Monitoring long-term trends in exposure to Photosystem II (PSII) herbicides on the Great Barrier Reef using passive sampling techniques

Christie Bentley, Chris Paxman, Kristie Lee Chue, Jochen Mueller
Presentation Outline

- Introduction to the Great Barrier Reef
- The Reef Plan and the Passive Sampling Program
- What we do
- Site and regional data summaries
- Relationship between Rain, River and Reef
- Key findings and conclusions
Introduction to the Great Barrier Reef (GBR)

- UNESCO World Heritage Site 1981
- 3000 reefs and 900 islands
- 1.6 million visitors/ year
- Huge economic value - $5 Billion, 63 000 jobs
Australia and Europe area comparison

Australia’s area: 7.7 million sq km
Europe’s area (shown): 3.5 million sq km

Darwin to Perth 4396 km • Perth to Adelaide 2707 km 8 • Adelaide to Melbourne 726 km
Melbourne to Sydney 887 km • Sydney to Brisbane 972 km • Brisbane to Cairns 1748 km
THE GBR Catchment

76% of the GBR catchment

17% of the GBR catchment
Past to present - pesticides on the GBR

- 1980’s – low levels of pesticides (DDT)
- Late 1990’s – diuron in-shore sediments
- Toxicity of diuron tested on organisms (seagrass & zooxanthelie)
- Early 200X’s diuron detected off-shore in grab samples (and PSII inhibition assay developed).
- Passive sampler developed and calibrated - first data from the reef
- Reef Monitoring Plan established (incl. pesticide monitoring)
- 2011 - Diuron temporarily suspended
History of the Reef Plan

- 2001 Report released highlighting the decline in water quality in the GBR
- 2003: 2003 Reef Water Quality and Protection Plan (65 actions)
- 2009: Updated 2009 Reef Water Quality and Protection Plan
- Revised to 11 actions
- 2010: Program review
- 2013: Program review
- 2020: Goal

GOAL
The Reef Plan

- **GOALS**
  - To halt and reverse the decline in water quality entering the reef by 2013.
  - To ensure that by 2020 the quality of water entering the reef from adjacent catchments has no detrimental impact on the health and resilience of the Great Barrier Reef.

- Water Quality and Land Management targets
- Collaborative program of coordinated projects and partnerships to improve the WQ in the GBR though improved land management in reef catchments
Introduction to the Passive Sampling Program

- Routine monitoring and Terrestrial run-off assessments
- Current program - 12 inshore reef sites
- Various Locations
- Monitoring record at some sites since 2005. Valuable!
- ‘Wet’ and ‘dry’ season deployments – 9 per year
- Community involvement
Why use passive samplers?

Many advantages
- $$$
- Valuable continuous monitoring record
- Sensitive detection tool for a fragile ecosystem

Important to recognise their limitations:
- Need good calibration data
- Interference and damage
- Loss of resolution (grabs better)
- Human error when deploying
Types of Passive Samplers

- **Passive flow monitors (PFMs)**
  (in-situ calibration technique for flow) in duplicate

- **Chemcatchers**
  (relatively polar chemicals such as PSII herbicides)
  SDB-RPS Empore Disks™, PES membrane 0.45 μm in duplicate

- **PDMS/SPMDs**
  (moderately polar to non-polar chemicals) in duplicate
Quality Control

- Samplers handled with care.... Or not!!!
- Passive samplers deployed in duplicate
- One Chemcatcher extract archived
- 10% of duplicate Chemcatcher extracts are analysed
- Blanks for each deployment
- Replicate PDMS/ SPMDs are combined
### Priority Chemicals identified for the MMP

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Description</th>
<th>SPMD</th>
<th>PDMS</th>
<th>ED</th>
<th>GRAB</th>
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<tr>
<td>Bifenthrin</td>
<td>Pyrethroid insecticide</td>
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<td>Bromacil</td>
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<td>Conazole fungicide</td>
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<td>Tebuconazole</td>
<td>Conazole fungicide</td>
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<td>Chloracetanilide herbicide</td>
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<td>Propoxur</td>
<td>Carbamate insecticide</td>
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</table>
Concentrations of PSII herbicides

GREEN ISLAND
WET TROPICS

- Diuron
- Hexazinone
- Atrazine
- Desethyl atrazine
- Desisopropyl Atrazine
- Tebuthiuron
- Ametryn
- Prometryn
- Simazine
- Metolachlor
- Terbutryn
- Bromacil
- Flumeturon
- Imidacloprid

No sampler deployed/ returned this sampling period
Maximum concentrations 2009 - 2012

Concentration in water (ng.L⁻¹)

- Low Is
- Green Is
- Fitzroy Is
- Normanby Is
- Dunk Is
- Orpheus Is
- Magnetic Is
- Cape Cleveland
- Pioneer Bay
- Outer Whitsunday
- Sarina Inlet
- North Keppel Is

- Diuron
- Hexazinone
- Atrazine
- DE atrazine
- DI atrazine
- Terbutryn
- Bromacil
- Midacloprid
- Ametryn
- Prometryn
- Simazine
- Metolachlor
- Terbutryn

* Unreliable: 1/6 wet season sampling periods successful

No successful sampling periods 11-12
No monitoring 08-09

[Diagram showing concentration levels for various locations and chemicals]
**PSII-Herbicide Equivalent (PSII-Heq) Index**

- Derived using relative potency factors (REP) for each chemical with respect to a reference PSII herbicide diuron
- REP derived from studies obtained using corals, Phaeodactylum and Chlorella
- Assumed herbicides act additively
- PSII-HEq (ng.L⁻¹) is the sum of the individual REP-corrected concentrations of each individual PSII herbicide

<table>
<thead>
<tr>
<th>PSII Herbicides</th>
<th>Mean/Preliminary Consensus (REP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diuron (reference)</td>
<td>1</td>
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<tr>
<td>Ametryn</td>
<td>1.31</td>
</tr>
<tr>
<td>Atrazine</td>
<td>0.16</td>
</tr>
<tr>
<td>Desethyl-atrazine</td>
<td>0.11</td>
</tr>
<tr>
<td>Desisopropyl-atrazine</td>
<td>0.003</td>
</tr>
<tr>
<td>Flumeturon</td>
<td>0.04</td>
</tr>
<tr>
<td>Hexazinone</td>
<td>0.38</td>
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<tr>
<td>Prometryn</td>
<td>1.05</td>
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<tr>
<td>Simazine</td>
<td>0.07</td>
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<tr>
<td>Tebuthiuron</td>
<td>0.08</td>
</tr>
<tr>
<td>Terbutylazine</td>
<td>0.3</td>
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</table>

*(Jones and Kerswell 2003); (Muller et al. 2008); (Bengtson-Nash et al. 2005); (Schmidt 2005); Macova et al., unpublished data (Entox);*
Converting concentrations into PSII-HEq
PSII-Heq Max 2005 - 2012

- Diuron
- Hexazinone
- Atrazine
- Tebuthiuron
- Prometryn
- Ametryn
- Simazine
- Desethyl atrazine
- Desisopropyl atrazine

PSII-Heq INDEX

1. 50 x PSII-Heq <= 250
2. 25 x PSII-Heq <= 250
3. PSII-Heq <= 250
4. 10 x PSII-Heq <= 250
5. PSII-Heq < 250

Regions:
- Wet Tropics
- Burdekin
- Mackay Whitsunday
- Fitzroy
- Low Isles
- Green Island
- Fitzroy Island
- Normanby Island
- Dunk Island
- Orpheus Island
- Magnetic Island
- Cape Cleveland
- Pioneer Bay
- Outer Whitsunday
- Sarina Inlet
- North Keppel Island

No sampling
Rain, River and Reef

- Rivers deliver pollutants to inshore reef
- High flow can often lead to increased pesticide levels, sustained over several months
- High levels of PSII herbicides detected in flood plumes
Understanding sampler behaviour – past and present work

- Fluctuating concentrations and flood event sampling
  - Considerations: sampler configuration, deployment times

- Grabs vs passive sampling for accurate load estimation ongoing
  - How many grab samples do you need?

- Calibrating for environmental conditions – flow, temperature, salinity, biofouling etc
  - Traditional PRCs not suitable
Conclusions…

- Numerous PSII herbicides detected in inshore GBR waters using Chemcatcher
- PSII herbicide profiles detected reflected land use in the adjacent catchment
- Captures seasonal variation, regional variation
- PSII herbicide levels detected increased with rainfall
- Long-term sampling records for most sites

But…..

- How do we assess true change/ trends? Can we achieve Reef Plan goals?
Thanks to . . .

<table>
<thead>
<tr>
<th>Whitsunday Moorings</th>
<th>Fitzroy Island Resort</th>
<th>Great Barrier Reef Marine Park Authority</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taylor’s Beach Caravan Park</td>
<td>Ingham Travel</td>
<td>Australian Centre for Tropical and Freshwater Research</td>
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<tr>
<td>Sarina Bait Supplies</td>
<td>Frankland Island Cruise &amp; Dive</td>
<td>North Keppel Island Environmental Education Centre</td>
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<td>Jace Services</td>
<td>Reef Safari Diving</td>
<td>Department of Environment and Resource Management</td>
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<td>Reef Fleet Terminal</td>
<td>Orpheus Island Research Station</td>
<td>Australian Institute of Marine Science</td>
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<td>Low Isles Caretakers</td>
<td>Big Cat Green Island</td>
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<td>Quicksilver Connections</td>
<td>Hamilton Island Enterprises</td>
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<tr>
<td>Raging Thunder</td>
<td>Mission Beach/ Dunk Island Water Taxi</td>
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</tbody>
</table>
Thank you to

- Past and present team at Entox
- Past and present program managers and regional co-ordinators – Katherine Martin, John Rainbird, Cath McLean, Phil Laycock, Carolyn Thompson, Warwick Sheldon
Passive flow monitors (PFMs)

- Alternative method to PRCs to calibrate samplers in-situ
- Calibrates the effect of flow (3.4 cm/s – 24 cm/s) and salinity on the uptake of chemicals into the sampler
- Fresh or marine water
- Co-deployed with Chemcatchers, PDMS and SPMDs

\[ v \text{ (cm/s)} = \frac{r_{PFM} - 0.065}{0.164} \]