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Herbicide contamination and the potential impact to seagrass meadows in Hervey Bay, Queensland, Australia

Kathryn McMahon [a,*], Susan Bengtson Nash [b], Geoff Eaglesham [c], Jochen F. Müller [b]
Norman C. Duke [a], Steve Winderlich [d]

[a] *Centre for Marine Studies, University of Queensland, Brisbane, Queensland 4072, Australia*
[b] *National Research Centre of Environmental Toxicology, University of Queensland, Brisbane, Queensland 4108, Australia*
[c] *Queensland Health Scientific Services, 39 Kessels Road, Coopers Plains, Queensland 4108, Australia*
[d] *Queensland Environmental Protection Agency, PO Box 101, Maryborough, Queensland 4650, Australia*

Abstract

Low concentrations of herbicides (up to 70 ng l^{-1}), chiefly diuron (up to 50 ng l^{-1}) were detected in surface waters associated with inter-tidal seagrass meadows of *Zostera muelleri* in Hervey Bay, south-east Queensland, Australia. Diuron and atrazine (up to 1.1 ng g^{-1} dry weight of sediment) were detected in the sediments of these seagrass meadows. Concentration of the herbicides diuron, simazine and atrazine increased in surface waters associated with seagrass meadows during moderate river flow events indicating herbicides were washed from the catchment to the marine environment. Maximum herbicide concentration (sum of eight herbicides) in the Mary River during a moderate river flow event was 4260 ng l^{-1}. No photosynthetic stress was detected in seagrass in this study during low river flow. However, with moderate river flow events, nearshore seagrasses are at risk of being exposed to concentrations of herbicides that are known to inhibit photosynthesis.

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Keywords: Seagrass; Herbicide; *Zostera muelleri*; Hervey Bay; Queensland; Diuron; Flood

1. Introduction

Herbicides including diuron (3-(3,4-dichlorophenyl)-1, 1-dimethyl-urea), atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine), ametryn (2-ethylamino-4-isopropylamino-6-methylmercapto-*s*-triazine) and Irgarol 1051 (2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine) have been detected in coastal sediments and seagrasses along the coast of Queensland (Duke et al., 2001; Duke and Bell, in press; Duke et al., 2003; Haynes et al., 2000a; Scarlett et al., 1999). These herbicides are known to inhibit photosynthesis of plants (Oettmeier, 1992). The concentration of herbicide detected in seagrass sediments of the Great Barrier Reef Marine Park has been recorded as high as 1.7 μg kg^{-1} for diuron and 0.3 μg kg^{-1} for atrazine (Haynes et al., 2000a). Potential concentrations of herbicides in water have been inferred from this data as 100 ng l^{-1} of diuron. Irgarol has been detected in seagrass tissue up to 790 μg kg^{-1} dw (Scarlett et al., 1999).

Studies in a variety of seagrass species have shown photosynthesis is inhibited within hours by exposure to 10000 ng l^{-1} of the herbicides diuron, atrazine and simazine (Haynes et al., 2000b; Macinnis-Ng and Ralph, 2003). Smaller species such as *Halophila ovalis* seem to be impacted by water concentrations as low as 100 ng l^{-1} of diuron (Haynes et al., 2000b). With removal of herbicides seagrass photosynthesis can recover, although with exposure to higher concentrations

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[*] Corresponding author. Fax: +61 7 3365 7321.
E-mail address: k.mcmahon1@uq.edu.au (K. McMahon).

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recovery is slower or with 100 000 ng l^{-1} there may be no recovery in some species (Haynes et al., 2000b; Macinnis-Ng and Ralph, 2003).

Haynes et al. (2000a) proposed that herbicide concentrations detected in Queensland coastal sediments have the potential to impact the local seagrass communities. The coastal seagrass meadows support fourteen seagrass species out of the possible fifteen species present in Queensland (Carruthers et al., 2002). This habitat is also highly productive, supports a high biodiversity and provides an important nursery ground for commercial fisheries (Loneragan et al., 1994). Coastal seagrass habitats are dynamic and variable, with episodic cyclones, storms and floods causing severe impacts at a local scale (Carruthers et al., 2002; Preen et al., 1995). This habitat is also one of the most likely to be impacted by herbicides originating from the catchment or from leaching of antifoulant paints on boats (Haynes and Michalek-Wagner, 2000; Scarlett et al., 1999).

Major seagrass loss has occurred in Hervey Bay, south-east Queensland, Australia in 1992 and again in 1999 where up to 90% of the existing meadows were lost due to cyclone and flood events (Campbell and McKenzie, 2004; Preen et al., 1995). During both events seagrass was lost due to turbid river plumes lowering light reaching the seagrass, and from physical removal of seagrass caused by the cyclone and storms (Preen et al., 1995; Longstaff et al., 1999). Many of the intertidal seagrass meadows were completely lost after the flood. The combined effect of reduced ambient light and the potential flood-associated surge in herbicide concentration may have greatly impacted the seagrass, causing the massive losses observed.

This paper investigates the relationship between herbicide contamination and seagrass health in intertidal seagrass meadows of Hervey Bay, three years after the 1999 flood that resulted in extensive seagrass loss. The concentration and composition of herbicides present over a range of flow conditions and the potential impacts to seagrass is discussed. This paper is complimented by the concurrent investigation by Bengtson Nash et al. (in press, this issue) which assesses herbicide contamination using a novel phytotoxicity test.

2. Methods

2.1. Regional description

The Hervey Bay region has a sub-tropical climate with most rain falling between January and April and the highest river flows at this time, although there is a high inter-annual variability in the amount of rainfall. River flow is positively correlated with rainfall events. Hervey Bay is a large (3940 km^2), U-shaped bay formed by a sand island to the east (Fraser Island) and mainland Australia to the west (Fig. 1). Maximum water depth within the bay is 30 m with a tidal range of 4.1 m. Extensive inter-tidal banks of fine to medium grained sands fringe the landward side of the bay, supporting extensive though sparse seagrass meadows. The Mary and Burrum rivers flow into Hervey Bay. The Great Sandy Straits is a sand passage estuary of 931 km^2 between the mainland and Fraser Island. There were 55 km^2 of dense inter-tidal seagrass meadows in 1999 (McKenzie et al., 2000). The Great Sandy Straits is more protected than Hervey Bay with the Mary River draining to this region, however many smaller creeks also discharge into it. The Mary River has a catchment of 9595 km^2 with the main activities dry land grazing (60%), native forestry (27%), plantation forestry (7%) and agriculture (8%) (EPA, 2001). The Burrum catchment is 3118 km^2 with native forestry and agriculture the major activities. Most intensive agriculture is located in the lower catchment of both rivers. Annual diuron application rates in sugar cane cultivation areas in the 1990s were reported as 9600 kg/active ingredient for

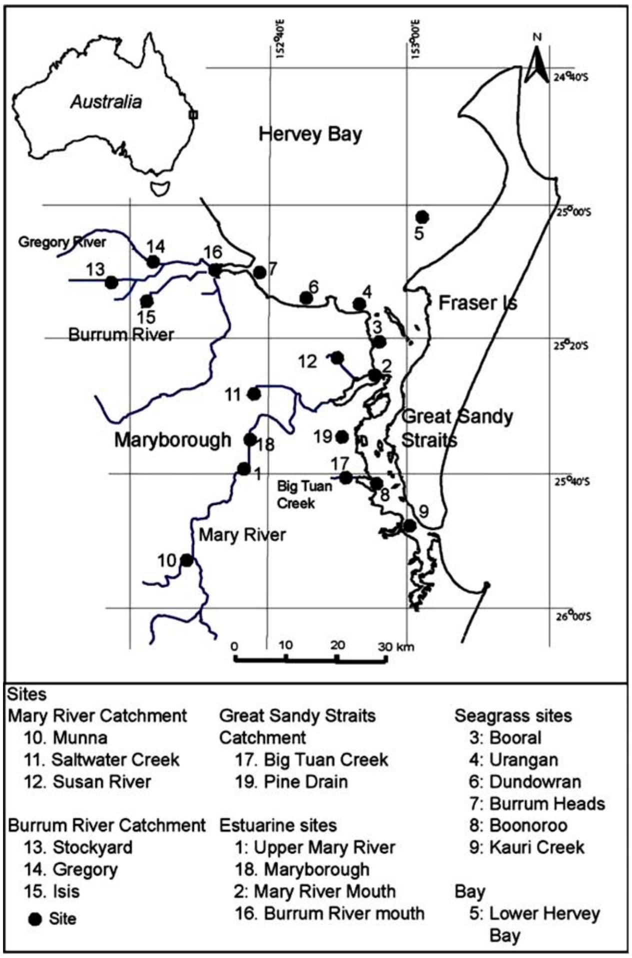

Fig. 1. Location of sites in the fresh and estuarine sections of the Mary and Burrum rivers and the tributaries of the Great Sandy Straits and the marine sites in Hervey Bay and the Great Sandy Straits where samples were collected for this study.

the Mary River catchment and 3300 kg/ai for the Burrum River catchment (Hamilton and Haydon, 1997). There is no census on application rates of other herbicides in the region or with other catchment activities.

2.2. Sampling strategy

Field sampling was conducted over four periods (Table 1). April 22–May 1, 2002 and December 10–17, 2002 were low river flow periods (total monthly discharge 2280 and 2080 ML respectively) and February 2003 and 2004 were moderate river flow periods (total monthly discharge 347 890 and 216 581 ML respectively) (DNRM, 2004). There was low rainfall in 2002 and the preceding two years in the study region (Bureau of Meterology, 2004). The first river flush for over one year occurred in February 2003, peaking at 500 $m^3 s^{-1}$ and followed the highest monthly rainfall since the 1999 flood, 350 mm. In February 2004 there was another large rainfall event, with a monthly total of 300 mm and a peak river flow of 450 $m^3 s^{-1}$ (Bureau of Meterology, 2004; DNRM, 2004).

Nine sites, estuarine and marine, were sampled in April and December for surface water herbicide contamination and additionally, six of these sites for seagrass photosynthetic measures. The sampling location in the seagrass meadows was standardised by selecting the part of the meadow closest to shore. April was identified as a low growing season for seagrass and a potentially low herbicide application period, December as a peak growing season for seagrass and a potentially high herbicide application period, where herbicides are applied to combat pre-emergent weeds at the start of the wet season (Jones and Kerswell, 2003). In December 2002 a number of fresh water tributaries in the Mary River, Burrum River and Great Sandy Straits catchment were sampled to assess herbicide contamination in surface water. Opportunistic sampling was conducted in February 2003 and February 2004 to examine the relationship between rainfall, river flow and herbicide contamination in surface waters. To examine the temporal variation in herbicide contamination over a river flow event, six samples were collected at one location in the Mary River. Sediment samples were collected at a number of sites in April and December and analysed for herbicide contamination (Table 1, Fig. 1). No herbicide determination was conducted on seagrass leaves.

Table 1
Sampling strategy employed for this study including the number of samples collected at each site for each period

	Surface water Apr & Dec 2002	Sediment Apr & Dec 2002	Surface water tributaries Dec 2002	Surface water Feb 2003	Surface water Feb 2004	Seagrass health Apr & Dec 2002
Mary River catchment						
10. Munna			1			
11. Saltwater Creek			1			
12. Susan River			1			
Burrum River catchment						
13. Stockyard			1			
14. Gregory			1			
15. Isis			1			
Great Sandy Straits catchment						
17. Big Tuan Creek			1	1	1	
19. Pine Drain					1	
Estuarine sites						
1. Upper Mary River Maryborough	1	1		1		
18. Mary River, Maryborough				6	1	
2. Mary River mouth	1					
16. Burrum River mouth			1			
Seagrass sites						
3. Booral	1	1			1	√
4. Urangan	1			1		√
6. Dundowran	1	1				√
7. Burrum Heads	1	1			1	√
8. Boonoroo	1				1	√
9. Kauri Creek	1				1	√
Bay						
5. Lower Hervey Bay	1	1[a]				

[a] Samples only collected in December 2002.

2.3. Herbicides

Surface water samples were collected, treated and analysed as described in Bengtson Nash et al. (in press, this issue). All water samples from fresh, estuarine and marine sites were collected following high tide, on the out-going tide, except at Maryborough (site 18) for the river flow sampling, where six samples were collected over the in-coming and out-going tide. This site was located 55 km upstream of the Mary River mouth, so any discharge from downstream tributaries may influence this site, however, due to the large distance from the river mouth, it is highly unlikely marine sources would reach this site. The surface water samples were analysed for eight herbicides by Liquid Chromatography–Mass Spectrophotometry (LC–MS), diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea), atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine), hexazinone (3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazine-2,4 (1*H*,3*H*)-dione), ametryn (2-ethylamino-4-isopropylamino-6-methylmercapto-*s*-triazine), tebuthiuron (1-(5-*tert*-butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea), simazine (6-chloro-N^2,N^4-diethyl-1,3,5-triazine-2,4-diamine), flumeturon (1,1-dimethyl-3-(a,a,a-trifluoro-*m*-toly) urea) and prometryn (N^2,N^4-diisopropyl-6-methylthio-1,3,5-triazine-2,4-diamine). The limit of detection was set at three times the baseline; here we report the limit of quantification (LOQ) as 5 ng l^{-1}. The majority of these herbicides are used for weed control and target herbaceous plants, except tebuthiuron, which targets woody plants.

Three sub-samples of sediment were collected with a benthic grab, pooled and mixed thoroughly to make up the site sample. The herbicide content of around 50 g for each sample was extracted by adding 100 ml of acetone and shaking for 12 h. The solution was transferred to a separating funnel. A further 100 ml of acetone was used to rinse the glassware and was added to the separating funnel. 200 ml of dichloromethane (DCM) was added to the funnel, the solution mixed thoroughly and left to settle out in phase. The organic layer was removed and evaporated using a rotary evaporator. The concentrate was transferred to test tubes and 6 ml of hexane added. Exactly 1 ml of deionised water was added and the organic layer removed under a gentle stream of nitrogen gas. Finally 1 ml of methanol was added to make up a final extract volume of exactly 2 ml. This extract was analysed by LC–MS as described in Bengtson Nash et al. (in press, this issue).

2.4. Impacts to seagrass

The seagrass, *Zostera muelleri* Irmisch ex Ascherson (formally *Z. capricorni*) was examined at each site in April and December 2002, except for Dundowran (site 6) in April 2002 where only *Halodule uninervis* (Forsskål) Ascherson seagrass was present. The maximum quantum yield of photosystem II (F_v/F_m) (dark adapted) of 10 plants were measured at each site with a diving PAM (WALZ). Values below 0.75 indicate photoinhibition of the plant and dark adapted maximum quantum yield indicate damage to the plants photosystems or photosynthetic stress (see Bolhar-Nordenkampf et al., 1989; Maxwell and Johnson, 2000). Different herbicides have different modes of action on how they affect plants and can interfere with unique pathways of the photosynthetic cycle (Ralph, 2000). However, the outcome of each action, if the amount of herbicide is high enough will be to cause photoinhibitory damage (Maxwell and Johnson, 2000). In other studies effective quantum yield ($\Delta F/F'_m$) has been used to determine the impact of herbicides on seagrass photosynthesis (Haynes et al., 2000b; Macinnis-Ng and Ralph, 2003). The nature of the current study was to sample across a range of sites at low tide and only one site could be sampled in a day. Therefore the time of sampling and the recent light history that affects photosynthetic parameters varied between sites, and light adapting the plants before measurement was not feasible. As a consequence effective quantum yield, a more precise measure of the instantaneous photoinhibition was not considered a suitable measure and the more conservative dark adapted maximum quantum yield was chosen as an indicator of photosynthetic stress. Intact plants were removed from the meadow, stored in moist plastic bags and transported back to shore. The plants were dark adapted for 15 min within one hour of collection and then one leaf from each shoot was measured directly above the leaf sheath. If leaves were less than 1mm wide all the leaves from the shoot were used in the measurement. Leaf width (mm) varied between sites, 0.5 ± 0.1 to 2.7 ± 0.2 (site average with standard error) (McMahon et al., 2003).

Chlorophyll concentrations were assessed at each site from a sub-set of five plants collected for maximum quantum yield measures. Following PAM measurements the plants were stored in moist plastic bags in the dark at 0 °C and a piece of basal leaf from each plant was weighed and frozen in the dark within 12 h of collection. The leaf material was ground in 10 ml of 90% acetone and stored overnight in the dark at 0 °C. The solution was centrifuged at 2000 rpm for 15 min. Absorbance was measured with a spectrophotometer at wavelengths of 725, 663 and 645 (Dennison, 1990) and Chlorophyll *a* and *b* calculated according to Arnon (1949) and expressed as mg Chl g fresh weight^{-1} seagrass leaf. A two-way analysis of variance was conducted to determine if there were significant differences in chlorophyll concentration between site and sampling time on the statistical package R1.9.0. No seagrass measures were taken in February 2003 and 2004 due to logistical constraints.

3. Results

3.1. Herbicide contamination of surface water during low river flow conditions

In April 2002 with low river flow, total herbicide concentration ranged from <5 to 65 ng l^{-1} and in December 2002 also with low river flow, concentrations ranged from <5 to 165 ng l^{-1} at estuarine and marine sites (Table 2). Five of the eight herbicides, diuron, atrazine, simazine, ametryn and hexazinone, were detected in the Mary River during this time. The herbicide with the highest concentration was diuron (Table 2). Diuron was the only herbicide detected in coastal waters above seagrass meadows in April and December (Table 2).

The Upper Mary River (site 1) consistently had the highest total herbicide concentrations. Water was brackish at 5 ppt salinity and the tidal range was 3 m. The sites with the lowest herbicide concentrations were in the coastal waters, <5–25 ng l^{-1}. At Booral (site 3), Dundowran (site 6), Burrum Heads (site 7), Kauri Creek (site 9) and Lower Hervey Bay (site 5), the concentration did not exceed 5 ng l^{-1} (Table 2).

3.2. Herbicide contamination of surface water during moderate river flow events

In February 2003 following rainfall, the total monthly river discharge was seven times greater than the April and December 2002 sampling. Five herbicides, diuron, simazine, atrazine, hexazinone and ametryn, were detected in the flowing fresh water in the Mary River, Maryborough (site 18) at this time (Table 3). These water samples were collected 35–62 h after the peak river flow (500 m^3 s^{-1}) equating to approximately half (230 m^3 s^{-1}) and a fifth (90 m^3 s^{-1}) of the peak discharge. There was no correlation with river discharge rate and concentration of total herbicides. Simazine was found at the highest, and also the most variable concentration, ranging from below detection to 4150 ng l^{-1}, with a mean 1870 ng l^{-1} at Mary River (site 18). The highest concentrations of simazine were detected on the in-coming tide. Diuron was also variable over time, 20–105 ng l^{-1}, with a mean of 55 ng l^{-1}. Atrazine remained steady over time at 5–10 ng l^{-1} whereas concentrations of hexazinone and ametryn were detectable but below the limit of quantification of 5 ng l^{-1} (Table 3).

Table 2
Herbicide composition and concentration from surface water samples collected in April and December 2002 with low flow of the Mary River

	Diuron		Atrazine		Simazine		Hexazinone		Ametryn		Tebuthiuron		Total	
	Apr	Dec	Apr	Dec	Apr	Dec	Apr	Dec	Apr	Dec	Apr	Dec	Apr	Dec
Mary River catchment														
10. Munna	–	<5	–	<5	–	50	–	nd	–	<5	–	nd	–	55
11. Saltwater Creek	–	25	–	10	–	<5	–	nd	–	nd	–	55	–	90
12. Susan River	–	25	–	nd	–	nd	–	nd	–	nd	–	nd	–	25
Burrum River catchment														
13. Stockyard	–	<5	–	10	–	nd	–	nd	–	nd	–	nd	–	10
14. Gregory	–	60	–	110	–	nd	–	nd	–	10	–	nd	–	180
15. Isis	–	<5	–	<5	–	nd	–	nd	–	nd	–	nd	–	10
Great Sandy Straits catchment														
17. Big Tuan Creek	–	10	–	nd	–	nd	–	nd	–	nd	–	nd	–	10
Estuarine sites														
1. Upper Mary River	45	80	10	25	10	30	<5	nd	nd	<5	nd	nd	65	165
2. Mary River mouth	<5	5	nd	nd	nd	<5	nd	nd	nd	nd	nd	nd	<5	10
16. Burrum River mouth	–	<5	–	nd	–	nd	–	nd	–	nd	–	nd	–	<5
Seagrass sites														
3. Booral	<5	<5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	<5	<5
4. Urangan	5	10	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	5	10
6. Dundowran	<5	<5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	<5	<5
7. Burrum Heads	nd	<5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	<5
8. Boonoroo	<5	25	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	<5	25
9. Kauri Creek	nd	<5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	<5
Bay														
5. Lower Hervey Bay	<5	5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	<5	5

Concentration in ng l^{-1}, nd = not detected, – = no samples collected.

Table 3
Herbicide composition and concentrations during a river flow event in February 2003 in the Mary River, Maryborough (18)

Date	Time	River flow	Tides	Diuron	Atrazine	Simazine	Hexazinone	Ametryn	Total
7th	11:50	240	In-coming	60	5	3240	<5	<5	3310
	17:00	200	Out-going	30	5	nd	nd	nd	35
	19:15	200	Out-going	25	10	<5	nd	nd	35
8th	10:30	100	Low	20	5	5	nd	<5	30
	12:30	90	In-coming	85	10	3825	5	<5	3925
	14:30	80	High	105	5	4150	nd	nd	4260

River flow is the instantaneous discharge measured in m^{3} s^{-1} at Home Park gauging station (DNRM, 2004) and tide direction is calculated from tide tables (Bureau of Meterology, 2004). Herbicide concentration is in ng l^{-1}, nd = not detected.

In February 2004, following another rainfall event of 152 mm, three herbicides were detected in the Mary River (site 18), diuron, atrazine and simazine (Table 4). These water samples were collected 160 h after the rainfall event on 3rd February. The Mary River had moderate concentrations of diuron (35 ng l^{-1}) and simazine (25 ng l^{-1}) and low concentrations of atrazine (<5 ng l^{-1}) (Table 4).

3.3. Herbicide contamination in catchments

In December 2002 five herbicides, diuron, atrazine, simazine, tebuthiuron and ametryn, were detected in the fresh water tributaries leading into the Mary River and the Burrum River and also Big Tuan Creek leading into the Great Sandy Straits near Boonoroo (Table 2). Each catchment had a unique combination of herbicides. All five herbicides were detected in the Mary River tributaries. Diuron, atrazine and ametryn were detected in the Burrum River tributaries and diuron was detected in Big Tuan Creek (site 17). Once again diuron was the most common herbicide detected. The highest total concentration of herbicides detected was in the Gregory River (site 14), a tributary of the Burrum River at 180 ng l^{-1}, predominantly atrazine, 110 ng l^{-1} and diuron 60 ng l^{-1}. This site was surrounded by sugar cane fields (Table 2).

During the rainfall and river flow event Big Tuan Creek (site 17) was also surveyed. In February 2003 diuron (50 ng l^{-1}) and atrazine (10 ng l^{-1}) were detected (Table 4). In February 2004 only simazine (355 ng l^{-1}) was detected (Table 4). The highest concentration of diuron in this study, 895 ng l^{-1} was detected at Pine Drain (site 19) during the February 2004 rainfall event (Table 4).

3.4. Herbicide contamination in seagrass meadows

Diuron was the main herbicide detected in waters associated with seagrass meadows, ranging from <5 to 50 ng l^{-1} (Table 2 and 4). Simazine and atrazine were detected only during moderate river flow events, with 10–30 ng l^{-1} and <5–10 ng l^{-1} respectively (Table 4). Surface water concentrations were higher during moderate river flow events, maximum of 70 ng l^{-1} compared to low river flow periods, maximum of 25 ng l^{-1} (Fig. 2). The seagrass sites Booral (site 3), Urangan (site 4) and Boonoroo (site 8) had the highest herbicide concentrations (Tables 2 and 4). Both diuron (0.1–0.2 μg kg^{-1} dry weight) and atrazine (0.2–1.1 μg kg^{-1} dry weight)

Table 4
Herbicide composition and concentration following a rainfall event and moderate river flow in February 2003 and 2004 at a number of river, catchment and coastal sites

	Date	Diuron	Atrazine	Simazine	Flumeturon	Total
Great Sandy Straits catchment						
17. Big Tuan Creek	6 Feb 2003	50	10	nd	nd	60
17. Big Tuan Creek	8 Feb 2004	nd	nd	355	nd	355
19. Pine Drain	6 Feb 2004	875	20	nd	<5	895
Mary River estuarine sites						
1. Upper Mary River	19 Feb 2003	25	<5	45	nd	70
18. Maryborough	10 Feb 2004	35	<5	25	nd	65
Seagrass sites						
4. Urangan	8 Feb 2003	20	10	5	nd	35
3. Booral	9 Feb 2004	50	10	10	nd	70
7. Burrum Heads	9 Feb 2004	nd	nd	nd	nd	nd
8. Boonoroo	8 Feb 2004	10	<5	25	nd	40
9. Kauri Creek	11 Feb 2004	10	<5	10	nd	25

Concentration in ng l^{-1}, nd = not detected.

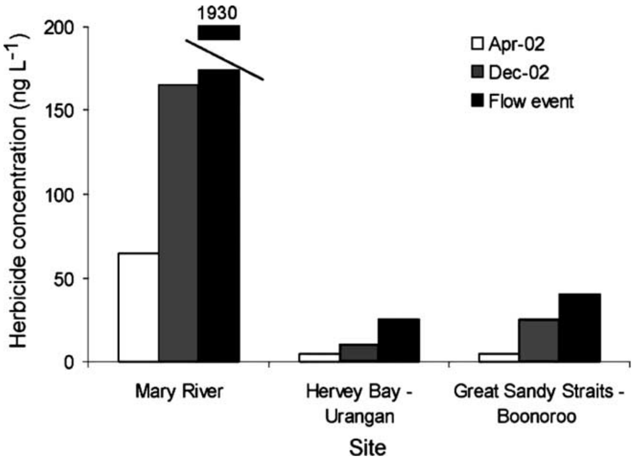

Fig. 2. Temporal variation in the total herbicide concentration of surface waters at three selected sites, Mary River, Urangan in Hervey Bay and Boonoroo in the Great Sandy Straits. Samples were collected in April and December 2002, following low river flow and rainfall and then in February 2003 (Mary River, $n = 6$; Urangan, $n = 1$) and 2004 (Boonoroo, $n = 1$) following rainfall events of >200 mm. Concentrations are expressed as the sum of eight herbicides (ng l^{-1}). Where more than one sample was analysed the mean concentration is displayed. For further details of herbicide composition consult Table 2.

were detected in sediments associated with seagrass but only the sites Booral (site 3), Dundowran (site 6) and Burrum Heads (site 7) were sampled (Table 5).

3.5. Seagrass photosynthetic measures

There was no indication of photosynthetic stress to seagrass at any of the sites in both April 2002 and December 2002. Dark adapted maximum quantum yield (F_v/F_m) was consistently above 0.7 (Table 6). There was no correlation detected between F_v/F_m and herbicide concentration in the water at the site.

Chlorophyll concentration varied between sites ($F = 9.92$, df = 5, $p < 0.00$) and also between sampling times ($F = 4.7$, df = 1, $p = 0.03$). Concentrations ranged from 1.22 ± 0.11 to 4.66 ± 0.29 mg Chl ($a + b$) g wet wt^{-1}. The seagrass at Dundowran (site 6), with very small morphology and leaf widths <0.5 mm, had significantly higher chlorophyll per weight of leaf than seagrass collected at all other sites. There was no correlation between herbicide concentration in the water and chlorophyll concentration (Table 6).

Table 5
Sediment herbicide concentrations of diuron and atrazine (μg kg^{-1} dry weight sediment) at 5 sites in Mary River, Hervey Bay and the Great Sandy Straits in April and December 2002

Site	Diuron		Atrazine	
	April	Dec	April	Dec
Mary River estuarine site				
1. Upper Mary River	0.4	1.5	nd	nd
Seagrass sites				
3. Booral	0.1	nd	nd	0.4
6. Dundowran	nd	0.2	nd	0.2
7. Burrum Heads	nd	nd	1.1	0.4
Bay				
5. Lower Hervey Bay	–	nd	–	0.4

nd = not detected, – = no sample collected.

4. Discussion

Herbicides were detected in the catchment and marine environment of Hervey Bay and the Great Sandy Straits. There are a number of potential sources of herbicides in the marine environment. Herbicides can enter the aquatic environment from the catchment both dissolved in water and attached to sediment (Müller et al., 2000; Rayment, 2003) and through groundwater input (Finlayson and Silburn, 1996; Keating et al., 1996; Schwarzschild et al., 1994). There are many activities in the lower catchments adjacent to Hervey Bay and the Great Sandy Straits that use herbicides and are potential sources of these compounds; sugar cane and pineapple cultivation, forestry plantations and weed management for council, railways and residential areas. Herbicides can also be released from boat anti-fouling paint into estuarine and marine waters (Scarlett et al., 1999).

4.1. Herbicide sources

This study does not fully examine the sources of herbicides, but sheds light on potential sources requiring further investigation. The herbicides present in the marine environment of Hervey Bay are diuron, atrazine and simazine. Diuron can be sourced from both the catchment and also anti-fouling paints on boats, whereas atrazine and simazine are only likely to be sourced from the catchment. Different catchments in the region had a unique suite of herbicides in the surface waters. Mary River and Big Tuan Creek had relatively high simazine concentrations, the dominant herbicide with river flow following rain events. Sampling in the Mary River catchment indicated a potential source of simazine from Munna (site 10), approximately 55 km upstream from the town of Maryborough. Simazine may also be sourced from downstream of Maryborough as indicated from the peaks of simazine with the in-coming tide during the river flow event in February 2003. This downstream source is very unlikely to be from the marine environment, as the sampling occurred 50 km upstream of the river mouth, but may be from other tributaries leading in to the Mary River, immediately downstream of the sampling site. Simazine was also detected in coastal waters at Urangan (site 4), approximately 55 km from the Mary River site (site 18). The ratio of simazine to

Table 6
Average maximum quantum yield (F_v/F_m) and Chlorophyll $a + b$ (mg Chl g wet weight^{-1} of seagrass) of *Zostera muelleri* from 5 sites in Hervey Bay and the Great Sandy Straits and *Halodule uninervis* from Dundowran in April

Site	Maximum quantum yield (F_v/F_m)		Chlorophyll $a + b$ (mg Chl g wet wt^{-1})	
	April 2002	Dec 2002	April 2002	Dec 2002
3. Booral	0.764 ± 0.010	Not measured	2.37 ± 0.59	1.67 ± 0.24
4. Urangan	0.762 ± 0.007	0.760	1.84 ± 0.51	3.01 ± 0.29
6. Dundowran	Not measured	Not measured	4.29 ± 0.70	4.66 ± 0.29
7. Burrum Heads	0.747 ± 0.022	0.702 ± 0.018	1.22 ± 0.11	2.13 ± 0.19
8. Boonoroo	0.779 ± 0.007	0.762 ± 0.007	2.20 ± 0.35	2.02 ± 0.30
9. Kauri Creek	0.754 ± 0.012	0.706 ± 0.014	1.60 ± 0.25	2.00 ± 0.26

A yield value under 0.700 would indicate photosynthetic stress ($n = 10$). Chlorophyll readings $n = 5$. No yield measurements were taken at Dundowran and at Booral in December. Variation is expressed as standard error.

diuron decreased from the river (average 22) to the coastal site (2). This could indicate simazine is lost from the water column faster than diuron, or that additional sources of diuron are entering the plume before reaching Urangan (site 4). In December 2002, the surface waters of Saltwater Creek (site 11) and Susan River (site 12), tributaries downstream of Maryborough, contained predominantly the herbicide diuron, 25 ng l^{-1}, supporting the hypothesis of additional diuron inputs. Approximately 1 km from the Urangan site is a relatively large boat harbour with a maximum capacity of 176 berths. During moderate river flow events, diuron is delivered from the catchment, however during the low river flow periods the source of low concentrations of diuron is unclear. Residual inputs from previous river flow events and release from boat anti-fouling paints are two possible sources.

In the Burrum catchment, the Gregory River (site 14) had the highest concentration of herbicide from all the tributaries sampled. This is an intensive sugar cultivation region and previous studies have identified movement of herbicides from sugar cane cultivation (Rayment, 2003). Both diuron and atrazine were present in the tributaries where herbicides were detected. However, at the mouth of the Burrum River (site 16) and the nearby Burrum Heads (site 7) seagrass site, only diuron was present. This indicates atrazine was not reaching the marine environment at that time.

Diuron, atrazine and simazine were detected in Big Tuan Creek (site 17) and the adjacent seagrass site, Boonoroo (site 8). There are a number of potential sources of herbicides in this catchment. The catchment landuse of this tributary is predominantly pine plantation forestry. Big Tuan Creek is also a smaller harbour with 15 boats permanently moored.

4.2. Temporal variations in herbicide concentration

During the major sampling period of 2002, river flow was low with monthly river discharge of 2280 ML in April and 2080 ML in December. The maximum monthly discharge between these two sampling periods was 5000 ML. In February 2003, the monthly discharge was almost seven times greater at 34 800 ML (DNRM, 2004). This was induced by a rainfall event approximately 130 mm greater than the 10 year average (Bureau of Meterology, 2004). Herbicide contamination in rivers usually increases during rain and river flow events (Cooper and Riley, 1996; Finlayson and Silburn, 1996) and this was demonstrated in the current study.

Total herbicide concentrations in Mary River, Maryborough (site 18) during the flow event were up to 30 times those recorded in April and December 2002 in the Mary River (site 1). The dominant herbicide at this time was simazine, followed by diuron. Interestingly, there was a large variation in the concentration detected over the seven samples. This variation was mostly due to large fluctuations in simazine concentration. There was no relationship between flow rate and herbicide concentration, indicating that there is a complex relationship between river flow and herbicide delivery. The site where samples were collected during this event is under the influence of tides, and peak simazine concentrations were observed when samples were collected during the in-coming tide. This may indicate a source of simazine from a tributary immediately downstream of the sample collection point.

4.3. Significance of herbicides

Although there were differences in the concentration of herbicide detected between low flow (April and December 2002) and moderate flow (February 2003 and 2004), the concentrations were generally low. Studies have detected diuron concentrations as high as 8500 ng l^{-1} in other rivers in Queensland during flow events (White et al., 2003). During a flood event in the Mary River in January 1996 (total monthly flow 626 000 ML) a maximum of 200 ng l^{-1} of diuron was detected in surface waters. This is double the maximum concentration of diuron detected in the current study in the Mary River (Rayment et al., 1997). In February 2004 following 152 mm of rain, the highest concentration of diuron, 895 ng l^{-1} was detected in a small, ephemeral drain flowing from a pine plantation (site 19).

Simazine concentrations exceeded the Australian and New Zealand Environment and Conservation Council (ANZECC) water quality guideline 95% trigger value (ANZECC, 2000) during the moderate river flow event in February 2003 at Mary River (site 18) and the same guideline was exceeded with diuron during the 2004 rainfall event at Pine Drain (site 19). The ANZECC guidelines for diuron acknowledge that there is not enough information available to accurately set guidelines for this herbicide, not just in relation to seagrass but for the health of the entire ecosystem. Although the guidelines were not exceeded at other sites and times, it is unclear whether chronic exposure to low levels of herbicide and pulses of elevated herbicide during river flow and flood events are causing environmental effects.

4.4. Herbicide and seagrass

To our knowledge, this study provides the first account of herbicide concentrations for surface waters associated with coastal seagrass in Australia. No photosynthetic stress of seagrass was observed with the very low concentration of herbicides detected during low river flow periods. However, the photosynthetic measure of maximum quantum yield was a very conservative measure of photosynthetic stress. Effective quantum yield would be a more sensitive indicator of stress. The herbicide concentrations present in seagrass habitats are below the concentrations which are known to impact seagrass photosynthesis, based on laboratory and field studies (Chesworth et al., 2004; Haynes et al., 2000b; Macinnis-Ng and Ralph, 2003; Ralph, 2000). However, these studies on impacts to seagrasses from herbicide focused on short-term exposure. It is not known whether there would be impacts to seagrass health from chronic exposure to 10–50 ng l^{-1} of herbicides such as diuron, atrazine and simazine.

To our knowledge, this study is also the first record of the herbicide atrazine in sediments associated with seagrass meadows in Australia. Diuron was also detected in these sediments, but at lower concentrations than those found by Haynes et al. (2000a). Little is known of the potential impacts to seagrass exposed to chronic levels in the sediments.

4.5. Conclusion

There are low background levels of herbicides, predominantly diuron in the water (<25 ng l^{-1}) and diuron and atrazine in the sediment (up to 1.1 μg kg^{-1} wet weight) associated with seagrass during low river flow periods (monthly discharge of ~2000 ML). From our studies there is no detectable impact to seagrasses at these low concentrations. Following rainfall and moderate river discharge (monthly discharge of ~200 000 ML), herbicides are delivered from the catchment and the herbicide concentrations in the waters above seagrass meadows increase up to 70 ng l^{-1}, close to the concentrations known to impact seagrass photosynthesis. The photosynthetic stress of seagrass was not determined during moderate river flow events. Considering up to 70 ng l^{-1} was detected in moderate river flow event, there is a risk that concentrations high enough to directly impact seagrasses are likely during a flood event.

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