

# Pesticide residues in the Great Barrier Reef

Australia's Great Barrier Reef (GBR) is one of the world's most iconic World Heritage-listed ecosystems but is currently under threat from a range of environmental insults including climate change and pollution. Recent research has shown that herbicides from agricultural runoff have been found in the GBR lagoon at concentrations capable of harming keystone marine plants. The agricultural sector and state and national governments have responded by encouraging the implementation of improved management practices across the GBR catchment area. **Stephen Lewis, Rob Milla, Jon Brodie, Zoë Bainbridge and Aaron Davis report.**

The Great Barrier Reef (GBR) off the Queensland coast in Australia is one of the world's most iconic World Heritage-listed ecosystems and hosts a great diversity of corals, seagrass, mangroves, fish, phytoplankton, invertebrates, reptiles, birds and mammals<sup>1</sup>. A large number of watersheds drain directly into the GBR lagoon collectively referred to as the GBR catchment area. This area was settled progressively northwards by Europeans from the 1850s and the lands were developed largely for sheep and cattle pastures<sup>2</sup>. Sugarcane became an important crop along the coastline and a sugarcane industry grew from the 1890s. Over 100 years later, beef grazing and sugarcane remain the key agricultural industries within the GBR catchment area.

Pesticide use in these two major industries has been ever evolving. The main 'pests' in beef grazing include ticks and fleas on cattle and woody regrowth vegetation and weeds. Within the sugarcane industry the greyback cane grub/beetle and an array of broad leaf weeds, grasses and vines are the major pests. From the 1940s-50s both industries mainly used organochlorine insecticides (such as DDT, dieldrin, lindane) to control insect pests until these were widely banned/restricted in the late 1980s due to significant levels measured in beef exports and other environmental concerns. A number of alternative chemicals are now available for the treatment of cattle including pyrethroids, biopesticides (such as abamectin) and benzoylphenyl urea (such as fluzazuron), while organophosphates (such as chlorpyrifos) and chloronicotinyls (such as imidacloprid) are used to control the greyback grub in the sugarcane industry.

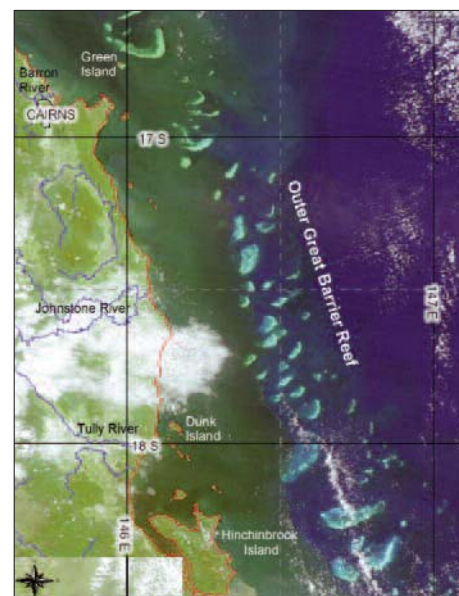
Weed control in the beef and sugarcane industries was largely through blade ploughing, chaining and cultivation. Changing practices in the sugarcane industry to reduce soil erosion (such as minimal tillage) has caused an increased reliance on herbicide application particularly since the 1980s-90s. Some of the key herbicides used

include paraquat, diuron, atrazine, glyphosate, hexazinone and ametryn. Herbicides to control woody vegetation regrowth and weeds (particularly tebuthiuron) are also used in the grazing industry.

Research on the environmental runoff and potential impacts of pesticides in the GBR catchment area and lagoon can essentially be separated into two eras: the pre 1990s where organochlorines were the pesticides of concern and the post 1990 period where an array of pesticides have the potential to move offsite at potentially harmful concentrations. While the long-banned organochlorine insecticides still persist at low concentrations in the soils<sup>3</sup> and biota<sup>4,5</sup> within the GBR catchment area and lagoon, they are thought to pose little risk to its ecosystems. So instead we focus on the pesticides currently used in the GBR catchment area and lagoon including data from monitoring programmes, toxicity studies and pesticide risk assessments. We also examine the alternative farming practices and new products available to reduce pesticide runoff as well as government policies and regulation of pesticide use.

## Pesticide monitoring in the area

Sporadic monitoring of sediments, surface waters and groundwaters in the 1990s uncovered that a particular suite of herbicides in common use in the sugarcane industry such as diuron, atrazine, hexazinone and ametryn were regularly above analytical detection limits across several regions of the GBR catchment area<sup>6,7,8,9</sup>. These herbicides are all designed to inhibit photosynthesis via the photosystem II apparatus of the target plant and provide residual control of broad leaf weeds and grasses. However, it was difficult to place the concentrations of the herbicides detected in these initial monitoring programmes into an environmental context until more recently when research revealed that concentrations of diuron as low as 100 ngL<sup>-1</sup> had negative effects on the photosynthesis of certain sea-



MODIS satellite image (developed by CSIRO) from the Wet Tropics region of the Great Barrier Reef catchment area and lagoon on the 11 February 2007. The coastline can be seen with the haze of an algal bloom stretching far into the sea. It highlights the extent of the nutrient-enriched river water plumes in the GBR lagoon. Monitoring programmes over the last five to seven years have examined the concentrations of pesticides within these plumes.

grass species commonly found within the GBR<sup>10</sup>. The presence of diuron residues were then found in sediments and in seagrass leaves within the GBR<sup>11</sup>. These findings triggered a more focused monitoring approach to trace pesticides from a particular land use source to the river catchment and then to the GBR lagoon<sup>12,13,14</sup>. These 'paddock to reef' studies found that considerable loadings of diuron and atrazine associated with the sugarcane industry, atrazine associated with dryland cropping (mainly grains) and tebuthiuron used on beef grazing lands are exported to the GBR lagoon during wet season runoff events, typically between December and April. Concentrations of diuron, atrazine and tebuthiuron also exceeded national ecological protection trigger values<sup>15</sup> in some waterways within the GBR catchment area<sup>16,17</sup>. Other pesticides regularly detected in the monitoring programmes included hexazinone, ametryn, simazine, metolachlor, 2,4-D, bromacil (all herbicides) and imidacloprid (insecticide)<sup>18,19,20,21</sup>.

The monitoring studies have used two separate techniques: grab samples taken in river water plumes where the highest concentrations of pesticides are detected, and Chemcatchers®, passive samplers which can be deployed for a period of a few days up to one month. These samplers accumulate residues and an 'average' pesticide concentration may be calculated over the period of deployment<sup>22,23</sup>. The passive samplers also provide much lower detection limits (0.1 ngL<sup>-1</sup>) for the herbicides of concern compared to grab samples (10 ngL<sup>-1</sup>). In fact, monitoring data from passive samplers

deployed throughout the GBR lagoon show that herbicide residues at some inshore sites may persist at very low concentrations (~1-10 ngL<sup>-1</sup>) throughout the year<sup>24,25</sup>. Residues of the herbicides diuron, atrazine, hexazinone, ametryn, simazine and tebuthiuron have all been detected in passive samplers deployed in the GBR lagoon with concentrations between 1-20 ngL<sup>-126</sup>.

The grab samples taken within river water plumes detect these same herbicides at much higher concentrations in the order of 10-1700 ngL<sup>-1</sup>. The higher range concentrations occur close to the mouth of rivers before being progressively diluted as the river waters mix with seawater<sup>27,28</sup>. The herbicides detected display 'conservative' mixing behaviour in the river water plumes; this suggests that the herbicide residues are dissolved in the water column or attached to very fine sediment/colloidal particles in the plume and that, at least in the early stages of river plume behaviour, herbicides are not removed via sedimentation.

### Toxicity studies

Prior to the research showing the effects of diuron exposure on seagrass, there was virtually no information on the impact of these herbicides to relevant marine plant species in the GBR lagoon. Over the last 10 years, there have been several laboratory-based studies on the acute (short term) effects of the commonly detected herbicides on species of seagrass<sup>29,30</sup>, mangroves<sup>31</sup>, corals<sup>32,33</sup> and algae<sup>34,35</sup>, all important species in the GBR ecosystem. All of these studies use a technique known as pulse amplitude modulation chlorophyll fluorescence (PAM) which measures the amount of photosynthesis in the target plant. This can measure the lowest concentration of a particular herbicide that will have a 'negative effect' on the plant species through its ability to photosynthesise; this is known as the 'lowest observable effect concentration' or LOEC. The data from the grab samples taken from the river water plumes show that some concentrations exceed the LOEC measured for diuron on many of the plant species of the GBR<sup>36</sup>. Another study showed that isolated coral zooxanthellae were negatively affected when exposed to river plume waters collected from the Mackay Whitsunday region<sup>37</sup>. Many of the plant species appeared to fully recover once removed from herbicide exposure, while some did not. This finding implies that, at least temporarily, there are negative effects to some plant species (such as seagrass and the algal symbionts of coral - zooxanthellae) from herbicide exposure in the GBR lagoon, and possibly longer-term effects on others.

Other studies have examined the effects of herbicide exposure in combination with other potentially relevant environmental influences such as seawater temperature, salinity and sedimentation. One such study showed that diuron attached to sediment particles can produce an enhanced effect on

the sedimentation stress on crustose coralline algae<sup>38</sup>. Another study examined longer term effects on the exposure of diuron on the reproductive potential of corals<sup>39</sup>. These types of research questions are being addressed through the Australian Government's Marine and Tropical Sciences Research Facility.

### Risks of herbicide exposure

Risk assessments of herbicide exposure in the GBR lagoon before 2008<sup>40,41</sup> were limited to comparing the particular herbicide concentration to the Australian and New Zealand Water Quality Guidelines<sup>42</sup> which, for most herbicides, defaults to the freshwater ecological protection trigger value. As these guidelines are not particularly suitable for the GBR lagoon, previous studies particularly used the LOEC developed for seagrass and coral species to assess risk<sup>43,44</sup>. In 2008/09 the Great Barrier Reef Marine Park Authority (GBRMPA), the managing body for the GBR, developed locally-derived ecological trigger values for the protection of the GBR<sup>45</sup>. These trigger values were developed under extensive consultation and peer review with ecotoxicologists, water quality scientists, managers and pesticide manufacturers and include all available 'toxicity' data for relevant marine plants and animals of the GBR. However, data produced using the PAM technique were not included. PAM measures the effect of a herbicide on the photosynthesis (or photoinhibition) of the target plant. Since most marine plants appear to be able to recover from low level herbicide exposure under laboratory conditions<sup>46,47,48</sup> its use as a 'toxicity' measure is questionable. However, a recent study on macroalgae has shown that the PAM technique compares closely to the more established toxicity measures such as growth rates and biomass increase<sup>49</sup>. GBRMPA recognised that this technique may soon become more widely accepted and produced an alternative set of guidelines incorporating the PAM data. Importantly, there is considerable variation between the alternative ecological trigger values and the currently adopted guidelines for most of the herbicides which inhibit photosynthesis through photosystem II (Table 1). While the development of the GBRMPA guidelines has been a fundamental step towards understanding the risk of herbicide residues in the GBR lagoon, there is confusion about which set of guidelines

is acceptable to protect the GBR. If the alternative guidelines that incorporate the PAM data are eventually adopted, the area of the GBR considered at risk from herbicide exposure would increase considerably<sup>50</sup>. This issue is currently the biggest challenge facing ecotoxicologists that study the GBR.

Other factors such as exposure/dosage time, additive effects and potential synergistic (enhanced) effects also make the assessment of risk in the GBR lagoon very difficult. Areas of the GBR may exceed the current guideline value for 12 hours to a couple of days, while the alternative GBR guideline (as well as LOEC for certain GBR plant species) may be exceeded from a few days up to one month<sup>51,52</sup>. It is presently unclear what implications long-term herbicide exposure may have on GBR ecosystems. In addition, the key herbicides detected in the GBR lagoon are all photosystem II inhibitors and thus, in combination, would have additive effects. Current research efforts are examining this<sup>53</sup>. There is also active research investigating the effects of herbicide exposure on corals in combination with different seawater temperatures predicted by future climate change scenarios.

Whilst considerable advances have been made in the last five years in understanding the risk of herbicide residues in the GBR lagoon, the impact of herbicide exposure to freshwater wetlands is much less certain. The current Australian and New Zealand ecological protection guidelines<sup>54</sup> for most of the key herbicides are of low reliability or not available. There are several coastal wetlands in the GBR catchment area that have been recognised as having international (RAMSAR) or national (that is listed on Australia's National Directory of Important Wetlands: ANCA) ecological significance and their management is imperative given their connectivity to the GBR<sup>55</sup>. Concentrations of herbicide residues are generally much higher in streams draining directly into these freshwater wetlands and so they are potentially even more threatened than the GBR lagoon. In addition, insecticides such as chlorpyrifos, diazinon and fipronil, other non-photosystem II inhibiting herbicides such as metolachlor and pendimethalin and the fungicide propiconazole have also been detected in passive samplers deployed at some river mouths<sup>56</sup>. The impact of this

**Table 1. Current and alternative GBRMPA guidelines for the protection of the Great Barrier Reef**

Herbicide	Current GBRMPA trigger value	Alternative GBRMPA trigger value
Diuron	900 ngL <sup>-1</sup>	10 ngL <sup>-1</sup>
Atrazine	600 ngL <sup>-1</sup>	500 ngL <sup>-1</sup>
Hexazinone	1200 ngL <sup>-1</sup>	90 ngL <sup>-1</sup>
Ametryn	500 ngL <sup>-1</sup>	200 ngL <sup>-1</sup>
Simazine	200 ngL <sup>-1</sup>	4300 ngL <sup>-1</sup>
Tebuthiuron	20 ngL <sup>-1</sup>	1800 ngL <sup>-1</sup>



The control of weeds using shielded sprayers is being encouraged as an improved management practice in the sugar industry. This approach targets weeds early, reduces the total amount of herbicide applied, uses products less susceptible to runoff (such as glyphosate), and reduces the need for residual herbicide control.

Photo: Rob Milla

'cocktail' of pesticides in freshwater ecosystems has not been studied.

### New farming management practices

The lower Burdekin sugarcane industry is implementing a variety of improved management practices in order to address concerns of potential losses of herbicides to the GBR. These practices include improvements in application methodologies and timings as well as a move towards less environmentally persistent products. The main principle of improved weed management is to control weeds early in the crop cycle – particularly during the fallow period when cheaper and less persistent products such as glyphosate and paraquat can be used. When this principle is combined with other changes such as minimum tillage and the use of legume fallow crops, weed seed germination is greatly reduced. This means there is less need for residual herbicides due to decreased weed pressure.

Queensland Primary Industries and Fisheries are promoting this improved farming system including a greatly reduced reliance on residual herbicides through the Demonstration Farms Project. This project showcases best management practices for water quality on two commercial scale farms in the lower Burdekin demonstrating significant economic and water quality benefits of the improved farming practices.

One of the methods used to control weeds using less residual herbicide is a shielded sprayer. Shielded sprayers utilise a shroud to cover spray nozzles in the furrow – meaning that a contact herbicide such as glyphosate or paraquat can be used with minimal potential for crop damage. If the weed pressure warrants the use of a residual

herbicide, this can be band sprayed over the crop area and not the furrow, thus minimising total product use over the paddock by up to 60%. The use of such tools allows farmers to achieve both cost savings and environmental improvements while maintaining appropriate levels of weed control.

A 'new' suite of herbicide active ingredients have been proposed as potential replacements for diuron, atrazine, hexazinone and ametryn in the sugarcane industry. These herbicides, which typically have much shorter half lives in surface waters (< three days), include imazapic, isoxaflutole and metribuzin. These products are highly soluble, highly mobile and, similarly to the currently used residual herbicides, have moderate-high toxicity to plants<sup>57</sup>. However, the shorter half lives suggest that their exposure in the environment should be much shorter than the current residual herbicides in widespread use.

### Government policy

The herbicides which have been identified as of concern to the GBR have been recognised by the Australian Federal and Queensland State Governments, both of which have committed to reducing herbicide runoff through the Reef Protection Plan<sup>58</sup>. The Federal Government has identified the wider water quality issues through the development of regional Water Quality Improvement Plans and has recently made funding available to assist graziers, sugarcane growers and horticulturists to adopt improved management practices that will reduce herbicide runoff. The Queensland Government has adopted a regulatory approach to herbicide management and plans to reduce the loads of the photosystem II inhibiting herbicides entering the

GBR by half by 2013, although the specific requirements for farmers have not yet fully emerged.

The Australian regulatory body for pesticide management, the Australian Pesticides and Veterinary Medicines Authority (APVMA) has recently completed a review of the herbicide atrazine primarily due to concerns about human and animal health (potential carcinogen), as well as environmental impacts including its potential to contaminate ground and surface waters<sup>59</sup>. The review concluded that amendments were required to product labelling including that atrazine is no longer to be used along drainage lines and it is to not be mixed, applied or handled in areas susceptible to runoff. However, no further restrictions to those implemented in 1997 were required on atrazine rates applied in the sugarcane industry or in dryland cropping. The use of diuron has also been under review. A preliminary report released in 2005 suggests that, at current application rates in the sugarcane industry, diuron is likely to have an unacceptable environmental impact<sup>60</sup>. However, any final recommendations have yet to be released.

### Conclusion

Residues of photosystem II herbicides including diuron, atrazine and tebuthiuron are present in the GBR catchment area and GBR lagoon at concentrations which exceed the appropriate LOEC and/or ecological protection trigger value guidelines. Therefore these residues are at levels which have the potential to harm freshwater and marine ecosystems of the GBR. While the knowledge of the sources, transport and fate of pesticide residues detected in the GBR has increased considerably over the last decade, there are several gaps in our knowledge base that limit the full appreciation of pesticide risk to both the freshwater and marine ecosystems of the GBR (such as freshwater wetlands, mangroves, seagrass and coral reefs). Advances in the fields of monitoring (passive samplers) and ecotoxicology (controlled environmental experimentation) are helping to improve risk assessments. New farming initiatives are being adopted in certain areas of the GBR catchment area to help reduce the use and offsite movement of these problematic herbicides with assistance from Federal and State Government's Reef Plan incentive funding.

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## Endosulfan one step closer to listing under POPs convention

The fifth meeting of the Persistent Organic Pollutants Review Committee of the Stockholm Convention was held from 12 to 16 October 2009 in Geneva. The 31 Committee members gathered to review the chemicals proposed for listing in the Convention (hexabromocyclododecane, endosulfan, and short-chained chlorinated paraffins).

The Committee reviewed and adopted a revised draft risk profile on endosulfan under which it agrees that the POP characteristics of the chemical warrant global action. The Committee decided to develop

a risk management evaluation document for endosulfan that includes an analysis of possible control measures for consideration at its next meeting and final recommendation to the Conference of the Parties (COP) to the Stockholm Convention for its listing in the Annexes of the Convention.

This meeting of the Review Committee will take place next year and will hopefully recommend endosulfan to the COP for inclusion in the Convention in 2011 leading to a global ban.

<http://chm.pops.int/>

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