}))</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>São Luiz, Maranhão, Brasil, 2011</td>
<td>SPE LC-MS/MS</td>
<td>20 – 4800</td>
<td>50 – 7800</td>
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<td>(DINIZ et al., 2014)</td>
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<tr>
<td>Malaysia, 2013</td>
<td>SPE LC-MS/MS</td>
<td>5 – 2021</td>
<td>1 – 285</td>
<td>-----</td>
<td>(ALI et al., 2013)(ALI et al., 2014)</td>
</tr>
<tr>
<td>California, USA, 2013</td>
<td>SPE LC-MS/MS</td>
<td>254</td>
<td>68</td>
<td>M1: 62</td>
<td>(SAPOZHKNIKOVA et al., 2013)</td>
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<tr>
<td>Bushelr, Iran, 2013</td>
<td>MF-LPME HPLC-UV</td>
<td>11 – 63</td>
<td>29</td>
<td>3,4-DCA: 47 – 289</td>
<td>(SALEH et al., 2015)</td>
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<tr>
<td>Seto Inland Sea, Japan, 2014</td>
<td>SPE HPLC-UV</td>
<td>3</td>
<td>31</td>
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<td>(KAONGA et al., 2016)</td>
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<td>Rio Grande, Brazil, 2014</td>
<td>SPE LC-MS/MS</td>
<td>6</td>
<td>21</td>
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<td>(DOMINGUEZ et al., 2014)</td>
</tr>
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<td>South Korea, 2014</td>
<td>LLE LC-MS/MS</td>
<td>14</td>
<td>35 – 1360</td>
<td>DCOIT: nd Zn/Cu pyrithione: nd</td>
<td>(KIM et al., 2014)</td>
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<tr>
<td>Panama, 2016</td>
<td>SPE LC-MS/MS</td>
<td>&lt;1 – 5</td>
<td>&lt;8 – 70</td>
<td>DCOIT: nd TCMTB: nd Dichlofluanid: nd</td>
<td>This study</td>
</tr>
</tbody>
</table>
References

References

6. NEXT STEPS

- Freeze dry sediment samples
- Sediment characterization
- MSPD validation
- MSPD in samples from Panama
- Dissertation
- PPCPs in sediment samples of the Americas
ACKNOWLEDGEMENTS