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Glyphosate persistence in seawater

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ABSTRACT

Glyphosate is one of the most widely applied herbicides globally but its persistence in seawater has not been reported. Here we quantify the biodegradation of glyphosate using standard "simulation" flask tests with native bacterial populations and coastal seawater from the Great Barrier Reef. The half-life for glyphosate at 25 °C in low-light was 47 days, extending to 267 days in the dark at 25 °C and 315 days in the dark at 31 °C, which is the longest persistence reported for this herbicide. AMPA, the microbial transformation product of glyphosate, was detected under all conditions, confirming that degradation was mediated by the native microbial community. This study demonstrates glyphosate is moderately persistent in the marine water under low light conditions and is highly persistent in the dark. Little degradation would be expected during flood plumes in the tropics, which could potentially deliver dissolved and sediment-bound glyphosate far from shore.

1. Introduction

1.1. Water quality and pesticides in the Great Barrier Reef

There has been increasing concern over the global loss of corals and seagrass and this has been particularly well documented for the World Heritage listed Great Barrier Reef (GBR) (De'ath et al., 2012; Orth et al., 2006). Management of this vast resource requires balancing coastal pressures from port and urban development, the extensive agriculture industry in GBR catchments, and needs to consider potential impacts on water quality from these activities (Brodie et al., 2013). Nearshore water quality around reefs and seagrass beds is most heavily impacted during the summer wet season from November to March when heavy rains deliver river runoff containing excess sediments, nutrients, and pesticides (Brodie et al., 2012a; Brodie and Waterhouse, 2012; Lewis et al., 2009). Satellite imagery effectively captures these events and their associated flood plumes migrating up to 50 km offshore as far as the midshelf coral reefs (Bainbridge et al., 2012).

A wide spectrum of pesticides have been detected in waters of the GBR, but herbicides are often more water soluble and mobile than contemporary insecticides and fungicides, and as a consequence, are more frequently detected in the river mouths and GBR lagoon (Brodie et al., 2012b; Davis et al., 2011; Lewis et al., 2009). The photosystem II herbicides have been the primary group detected in GBR waters; however, glyphosate (CAS number 1071-83-6) is the most widely used herbicide in Australia, in the GBR catchments and elsewhere, with approximately 15,000 tonnes applied annually to control agricultural, urban and roadside weeds (Beeton et al., 2006; Radcliffe, 2002). The popularity of glyphosate has increased steadily since its introduction in the mid 1970s as it exhibits: (i) relatively low toxicity to non-target organisms (Borggaard and Gimsing, 2008; Duke and Powles, 2008); (ii) apparent rapid microbial degradation to a major metabolite aminophosphonic acid (AMPA) (Giesy et al., 2000) and (iii) strong adsorption to soils and sediments potentially limiting runoff in surface water (Duke and Powles, 2008; Pérez et al., 2012; Solomon and Thompson, 2003).

1.2. Glyphosate monitoring and toxicity

Glyphosate has not often been included in regular monitoring programs as the stand-alone analytical methods are often cost-prohibitive, resulting in a long term deficiency in global datasets (Barceló and Hennion, 2003). However, glyphosate has been regularly detected in a diversity of waterbodies when samples were analysed (see Table 1). For example, glyphosate and AMPA were detected in 36% and 69% of water samples respectively, following extensive sampling of aquatic ecosystems in the Midwestern United States (Battaglin et al., 2005; Scribner et al., 2003).

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Table 1
Example, glyphosate concentrations in the aquatic and marine* environment. BDL = Below detection limit.

Concentration ($\mu g\ L^{-1}$)	Sample type, location	Reference
54 (peak)	Paddock Run-off, Queensland Australia	Davis et al. (2011)
BDL – 0.74	River Jauron, Central France	Pesce et al. (2008)
1.2 (peak)	Marennes-Oléron Bay, Atlantic coast, France*	Samain and McCombie (2008)
BDL – 4.5	Streams, Midwestern United States	Scribner et al. (2003)
BDL – 40.8	Surface water, Southern Ontario, Canada	Struger et al. (2008)
BDL – 0.59	Tributaries to River Ruhr, Germany	Skark et al. (1998)

Concentrations measured in field studies in Australia have been reported as high as 54 $\mu g\ L^{-1}$ (Davis et al., 2011). A similar concentration (40.8 $\mu g\ L^{-1}$) was measured in Canada (Struger et al., 2008), while field dissipation studies found concentrations as high as 1700 $\mu g\ L^{-1}$ (Mensink and Janssen, 1994; NHMRC, 2011). Glyphosate exhibits a relatively low toxicity to non-target marine organisms, with the LC_{50}s of glyphosate (lethal concentration which affects half of the sample population) in the 10–1000 $mg\ L^{-1}$ range. However, recent research suggests that low $\mu g\ L^{-1}$ concentrations can affect natural coastal microbial communities (Stachowski-Haberkorn et al., 2008). The toxicity of the glyphosate compound compared to glyphosate formulations has been extensively reviewed with multiple studies demonstrating that the formulations and surfactant additives are usually more toxic to test species (Barceló and Hennion, 2003; Giesy et al., 2000). The Australian guideline trigger values for the protection of 90% and 99% of freshwater species are 2000 and 370 $\mu g\ L^{-1}$ respectively (ANZECC and ARMCANZ, 2000) and these may in some instances be applied as "low reliability" guidelines in the absence of marine values.

1.3. Glyphosate persistence in water

As glyphosate is heavily used in the agriculture industry, the literature on its persistence is heavily weighted towards degradation in soil (see Table 2 for example half-lives). The average half-life in natural freshwaters for glyphosate is >60 days, with the most important route of degradation being mediated by bacteria (Bonnet et al., 2007). Increasingly, there has been evidence for off-site movement of glyphosate into aquatic ecosystems (Table 1), but no information has been published on glyphosate persistence in seawater. The aim of this study is to quantify the persistence of glyphosate in seawater in standard tests but under natural conditions and at environmentally relevant concentrations.

2. Methods

2.1. Simulation test conditions

A series of glyphosate degradation experiments were carried out in flasks according to the OECD methods for "simulation tests" (OECD, 2005). The tests were conducted in natural seawater containing a native bacterial community and no addition of nutrients or artificial inoculum to best mimic ecological conditions. The tests were conducted under three scenarios: (1) 25 °C in the dark which corresponds to the mean annual seawater temperature on the GBR (AIMS, 2013); (2) 25 °C in low light conditions and (3) 31 °C in the dark which is a summer maximum temperature for nearshore areas of the mid-northern regions of the GBR (AIMS, 2013). Three temperature-regulated incubator shakers (Thermoline TLM-530) were used in the experiments. A series of 6 × 900 mm LED strips (Superlight LED Lighting, Generation 3 High-Output LED Turbostrip) were fitted to one shaker, providing an even light environment of 40 µmol photons $m^{-2}\ s^{-1}$ over a 12:12 light day cycle. This is equivalent to 1.7 mol photons $m^{-2}\ day^{-1}$ which is within the range of light environments measured in shallow 3–6 m depths on turbid nearshore reefs of the GBR during the wet season (Uthicke and Altenrath, 2010). The position of flasks was randomised after every sampling period and flasks were consistently shaken at 100 rpm.

All glassware was washed at 90 °C with laboratory detergent, rinsed and oven dried at 100 °C, acid washed (10% HCl), rinsed × 5 with RO then Milli-Q water until pH neutral, oven dried a second time at 100 °C, baked in a muffle furnace at 350 °C for 30 minutes, and capped with aluminium foil until use. The glyphosate standard was purchased from Sigma–Aldrich, added to 2 mL of the carrier solvent ethanol (to assist in solubility), and made to 5 $mg\ L^{-1}$ concentration with Milli-Q water. Coastal water was collected from 19°16′ (S), 147° 03′ (E) and filtered to 20 µm to introduce the total bacterial diversity from this environment. The seawater was added to 500 mL Erlenmeyer flasks to a final volume of 300 mL and sample treatments were spiked with a final concentration of 10 $\mu g\ L^{-1}$ glyphosate. The same volume of carrier was added to control sample flasks and was 0.0004% (v/v). Each flask was stoppered with autoclaved silicone bungs to allow for aerobic conditions. The physical/chemical characteristics of the filtered seawater were measured for: pH, DIC, DOC, DIN, DON, TSS, bacterial counts (see below) and particle size distribution.

Table 2
Published glyphosate biodegradation half-life estimates in soil and fresh waters.

Half-life (days)	Matrix (if specified)	Reference
12	Soil (field)	FPPD (2012)
5–21	Soil (field)	FPPD (2012)
49	Soil (lab)	FPPD (2012)
4–180	Soil (lab)	FPPD (2012)
87 (2.5)	Water-sediment (water fraction only)	FPPD (2012)
47	–	Peterson et al. (1994), Wauchope et al. (2002), Wauchope et al. (1992)
60	Soil	Verschueren (2001)
30–174	Soil	Singh and Walker (2006)
<28	Soil-water	Mackay et al. (2006), Muir (1991), Rueppel et al. (1977)
>63	Lake water	Mackay et al. (2006), Muir (1991), Rueppel et al. (1977)
70	Pond water	Ghassemi et al. (1981), Mackay et al. (2006), Muir (1991)
63	Swamp water	Ghassemi et al. (1981), Mackay et al. (2006), Muir (1991)
49	Bog water	Ghassemi et al. (1981), Mackay et al. (2006), Muir (1991)
49–70	Natural waters	Ghassemi et al. (1981), Muir (1991)

2.2. Flow cytometry

Flow cytometry was used to quantify the microbial populations in the seawater used in the experiment. Samples were fixed with 5% formaldehyde and stored at 4 °C. Sub-samples were stained using Sybr Green, diluted to 1:10,000, and allowed to develop in the dark for 30 min. Samples were run using a BD Accuri C6 cytometer (BD Biosciences, CA, USA) equipped with a red and blue laser (488 nm, 50 mW maximum solid state; 640 nm, 30 mW diode) and standard filter setup. Flow rate was 14 μL min^{-1}, 10-μm core. The natural microbial community populations and their abundances were measured for the initial seawater as well as treatments for the experiment using the Accuri CFlow plus software.

2.3. Glyphosate analysis

For each sampling period, 5 mL control and glyphosate samples were collected and stored at 4 °C. The glyphosate samples were then sent to Queensland Health Forensic and Scientific Services (Coopers Plains, Australia) for analysis. Standards and blanks were derivatised with fluorenylmethylchloroformate. The derivatisation procedure follows a published method with minor adjustments for volume of sample available (Hanke et al., 2008). The sample was then concentrated on a SPE cartridge (Phenomenex Strata X 200 mg 3 m L^{-1}) prior to analysis by HPLC-MS/MS. The glyphosate and degradation product concentrations were determined by HPLC-MS/MS using an ABSciex 4000Q Trap mass spectrometer (ABSciex, Concord, Ontario, Canada) equipped with an electrospray (TurboV) interface and coupled to a Shimadzu Prominence HPLC system (Shimadzu Corp., Kyoto, Japan). Column conditions were as follows: Phenomenex Gemini-NX C18 column (Phenomenex, Torrance, CA) 3 μm 30 × 2.0 mm, 40 °C, with a flow rate of 0.35 mL min^{-1}. The column was conditioned prior to use and for analyte separation required a linear gradient starting at 0% B for 1.0 min, ramped to 100% B in 8 min then held at 100% for 2 min followed by equilibration at 0% B for 7 min (A = HPLC grade water, B = 95% methanol in HPLC grade water, both containing 5 mM ammonium acetate and 0.008% (v/v) 32% ammonia solution). The mass spectrometer was operated in the negative ion, multiple reaction-monitoring mode (MRM) using nitrogen as the collision gas. The transition ions monitored after sample derivatisation were 390/168, 390/150 for glyphosate and 332/110, 332/136 for AMPA.

Detection of glyphosate and/or its metabolite in a given sample were confirmed by retention time and by comparing transition intensity ratios between the sample and an appropriate concentration standard from the same run. Samples were reported as positive if the two transitions were present, retention time was within 0.15 min of the standard and the relative intensity of the confirmation transition was within 20% of the expected value. The value reported was that for the quantitation transition. The limit of detection for the method was typically less than 0.1 μg L^{-1}, with a reporting limit of 0.2 μg L^{-1} in the sample. Response was linear to at least 100 μg L^{-1} which is within the range of the samples with r^2 from 0.995 to 0.999. Sample sequences were run with a standard calibration at the beginning and end of each sequence with, with additional mid-range standards run every 10 samples.

2.4. Data analysis

Half-life ($T_{1/2}$) calculations assumed first order kinetics and were estimated from the decline in experiment concentration of glyphosate in seawater using the rate constant (k) (slope of the data obtained from plots of the natural logarithm of the concentrations versus time (T), where $T_{1/2} = \ln(2)/k$) (Beulke and Brown, 2001; Lazartigues et al., 2013). Glyphosate concentrations approaching the detection limit were removed from the analysis.

3. Results and discussion

3.1. Microbial abundance

The pH and dissolved oxygen (DO) levels of seawater in the flasks were similar between controls, treatments and freshly-collected natural seawater at the end of the 330 day experiment (Table 3). Other water quality properties can be found in Table S1 (supporting online material). The seawater in flasks contained identical bacterial abundance at the end of the experiment compared with natural seawater (Table 3) and is consistent with the range expected for seawater (Amaral-Zettler et al., 2010; Glöckner et al., 2012; Miller, 2009). The high densities of bacteria measured at the end of the experiment in each of the treatments indicate that the presence of 10 μg L^{-1} glyphosate did not reduce the microbial populations.

3.2. Glyphosate degradation and the formation of AMPA

Glyphosate degraded most rapidly under low light conditions at 25 °C with none detected by day 180, and most slowly in the dark at 31 °C where 52% remained by day 330 (Fig. 1). The major biodegradation metabolite of glyphosate is AMPA (Barceló and Hennion, 2003; Pérez et al., 2012; Wright, 2012) and this was detected in flasks in each of the treatments. In the dark at 25 °C AMPA increased over the course of the experiment duration to 1.42 μg L^{-1} by day 330, approximately 15% of the initial glyphosate concentration (Fig. 1). Similar results were obtained for the generation of AMPA at 31 °C in the dark. Under low light conditions, AMPA was only detected (0.35 ± 0.01 μg L^{-1} SE) at day 28 (Fig. 1).

Biodegradation is the primary pathway for glyphosate loss (Bonnet et al., 2007) and the detection of AMPA in each of the temperature and light treatments confirms that degradation of glyphosate in the flasks was mediated by bacteria from the native microbial communities. While glyphosate can also be lost due to hydrolysis and photodegradation (Lund-HØie and Friestad, 1986; Mallat and Barceló, 1998), these pathways are considered less important. The more rapid degradation of glyphosate under low light conditions (relevant to nearshore levels in the wet season) was likely due to differences in microbial community populations. Differences in microbial communities may also account for the slightly more rapid degradation of glyphosate in the dark at 25 °C compared to 31 °C. These results indicate that the available light will affect glyphosate persistence in the field and very low light levels expected during flood plumes may slow degradation.

3.3. Glyphosate persistence in seawater

The half-lives ($T_{½}$) for glyphosate were calculated by plotting the natural logs of the concentrations against time (Fig. 2). The linear correlations of each of the plots were high ($r^2 \geqslant 0.82$) and the resulting slopes were −0.0026, −0.0022 and −0.0149 for the dark 25 °C, dark 31 °C and light 25 °C treatments respectively (Fig. 2). Assuming first order kinetics (Beulke and Brown, 2001; Lazartigues et al., 2013) the $T_{½}$ for glyphosate were estimated as 267 ± 21 (SE) days for the dark at 25 °C, 315 ± 29 days for the dark 31 °C and 47 ± 7 days for light 25 °C treatments (Fig. 2). The half-life ($T_{½}$) for glyphosate of 47 days under low-light conditions was similar to reports for fresh water (Table 2); however, the persis-

Table 3
Mean and SEs for each treatment for pH, dissolved oxygen (DO), and total bacterial counts.

	Natural seawater	Control	Dark 25 °C	Dark 31 °C	Light 25 °C
Total bacterial counts ($\times 10^6$)	2.66 ± 0.4	2.65 ± 0.29	2.59 ± 0.02	2.61 ± 0.02	2.70 ± 0.02
pH	8.20 ± 0.01	8.22 ± 0.02	8.24 ± 0.02	8.33 ± 0.01	8.34 ± 0.01
DO (mg L^{-1})	6.5 ± 0.07	6.24 ± 0.15	5.95 ± 0.12	5.89 ± 0.18	6.13 ± 0.08

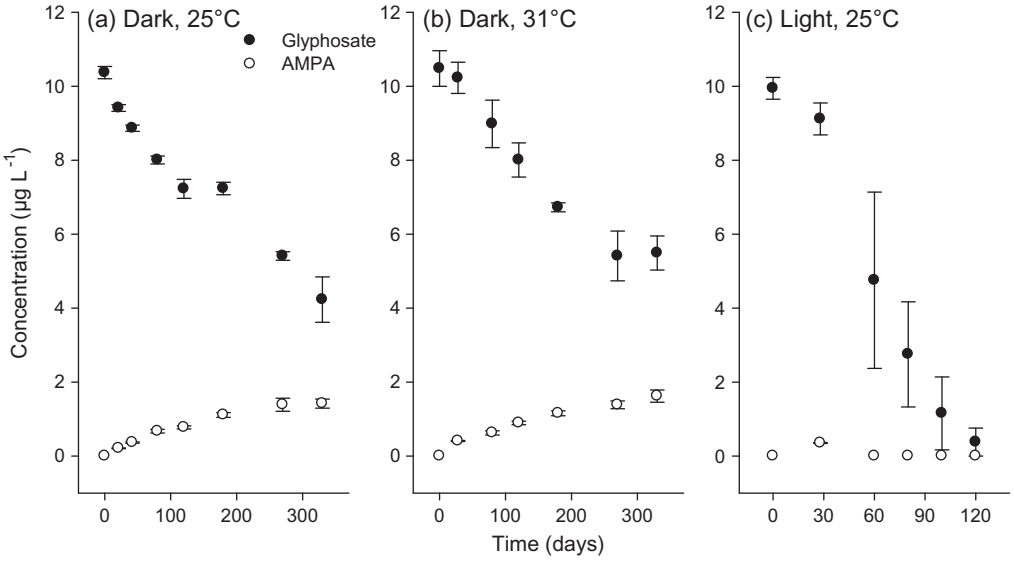

Fig. 1. Concentration of glyphosate and AMPA for each treatment: Dark 25 °C, Dark 31 °C, and Light 25 °C during the experiment duration. Concentrations reported in µg L^{-1}.

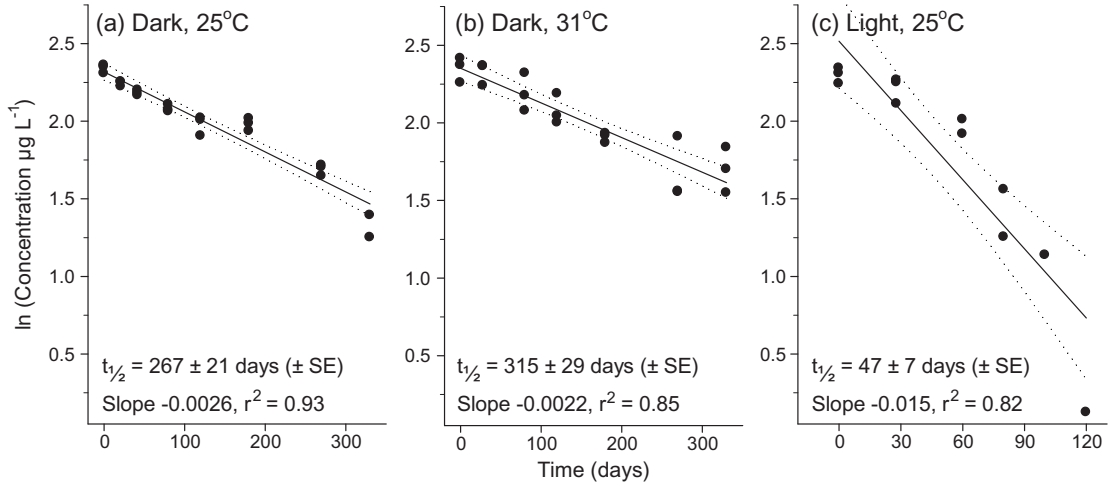

Fig. 2. Natural log of glyphosate concentrations (µg L^{-1}) and half-life ($T_{½}$) for each treatment: Dark 25 °C, Dark 31 °C, and Light 25 °C. Graphs show 95% confidence intervals for each slope.

tence in dark at both 25 °C and 31 °C (267 and 315 days) was by far the longest reported.

3.4. Application of results from the simulation test

The simulation tests performed in this study provide both standardized conditions required for inter-study comparisons and the most natural conditions possible in flask tests (native microbial communities without additional nutrients). The consistent bacterial densities between flasks at the end of the experiment and freshly-collected natural seawater confirmed the presence of abundant bacteria required for herbicide degradation. There is in the order of thousands of different bacteria in a litre of seawater (Sogin et al., 2006) so a high diversity of microbes would be expected to be available to facilitate biodegradation, and this should be confirmed using molecular techniques in future studies.

This study indicates glyphosate is moderately persistent in the marine environment under low light conditions and is highly persistent in the dark, with a minor influence of temperature between 25 °C and 31 °C. While these simulation tests mimic natural conditions better than many alternative "standard" tests, further work is needed to understand the persistence and fate of glyphosate in the marine environment. For example, glyphosate binds strongly to organic matter (Solomon and Thompson, 2003) and is therefore considered to have a low potential for offsite transport (Barceló and Hennion, 2003). However, this strong binding allows for long

distance transport and persistence in the environment as binding may help protect glyphosate from degradation (Solomon and Thompson, 2003). Furthermore, vast quantities of sediments (~17,000 ktonnes/yr), potentially contaminated with glyphosate and other pesticides, are transported into the GBR during monsoonal floods (Brodie et al., 2010; 2012b; Kroon et al., 2012; Lewis et al., 2009), representing an alternative transport pathway to the dissolved fraction.

Glyphosate is not generally considered in most marine monitoring programs despite it being one of the most widely used herbicides in GBR catchments and globally. Recent work has also reported that surfactants and wetting agents in commercial glyphosate formulations are themselves more toxic or increase the bioavailability and toxicity of glyphosate to non-target species (Pérez et al., 2012; Stachowski-Haberkorn et al., 2008). It is possible that the persistence of glyphosate may be affected by the toxicity of formulation surfactants if they influence microbial populations or alter the partitioning of the herbicide between water and particulates. However, the relevance of testing persistence in the presence of formulation surfactants is unknown as data on co-occurrence with glyphosate in the field is lacking. The long persistence of glyphosate in these flask experiments indicates that little degradation is likely during flood events which may deliver dissolved and sediment-bound herbicide far into the GBR lagoon. Further work is therefore needed to improve the monitoring and identify the fate of glyphosate for water quality risk assessments in marine ecosystems of high conservation value such as the GBR.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.marpolbul.2014.01.021.

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