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Critical Review

Pesticides in the Great Barrier Reef catchment area: Plausible risks to fish populations

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Abstract

Waterways that drain the Great Barrier Reef catchment area (GBRCA) transport pollutants to marine habitats, provide a critical corridor between freshwater and marine habitats for migratory fish species, and are of high socioecological value. Some of these waterways contain concentrations of pesticide active ingredients (PAIs) that exceed Australian ecotoxicity threshold values (ETVs) for ecosystem protection. In this article, we use a "pathway to harm" model with five key criteria to assess whether the available information supports the hypothesis that PAIs are or could have harmful effects on fish and arthropod populations. Strong evidence of the first three criteria and circumstantial weaker evidence of the fourth and fifth criteria are presented. Specifically, we demonstrate that exceedances of Australian and New Zealand ETVs for ecosystem protection are widespread in the GBRCA, that the PAI contaminated water occurs (spatially and temporally) in important habitats for fisheries, and that there are clear direct and indirect mechanisms by which PAIs could cause harmful effects. The evidence of individuals and populations of fish and arthropods being adversely affected species is more circumstantial but consistent with PAIs causing harmful effects in the freshwater ecosystems of Great Barrier Reef waterways. We advocate strengthening the links between PAI concentrations and fish health because of the cultural values placed on the freshwater ecosystems by relevant stakeholders and Traditional Owners, with the aim that stronger links between elevated PAI concentrations and changes in recreationally and culturally important fish species will inspire improvements in water quality. *Integr Environ Assess Manag* 2024;00:1–24. © 2023 Commonwealth of Australia and The Commonwealth Scientific and Industrial Research Organisation. *Integrated Environmental Assessment and Management* published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC).

KEYWORDS: Atrazine; Crustaceans; Diuron; Imidacloprid; Tropical ecotoxicity

INTRODUCTION

The Great Barrier Reef (GBR) is the world's largest coral reef ecosystem and a World Heritage site that is facing serious threats from multiple pressures, particularly climate change impacts (i.e., coral bleaching, cyclones, flood events, and ocean acidification), Crown of Thorns starfish, coastal development, and poor water quality. The catchment area adjacent to the GBR (the GBRCA) connects terrestrial habitats to the estuarine and marine ecosystems of the Reef. Rivers, creeks, and wetlands act as passageways for mobile and migratory aquatic species between freshwater ecosystems to seagrass and coral habitats (Arthington et al., 2015; Pearson et al., 2013; Waltham et al., 2019; Waltham, McCann, et al., 2020a). This network of waterways links human activities in the GBRCA to Reef ecosystems, transporting runoff and terrestrially derived pollutants to the marine environment (e.g., Lewis et al., 2021). The connecting waterways are also a cultural, social, and economic link between human and ecological systems of the GBRCA, providing commercial, recreational, and spiritual benefits (Gordon, 2007). The catchment and coastal ecosystems adjacent to the Reef are important components of a socioecological system (Gordon, 2007), a social system inextricably linked with the ecological system in which it is embedded (Walker & Salt, 2006). Fish are a highly valued organism for humans, and therefore the viability of their freshwater habitats is important to human needs.

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The close links between these human and ecological systems have placed significant pressure on the health and resilience of ecosystems of the Reef (Great Barrier Reef Marine Park Authority, 2019; Waltham & Sheaves, 2015; Waterhouse, Schaffelke, et al., 2017) and have led to considerable investments in managing the issue (Australian Government and Queensland Governments, 2018). Agriculturally sourced nutrients, sediment, and pesticide active ingredients (PAIs) present the greatest threats to the GBR's resilience against climate change pressures (Australian Government and Queensland Governments, 2018; Waterhouse, Schaffelke, et al., 2017). Management plans have been implemented for more than a decade by the Australian and Queensland governments with the intent of improving water quality (e.g., Australian Government and Queensland Governments, 2018). These management efforts have largely involved terrestrial-based programs and activities involving cooperation between landholders, communities, industry, regional management groups, and the Australian and Queensland governments to improve marine and coastal water quality and protect key Reef ecosystems (coral and seagrass habitats; e.g., Davis et al., 2017).

Changing land management practices to improve water quality entering and in the GBR lagoon is a complex and contentious issue that has challenged vested interests and established practices. Explanations to landholders and the community about why changing land management practices and environmental stewardship is necessary has focused on it in context of the need to protect the Reef's coral and seagrass ecosystems. Although the GBR catchments have significant environmental and human values in relation to the GBR, messaging to protect them from the impacts of poor water quality, independent of the Reef, has not been a focus. Indeed, focusing on the health of the catchments may be an effective avenue for change. According to Marshall et al. (2019), concern and value for ecosystems inspires environmental stewardship, and residents of the GBRCA have a greater concern for and connection to ecosystems they use more frequently (i.e., beaches and creeks) and the condition and status of freshwater fish and ecosystems, compared with coral reefs. Fish are particularly important in their value to people (e.g., Indigenous culture, recreational fishing, commercial fisheries, aesthetic) and to the environment playing an important role in ecological communities as well as being a mobile link between the riverine and marine ecosystems. Consequently, it may be beneficial to use links between declining water quality and the impacts on species that have high sociological value to inspire improvements in environmental stewardship.

Our goal in this article is to assess the hypothesis that elevated PAI concentrations might be jeopardizing recreational and culturally significant fisheries (both finfish and crustacean) in the freshwater and estuarine catchments of the GBR. These fisheries are highly valued by local communities and have a greater risk of exposure to PAIs than downstream seagrasses and corals. We hypothesize that fish populations could be affected by: (1) direct sublethal effects of PAIs; (2) indirect impacts on habitat and food webs; and/or (3) costressors that could affect fish already stressed via points (1) and/or (2) above. To support this hypothesis, demonstrating a plausible "pathway to harm" (e.g., a chain of events that would cause adverse outcomes to fish or crustaceans, as illustrated in Figure 1) would require: (1) observing concentrations of PAIs

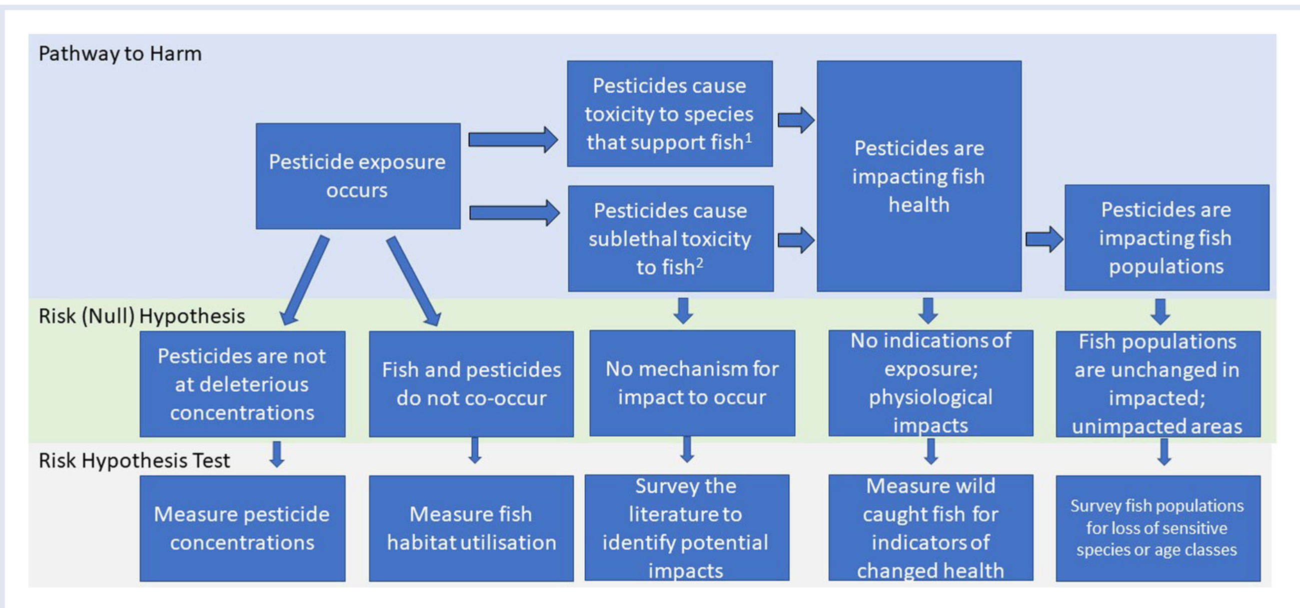

FIGURE 1 The "pathway to harm" model used in this study to assess the potential that pesticide active ingredient (PAI) exposure affects fish populations in the Great Barrier Reef catchment area. Essentially identical models would apply to crustaceans and other groups of organisms. "1" indicates that PAIs could exert an indirect impact on fish health by affecting species with a functional support role, for example, as prey items or habitat structure; "2" indicates direct toxic effects of the PAIs directly on the fish. Risk hypotheses are null hypotheses that, if disproven, suggest the risk has or is likely to occur. The risk hypothesis test is the evidence that would be required to support or refute these hypotheses. A similar pathway to harm model could be used for crustaceans

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in fish habitats high enough to harm fish species and/or species providing food or habitat functions; (2) demonstrating the temporal and spatial co-occurrence of PAIs with fish and/or crustacean species in their habitat; (3) demonstrating physiological mechanisms by which the observed PAIs could harm the organisms in question; (4) evidence that exposure to the observed PAIs has harmed individual fish and/or crustacea, and (5) measured changes in the fish and/or custacea population have occurred and are consistent with exposure to PAIs. We aim to follow a pathway to harm model that includes risk hypotheses and risk tests (Figure 1). Risk hypotheses are null hypotheses that, if disproven, suggest the risk has or is likely to occur. In this article, we will assess whether the available evidence is sufficient to demonstrate each of the five criteria in the proposed pathway to harm model, outlined above, for recreationally and culturally valued fish species of the GBRCA. In undertaking this assessment, we will focus on the regions and catchments where pesticide risk is greatest as estimated by Warne, Neelamraju, Strauss, et al. (2020) and Warne, Neelamraju, Turner, et al. (2020) and on PAIs that are of sufficient concentrations to pose environmental risk. For these high-risk situations, if the evidence is insufficient to establish a pathway to harm, then it could not be established for lower risk situations.

OBSERVED PAIs IN WATERWAYS OF THE GBRCA

The GBRCA consists of 35 basins that drain to the Great Barrier Reef lagoon, along approximately 2000 km of the east coast of Queensland, Australia. The total land area is approximately 424 000 km^2 and covers six different bioregions (i.e., South-East Queensland, Brigalow Belt, Central Queensland Coast, Wet Tropics, Einasleigh Uplands, and the Cape York Peninsula; Queensland Government, 2022) and three climate types (i.e., subtropics, dry tropics, and wet tropics). Agriculture is the dominant land use in the GBRCA (~77%) and includes cattle grazing (73%), cropping (2.8%), sugarcane (1.2%), and horticulture (0.2%; Warne, Neelamraju, Strauss, et al., 2020). Other important land uses are conservation (15%), forestry (4.6%), mines, wastewater treatment plants, landfills, industrial and commercial sites (2.4%), and urban (0.25%; Lewis et al., 2021; Warne, Neelamraju, Strauss, et al., 2020). Active ingredients (AIs) of herbicides, insecticides, and fungicides that have been detected in catchments and the inshore marine zone of the GBR are derived primarily from these agricultural land uses (Bainbridge et al., 2009; Lewis et al., 2009). Pesticides are an important tool in modern farming systems and biosecurity; they assist with protection of crops or animals from disease, insect infestation, and competition from weeds. Pesticide formulations applied in agriculture are complex mixtures of chemicals containing the AI (i.e., the chemical that exerts the toxic effect on the pest organism) and adjuvant chemicals designed to increase the effectiveness of the AI. The transport of AIs from the paddock to the Reef is discussed in the next section; here, we describe the evidence that PAIs are present in waterways of the GBRCA that drain into the Reef.

Currently, PAIs are monitored in rivers, creeks, and wetlands in the GBRCA (e.g., Davis & Neelamraju, 2019; Lewis et al., 2016; O'Brien et al., 2016; Spilsbury et al., 2020; Vandergragt et al., 2020; Warne, Neelamraju, Strauss, et al., 2020; Warne, Smith, et al., 2020; Water Quality and Investigations, 2020, 2021) and in the inshore waterways of the GBR lagoon (Thai et al., 2020, and references therein). Comprehensive, routine PAI monitoring has taken place since 2009 as part of the Paddock to Reef Integrated Monitoring, Modelling, and Reporting Program (e.g., Water Quality and Investigations, 2021). This targets the growing and wet season (typically October to March) runoff, and end-of-catchment sites downstream of agricultural land use. Other studies have evaluated PAI runoff dynamics near agricultural sites (Davis & Neelamraju, 2019; Lewis et al., 2016; O'Brien et al., 2016) and in individual catchments (e.g., O'Brien et al., 2016; Smith et al., 2012; Wallace et al., 2017). However, the number of PAIs detected and reported is limited to the methods used to monitor and detect chemicals. The numbers of pesticides present in waterways are likely to be much greater based on data in the Australian Public Chemical Registration Information System (PubCRIS; APVMA, 2019), which reports that at least 146 PAIs are registered for use on bananas, sugarcane, and rotational crops (i.e., mung beans, soybeans, corn, and rice). The pesticides that are registered for agricultural use data are the best available estimate of discharge patterns in Queensland because there is no tracking of the amounts sold. The following discussion of the PAIs present in the freshwaters of the GBRCA most likely underestimates the true number of PAIs present and the risk that they collectively pose.

From the end-of-catchment monitoring data, we know that PAIs occur ubiquitously during the growing and wet season (i.e., December to March in the GBRCA) in catchments downstream of agricultural land uses commonly applying pesticides. Almost all (~99.8%) 2600 samples collected from 15 sites between 2010 and 2015 contained at least one PAI (Warne, Smith, et al., 2020). The number, magnitude, and temporal variations of their concentrations differ between catchments and regions, depending on upstream land use and rainfall patterns (Warne, Smith, et al., 2020).

The most commonly measured PAIs in GBR rivers, creeks, and wetlands are herbicide AIs and one insecticide AI, which are (arranged alphabetically) 2,4-dichlorophenoxyacetic acid (2,4-D), atrazine, diuron, hexazinone, imidacloprid, metolachlor, and the degradation products isopropyl atrazine and desisopropyl atrazine (Spilsbury et al., 2020; Vandergragt et al., 2020; Warne, Smith, et al., 2020), although the concentrations and proportion of each compound depend on the upstream land use (Warne, Smith, et al., 2020). For example, atrazine and 2,4-D were detected in approximately 68% and approximately 52% of 3741 samples collected between 2011 and 2016, respectively (Spilsbury et al., 2020). The herbicide AIs detected vary in their modes of action, which include photosystem II (PSII) inhibitors (e.g., atrazine and diuron), synthetic auxins (e.g., 2,4-D and

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2-methyl-4-chlorophenoxyacetic acid [MCPA]), growth inhibitors (e.g., metolachlor), pigment inhibitors (e.g., isoxaflutole), amino acid synthesis inhibitors (e.g., glyphosate), and others (Smith et al., 2012; Warne, Neelamraju, Strauss, et al., 2020; Warne, Smith, et al., 2020). Many of these herbicides are routinely measured in flood plumes entering the GBR lagoon (Brodie et al., 2012; Kennedy et al., 2012; Thai et al., 2020).

At least 16 insecticide AIs including organophosphates, neonicotinoids, pyrethroids, and phenylpyrazoles have been measured in GBR catchments (Smith et al., 2015). Use patterns of these pesticides are changing. For example the organophosphate insecticide, chlorpyrifos is being phased out, and the use of neonicotinoids is increasing. Unlike the other classes of insecticides, which have chemical properties suggesting that they bind to sediment, neonicotinoids have a relatively high aqueous solubility (e.g., 0.61 g/L for imidacloprid; British Crop Production Council, 2012). Imidacloprid could be quantified in approximately 54% of more than 6500 samples from 14 GBR waterways, but occurred in some individual catchments in up to 99.7% of samples (Warne et al., 2022). In summary, pesticides are ubiquitous in the fresh, estuarine, and marine waters of the GBR region; therefore, the potential for exposure in aquatic organisms, particularly fish, to pesticides is high.

Concentrations and ecological risk of PAIs in the GBRCA

Hazards posed by PAIs. The presence of a PAI in an ecosystem does not indicate its potential to cause adverse outcomes. Pesticide AIs are only considered to pose a hazard if they occur at concentrations greater than those that cause toxic effects. In Australia, these limits are referred to as Default Guideline Values (DGVs; previously referred to as trigger values), which are the equivalent of water-quality criteria and standards. The cumulative frequency distribution of toxic values for at least five species that belong to at least four taxonomic groups (typically at the phyla level; Warne et al., 2018) are used to estimate the concentrations that should theoretically protect at least 80%, 90%, 95%, and 99% of aquatic species. The 99% species protection threshold is used to protect culturally and economically important species and areas, such as the Great Barrier Reef. Endangered species are not generally included in the derivation of DGVs because data for such species are lacking. Exceeding these concentrations indicates that less than 80%, 90%, 95%, and 99% of aquatic species are estimated to be protected from experiencing adverse effects from PAI exposure (Warne et al., 2018). Concentrations that should protect 80%, 90%, 95%, and 99% of aquatic species that were derived using the nationally endorsed method of calculating DGVs (Warne et al., 2018) but have not gone through the national endorsement process are referred to as ecotoxicity threshold values (ETVs). As both DGVs and ETVs are referred to in this article, the term ETV will be used as the generic term for both.

A method that uses the multisubstance potentially affected fraction (msPAF) method, the independent action model of joint action and a multiple imputation method are used to estimate the risk posed by mixtures of up to 22 PAIs frequently detected in GBR waterways. This method is termed the Pesticide Risk Metric (Warne et al., 2022). The Pesticide Risk Metric expresses the average daily risk over the wet season for either the percentage of aquatic (estuarine, fresh, and marine) species affected by or protected from harmful effects of pesticide mixtures. The Reef Water Quality Improvement Plan (Australian Government and Queensland Governments, 2018) has a pollutant reduction target for pesticides that is that at least 99% of aquatic species should be protected at the mouth of GBR waterways.

Dispersion of pesticide concentrations from paddock to reef. Pesticide AIs are transported predominantly into waterways via surface runoff during rain events and to a lesser extent by groundwater. Therefore, the volume, timing, and frequency of rainfall relative to the time of PAI application influences when and how many PAIs are transported to aquatic ecosystems. Application, runoff, and transport of PAIs from agricultural land to the GBR inshore marine zone, as well as the temporal exposure characteristics, have been described in detail elsewhere (e.g., Davis et al., 2017; Devlin et al., 2015; O'Brien et al., 2016; Skerratt et al., 2023; Smith et al., 2012). It was observed that the ecosystems closest to the source of PAI runoff (wetlands, creeks, drainage ditches, and upper reaches of rivers) were typically exposed to the highest concentrations of PAIs and therefore faced greater risk of impact than marine ecosystems (e.g., Devlin et al., 2015; Waterhouse, Brodie, et al., 2017), which is not unique to the GBRCA (O'Brien et al., 2016). For example, a study from the USA found agricultural ponds had atrazine concentrations as high as 500 μg/L, whereas adjacent rivers had concentrations between 1 and 25 μg/L (Rohr & McCoy, 2010). Similarly, in South-East Queensland, water quality (such as nutrients, turbidity, and dissolved oxygen) was better at the mouth of estuaries than further upstream (Graham et al., 2019). Most PAI monitoring data have targeted sites in the GBRCA located at the end-of-catchments (i.e., where concentrations are likely to be lower due to dilution), rather than upstream, because the sites were installed to evaluate the loads and then the risk of PAIs discharging directly into the GBR lagoon.

Spatial occurrence of PAIs in the GBRCA

Pesticide active ingredients are not uniformly distributed in GBR waterways with the numbers detected and concentrations of individual PAIs varying both in and between catchments, basins, and regions (e.g., Water Quality and Investigations, 2020). Exposure to PAIs in riverine aquatic ecosystems is affected by land use and is associated primarily with sugarcane, bananas, horticulture, and grains. The number of PAIs detected in end-of-catchment monitoring data was found to have a significant positive relationship with the proportion of sugarcane land use in a catchment and a negative relationship with the proportion of land used for conservation (Warne, Smith, et al., 2020).

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Waterways containing more PAIs, higher PAI concentrations (e.g., Warne, Smith, et al., 2020)—and therefore at a higher risk from PAIs—are typically smaller, located in the coastal plain, and have greater rainfall. Such waterways are found in the Mackay–Whitsunday, Lower Burdekin, Wet Tropics, and Burnett Mary regions (Neelamraju et al., 2022; Warne, Neelamraju, Strauss, et al., 2020; Warne et al., 2022). In comparison, waterways that drain catchments with large proportions of conservation or grazing typically have fewer PAIs, lower concentrations (Warne, Smith, et al., 2020), and are generally considered a low risk for PAI exposure (Neelamraju et al., 2022; Warne, Neelamraju, Strauss, et al., 2020; Warne et al., 2022).

Waterways of the O'Connell, Pioneer, Plane, and Proserpine Basins in the Mackay–Whitsunday region have some of the highest estimates of pesticide risk in the GBRCA, typically ranging from approximately 9% to 29% of aquatic species potentially experiencing adverse effects averaged over the wet season (Neelamraju et al., 2022; Warne, Neelamraju, Strauss, et al., 2020; Warne, Neelamraju, Turner, et al., 2020). However, Sandy Creek, located in the Plane Basin, is the most polluted waterway monitored for PAIs with individual samples estimated to affect up to 61% of aquatic species from mixtures containing an average of 14 PAIs (Neelamraju et al., 2022; Warne, Neelamraju, Strauss, et al., 2020; Warne, Neelamraju, Turner, et al., 2020; Warne, Smith, et al., 2020). The catchments drained by these waterways have large proportions (6%–45%) of sugarcane land use compared with other monitored GBR catchments (median of 1.1%, average of 6.3%; Warne, Neelamraju, Strauss, et al., 2020).

In the Burdekin region, the overall risk posed by pesticides is low (i.e., ranging from 1.7% to 2.3% of aquatic species being affected averaged over the wet season). However, the risk posed by pesticides in individual basins in the Burdekin region is relatively variable, ranging from very low (<1% species affected) to high (80% to <90% species affected). Barratta Creek, in the Haughton Basin and Lower Burdekin region, has the second highest average number of PAIs per sample (i.e., 13, Warne, Smith, et al., 2020), high PAI concentrations (O'Brien et al., 2016; Smith et al., 2012; Waterhouse, Brodie, et al., 2017; Warne et al., 2022), and high to very high risk (>20% species affected; Warne, Neelamraju, Strauss, et al., 2020). The lower Burdekin floodplains support irrigated sugarcane farming and therefore have an altered hydrology compared with nonirrigated catchments. Barratta Creek and similar small creeks pass through irrigated sugarcane farms before discharging into Bowling Green Bay, a Ramsar-designated wetland for its high conservation values. Farming practices in this area lead to irrigated water often being discharged into receiving creeks before the wet season begins, when water volumes are low, resulting in high PAI concentrations. Typically, PAI concentrations decrease quickly once the wet season begins (O'Brien et al., 2016; Smith et al., 2011).

Four of the seven basins in the Wet Tropics region have very low or low risk (<1% to 5% of species affected) from PAIs with the remainder facing a moderate risk (5%–10% of aquatic species affected; Neelamraju et al., 2022; Warne, Neelamraju, Strauss, et al., 2020; Warne, Neelamraju, Turner, et al., 2020). The Wet Tropics is well known for sugarcane farming, but the catchments in this region also have large areas of conservation land (e.g., the Tully catchment land use is 76% conservation and 11% sugarcane, Warne, Neelamraju, Strauss, et al., 2020), as well as relatively greater rainfall (average annual rainfall is ~2000 mm; Bureau of Meteorology [BOM], 2019a) than other GBR regions). These two factors are likely to increase the dilution of PAIs and decrease the risk compared with waterways in the Mackay–Whitsunday (average annual rainfall is 1540 mm [BOM, 2019b], 24% conservation, and 17% sugarcane [Warne, Neelamraju, Strauss, et al., 2020]), and Lower Burdekin (average annual rainfall is 680 mm [BOM, 2019c], 7% conservation, and 0.7% sugarcane [Warne, Neelamraju, Strauss, et al., 2020]) regions. The Wet Tropics also have relatively large proportions of bananas (of up to ~4%, Warne, Neelamraju, Strauss, et al., 2020) compared with other GBR regions, which have also been linked to PAI runoff in other tropical countries (e.g., Castillo et al., 2006). For example, imidacloprid can be applied to bananas at four times the permitted rate to sugarcane (APVMA, 2023).

Spatial occurrence of PAIs in important fish habitats (lacustrine and palustrine wetlands). Freshwater and estuarine ecosystems are important fish habitats for freshwater and migratory species (discussed below) including floodplain wetlands and the aquatic corridors (creeks, rivers, and estuaries) that allow fish to migrate to meet different life cycle requirements between freshwater and marine habitats. Our understanding of the occurrence and levels of PAIs in creeks, rivers, and estuaries is fairly robust—based on large-scale annual monitoring and several other studies, as described in the sections above. On the other hand, there are far fewer published studies of PAIs or other organic chemicals in freshwater lacustrine and palustrine wetlands in the GBRCA.

Devlin et al. (2015) discussed two small, unpublished studies. The first examined two wetlands and detected 19 PAIs, and the second study detected a maximum of two PAIs in sediments from seven of 11 monitored wetlands. Allan et al. (2017) reported detecting 14 PAIs in sugarcane drains and wetlands near the Mon Repos turtle breeding area, Burdekin, Queensland. In the most comprehensive study to date, PAIs and degradates were found in all 22 coastal palustrine wetlands monitored from the Wet Tropics to the Burnett Mary regions over two wet seasons (Vandergragt et al., 2020). In all, 59 PAIs and degradates were detected across all wetlands, with a minimum of 12, a maximum of 30, and an average of 21 PAIs and degradates per wetland (Vandergragt et al., 2020). Exceedances of ETVs (Australian and New Zealand Governments [ANZG], 2018), occurred only in the second wet season—with 10 wetlands having at least one PAI exceeding ETVs. Diuron concentrations were estimated to potentially affect up to 49% of aquatic species, and atrazine concentrations were estimated

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to affect up to 24% of aquatic species based on standardized toxicity tests (Vandergragt et al., 2020). It should be noted that one reason for selecting the wetlands in Vandergragt et al. (2020) was that moderate to high intensity land use (using the Australian Land Use and Management classifications, ABARES, 2016) was dominant within a radius of 1 km of each wetland. Therefore, the selected wetlands were expected to have greater exposure to PAIs and may not be representative of the exposure and risk posed by PAIs in wetlands surrounded by less intensive land uses. The risks posed by mixtures of PAIs in the 22 wetlands are currently being assessed but will most likely be greater than those posed by individual PAIs as was found for PAIs in rivers and creeks in the GBR region (Warne, Neelamraju, Strauss, et al., 2020; Warne et al., 2023; Figures 1 and 2).

Temporal variation in PAI concentrations

Although it is known that numerous herbicides occur at concentrations that exceed guideline values (frequently referred to as ETVs) in some GBR waterways (e.g., Water Quality and Investigations, 2020), the exposure is not the same throughout the year. Pesticides are applied seasonally, particularly at the beginning of the growing season, which is September to October in Tropical North Queensland and, as previously mentioned, runoff of PAIs is driven largely by rain events that occur predominantly in December–March (e.g., Water Quality and Investigations, 2021). These runoff characteristics result in low levels of exposure intermixed with episodic periods of high concentrations of varying duration (days to several months) during the wet season and/or growing season, as detailed in the sections below. For some catchments and PAIs, low level exposure (e.g., to concentrations below ETVs) can be expected year-round (e.g., Water Quality and Investigations, 2020). For example, analysis of 14 GBR waterways found very similar imidacloprid detection frequencies in both the wet and dry seasons (i.e., 64% and 56%, respectively; Warne et al., 2022). For freshwater systems receiving irrigation runoff (e.g., Barratta Creek, Figure 3), high PAI concentrations can occur before the wet season begins due to the limited dilution of irrigation runoff entering waterways. Such waterways may be at the greatest risk during the dry season (Davis et al., 2017).

End-of-catchment temporal variability. To evaluate the potential for fish and other organisms living in catchments to be exposed to fluctuating and potentially deleterious water quality, we examined the patterns of changing concentrations of nutrients, sediment, and PAIs throughout the year. The temporal variation in the concentration of atrazine (Figure 3A,B; Baratta Creek and Figure 4A,B; Sandy Creek), diuron (Figure 3C,D; Baratta Creek and Figure 4C,D; Sandy Creek), and imidacloprid (Figure 3E,F; Baratta Creek and Figure 4E,F; Sandy Creek) have been plotted for Barratta Creek (receives irrigated and rainfall runoff) and Sandy Creek (receives primarily rainfall runoff) as these waterways face the greatest risk from exposure to PAIs (Neelamraju et al., 2022; Warne, Neelamraju, Turner, et al., 2020; Warne, Smith, et al., 2020), and they are hydrologically different. Similar data for the other catchments are available in the Supporting Information. The ecosystems in these waterways face a moderate (5%–10% of species may experience harmful effects) to very high risk (>20% of species may experience harmful effects) from PAIs (Warne, Neelamraju, Strauss, et al., 2020).

As shown in Figures 3A and 4A, and corresponding figures in Supporting Information S1, at least occasional exceedances of the ETVs for atrazine occur in each waterway. The temporal pattern of atrazine concentrations in Barratta (Figure 3A) and East Barratta (Supporting Information S1: Figure S1) creeks, which have large irrigation systems, typically have two distinct peaks (in May–July and October–February) rather than one (typically October–February; Figure 4A) for nonirrigated waterways (values measured in Sandy Creek are plotted to be representative). Additionally, Barratta Creek and the lower Burdekin, the irrigated waterways in the dataset, have elevated atrazine concentrations over the nonirrigated waterways throughout the year (Figures 3A and 4A and Supporting Information S1: Figure S1) and very limited number of samples with concentrations at or below the limit of reporting (LOR, 0.02 µg/L). The additional peak of atrazine in Barratta and East Barratta Creeks is the result of irrigation during the dry season, which transports atrazine to the creeks where there is little dilution by rainfall. In Barratta Creek (Figure 3A), most samples contained atrazine at concentrations that exceeded the ETV that aims to protect 95% of freshwater species (ETV 95%) for four months (between October and January). In Sandy Creek (Figure 4A) and the Proserpine River (Supporting Information S1: Figures S1 or S2), approximately half the samples contained atrazine at concentrations that exceeded the ETV 95%. The plot of atrazine concentrations for all sites and years (Supporting Information S1: Figure S2) reveals that approximately 11% of samples exceeded the proposed ETV 95%.

Temporal trends in the distribution of diuron concentrations are more consistent across the waterways (Figures 3D and 4D and Supporting Information S1: Figures S3 and S4) with concentrations fluctuating but generally elevated in the wet season relative to the dry season. However, the magnitude of the increase and duration for which the concentrations are elevated is variable, being greatest in Barratta and Sandy Creeks (Figures 3D and 4D) and the Proserpine River (Supporting Information S1: Figure S3). The increase in diuron concentrations begins earliest in Barratta Creek, reflecting it being an irrigated region, whereas in most nonirrigated waterways diuron concentrations do not start increasing until at least November. As shown in Supporting Information S1: Figure S4, 30% of samples exceed ETVs for diuron.

Imidacloprid is highly toxic to freshwater insects and crustaceans and hence has very low - ETVs (i.e., the 99%, 95%, 90%, and 80% species protection concentrations are 0.05, 0.11, 0.19, and 0.38 µg/L, respectively; King et al., 2017). It should be noted that the ETVs for imidacloprid are currently being revised as considerable new toxicity data have become available since 2017 when King et al. (2017)

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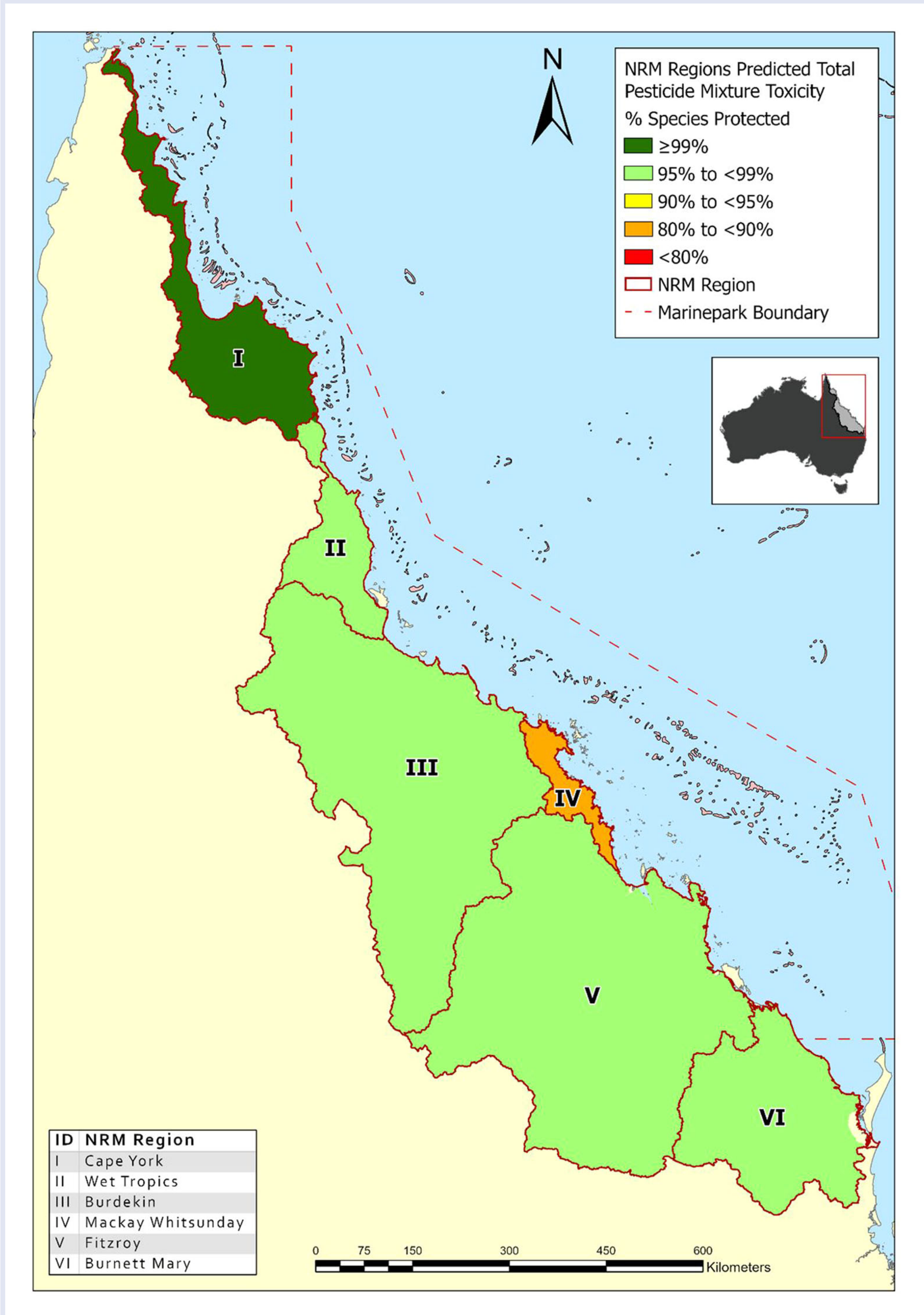

FIGURE 2 The estimated Total Pesticide Mixture risk based on concentrations of 22 pesticide active ingredients for the six Natural Resource Management Regions that constitute the Great Barrier Reef catchment area (Warne et al., 2023)

was published—how this will affect the resulting proposed ETVs is not known. Imidacloprid concentrations exceed the proposed ETVs (King et al., 2017) more frequently than any other PAI (Figures 3E and 4E and Supporting Information S1: Figure S5). Between 2009 and 2019, no exceedances of the proposed ETV for imidacloprid occurred in East Barratta and Plane Creeks (Supporting Information S1: Figure 5). Barratta Creek had considerably fewer exceedances that occurred sporadically through the year (Figure 3C), whereas the remaining waterways had numerous exceedances for 3–6 months continuously (Figure 4E).

Other PAIs that often exceeded their ETVs included hexazinone, imazapic, metolachlor, metribuzin, and metsulfuron-methyl (Supporting Information S1: Figure S6–S10). However,

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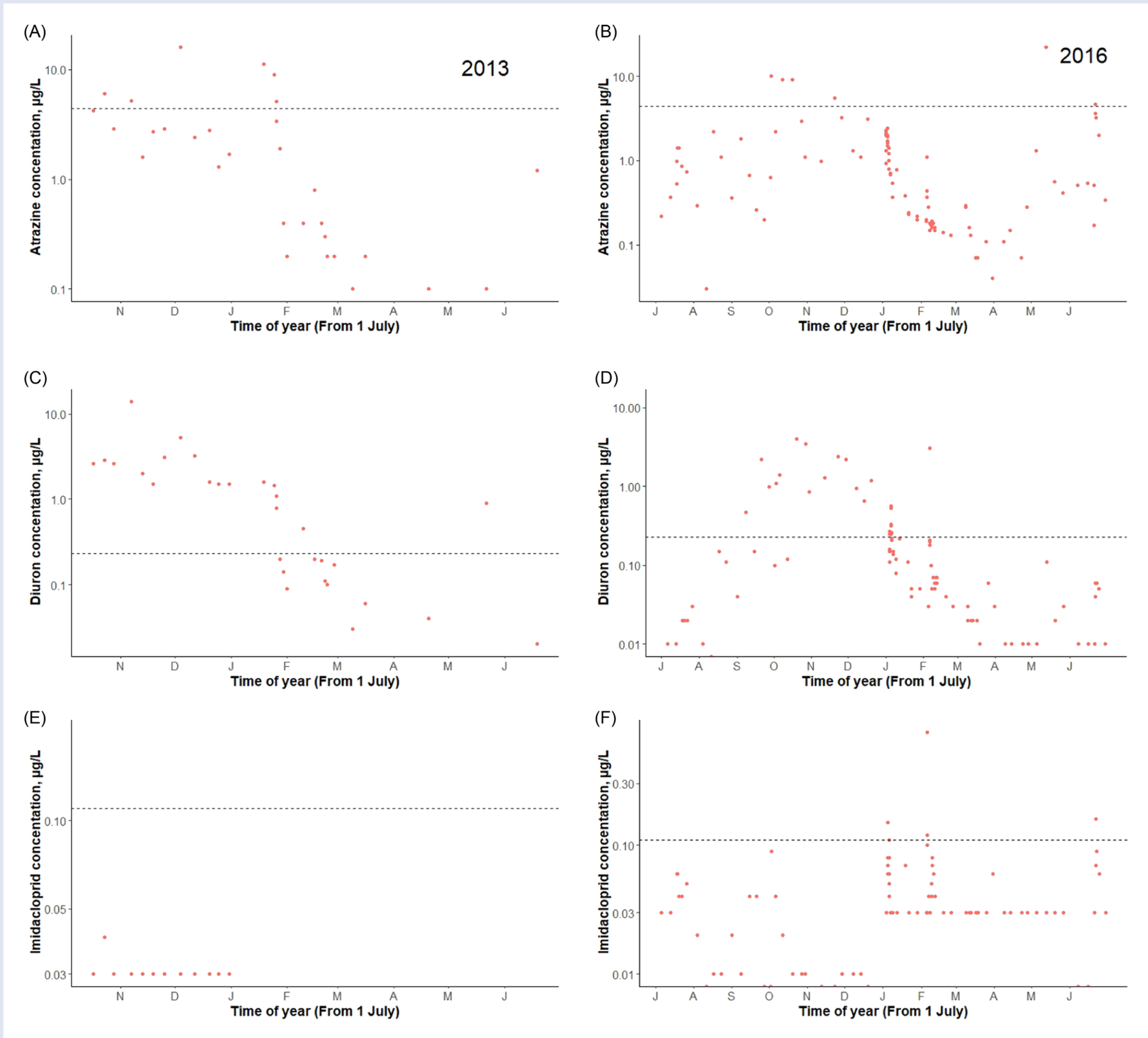

FIGURE 3 (A) Variation in atrazine concentrations in 2013 at Barratta Creek, the driest year between 2011 and 2019, compared with the atrazine ecotoxicity threshold value (ETV, horizontal line, to protect 95% of aquatic species). (B) The corresponding plot of atrazine concentrations in 2016, the wettest year. (C and D) Compilations of diuron (wet and dry years). (E and F) Imidacloprid (wet and dry years) and their ETVs. The ETVs are provided in Table S1. Data obtained from the Catchment Loads Monitoring Program (Queensland Department of Environment)

the percentage of samples that exceeded their proposed ETVs were markedly lower than for atrazine, diuron, and imidacloprid. The temporal trends in the concentrations of atrazine, diuron, and imidacloprid are representative of the other PAIs, although these other PAI concentrations infrequently exceed their corresponding ETVs.

Wetland temporal variability. Of the four studies of PAIs in GBR wetlands, only Vandergragt et al. (2020) has data on the temporal variation of PAIs. In nine of the 12 wetlands sampled during the wet seasons of both 2016/2017 and 2017/2018, the number of PAIs increased by between two and 11 PAIs, which represented a 10.5% to 68.8% increase in the number of PAIs detected. For the remaining wetlands, the number of PAIs decreased by between two and four, which represented a 9.1% to 18.8% decrease. The temporal variation in detected PAI concentrations was also large, ranging from less than 1% to 10 810% between the two years (Vandergragt et al., 2020). No explanation for the temporal variation was provided.

Temporal trends in nonpesticide stressors. Other stressors, such as suspended sediments and nutrients, are frequently elevated in waterways at the same times as PAIs (e.g., Supporting Information S1: Figures 3 and 4). The Proserpine River has elevated sediments year-round (Supporting Information S1: Figure S11) compared with the other waterways. Other waterways typically have

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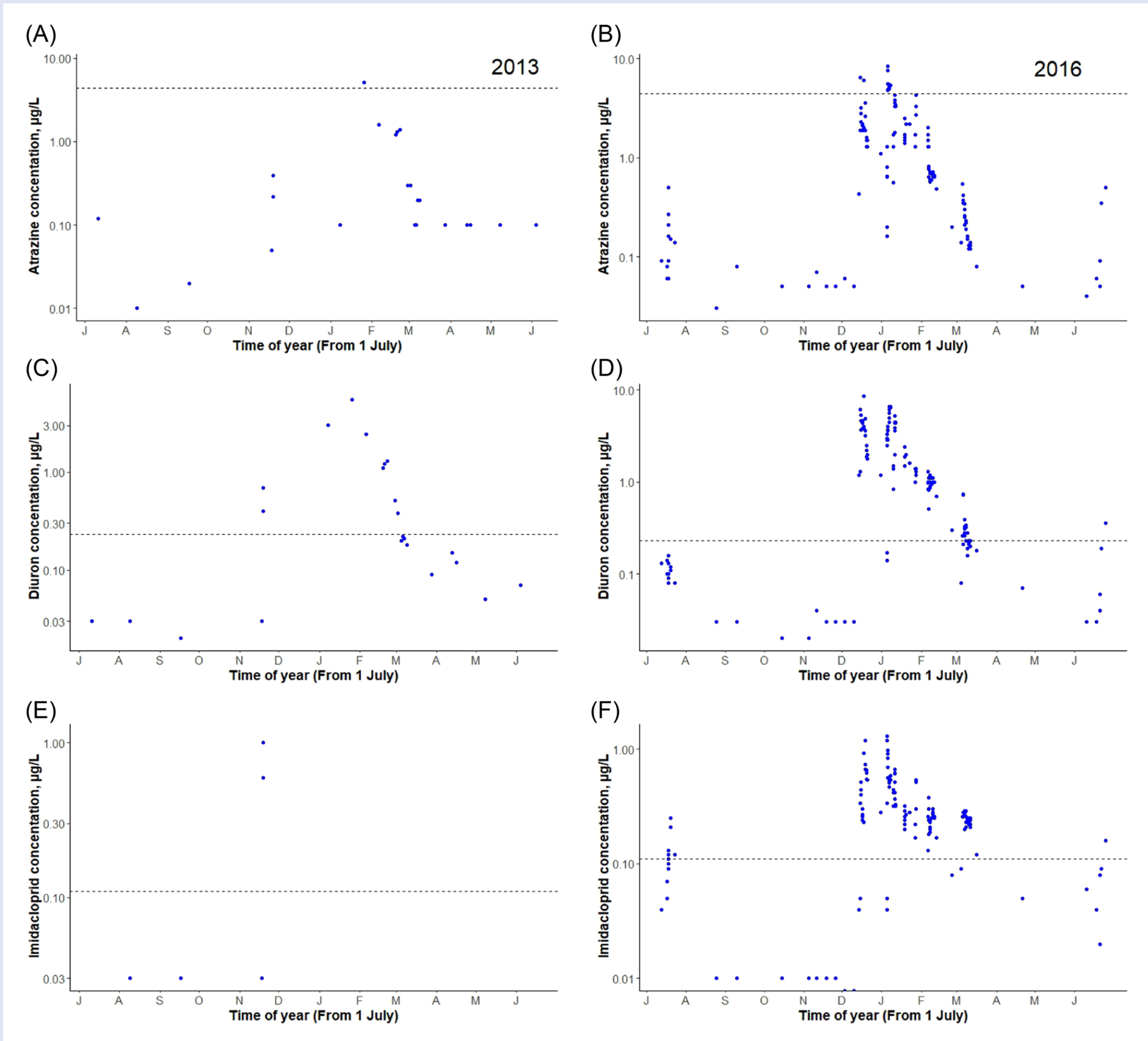

FIGURE 4 (A) Variation in atrazine concentrations in 2013 at Sandy Creek, the driest year between 2011 and 2019, compared with the atrazine ecotoxicity threshold value (ETV, horizontal line, to protect 95% of aquatic species). (B) The corresponding atrazine concentrations in 2016, the wettest year. (C and D) Compilations of diuron (wet and dry years). (E and F) Imidacloprid (wet and dry years) and their ETVs. The ETVs are provided in Table S1. Data obtained from the Catchment Loads Monitoring Program (Queensland Department of Environment)

lower sediment concentrations in August–October, during the dry season, and increased concentrations from November–April, during the wet season. Total nitrogen (TN) concentrations were also highly variable between and in the waterways, with the irrigated Barratta Creek having the highest TN concentrations (Supporting Information S1: Figure S12). Total nitrogen concentrations did not have a strong seasonal pattern in this irrigated catchment. High TN concentrations were also measured in the Pioneer and Proserpine Rivers and Sandy Creek (e.g., Supporting Information S1: Figure S12). As was observed for the PAIs, nitrogen concentrations often increased and remained elevated from November to March. Total phosphorus concentrations displayed a trend similar to TN concentrations (Supporting Information S1: Figures S12 and S13) in the same waterway.

In summary, the data described in this section indicate that, although PAI concentrations in the GBRCA fluctuate, they are frequently measured at concentrations that exceed DGVs. The multiyear temporal data demonstrate that peak PAI concentrations generally occur between October and March, and this peak period sees elevated concentrations of mixtures of herbicides and insecticides (Figures 3 and 4), increased nitrogen (Supporting Information S1: Figure S12), and TSS (Supporting Information S1: Figure S11), which is consistent for all waterways examined here. During a single wet season, several pulsed exposures to PAIs would occur during and after rainfall in

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most waterways downstream of agricultural land use (e.g., Smith et al., 2012; Water Quality and Investigations, 2020). In irrigated catchments, pulses of PAIs and nutrients would be linked to the irrigation events and may increase earlier in the growing season, as shown in Figure 3. The period of exposure to elevated pesticide concentrations in waterways with natural flow regimens can coincide with important events in the life cycle of aquatic organisms such as movement between habitats for fish and other mobile organisms, and higher summer temperatures and longer days triggering growth (Waltham et al., 2019). The pesticide monitoring program aims to collect 6–10 samples over each event; however, it is possible that the maximum concentrations are not sampled and thus are not included in the risk assessment. It is also possible that additional exposures near the paddock occur and that the PAI are degraded before they can be incorporated into monitoring programs. During the same period, fish and other freshwater organisms are likely to simultaneously encounter many sublethal stressors (i.e., elevated concentrations of multiple PAIs, nutrients, and suspended solids). This section demonstrates that the pesticide-related risk is plausible, based on concentration data, and that co-occurrence of pesticides and fishery species must be investigated.

CO-OCCURRENCE OF FISHERY HABITATS AND PAIs?

The previous section provided evidence that pulses of PAIs are regularly measured in many GBR waterways, and that, in some instances, these PAI pulses may present an environmental hazard. In the current section, we describe how these pulses intersect spatially with fish and crustacean habitats. The areas where PAI concentrations are high (i.e., the lower coastal floodplains of waterways) are habitat for many ecologically, recreationally, and sociologically important species of fish. A review of available published research revealed that GBR floodplain wetlands provide habitat to more than 80 fish species (Waltham et al., 2019). Some of these fish species remain entirely in freshwater ecosystems (e.g., Sooty grunter, *Hephaestus fuliginosus*), but at least 70 species of fish in the GBRCA have a diadromous life history, needing to migrate to fresh or estuarine and/or marine habitats at critical life stages (Russell & Hales, 1993; Russell et al., 1996a, 1996b, 2000). These species require connectivity to allow movement between marine and freshwater habitats. Any barrier or delay to migration could adversely affect future reproduction success for such species (Sheaves, 2009; Waltham et al., 2019). For example, the mangrove jack spawns on offshore coral reefs (Russell & McDougall, 2005), with larvae drifting into nearshore waters and estuaries where new recruits then use estuaries for feeding and shelter, while continuing further upstream to floodplain wetlands (see Figure 5). Mature mangrove jack eventually migrate back to the coast and inshore marine zone to complete their life cycle—this complex pattern of life-history connectivity between coral reefs and lowland freshwater wetlands emphasizes the requirement for connected and healthy waterways (Waltham et al., 2019). The barramundi, another fish species that is highly sought after in the GBRCA, also moves between freshwater floodplains and estuaries during its life history (Crook et al., 2017). Other diadromous fish species that are recreationally and/or commercially important include eels, mullet, and numerous smaller species that are important parts of the food chain (Bunn et al., 1997). Many fish species use a chain of habitats (Cappo et al., 1998) from freshwater to the reef with interrelationships between all habitats. Other species such as freshwater crustaceans remain on floodplains in both permanent and ephemeral waterbodies, occupying vegetated areas or channel banks in burrows, and would also be susceptible to PAIs (Bernays et al., 2014). Freshwater mussels also exist on the GBRCA floodplains, in sediments, and are important filter feeding species (Buelow & Waltham, 2020). As an example, the overlap between PAI occurrence and with fish habitat use is illustrated in the conceptual diagram in Figure 5.

Expansion and development of the human systems in the GBRCA has put pressure on these aquatic habitats by a range of stressors, in addition to chemical pollutants. A review of the Queensland Government Wetland Info mapping across the GBR catchments between 2001 and 2017 found a net loss of 7688 ha of natural wetlands, which consisted of riverine wetland (6255 ha), estuarine salt flats and saltmarshes (605 ha), and coastal and subcoastal tree swamps (1106 ha; Canning & Waltham, 2021). Most of the loss of wetland is the result of clearing and draining for urban and agricultural development. This rate of wetland loss has slowed in recent years (Canning & Waltham, 2021). Although the remaining wetlands are generally degraded, there have been major efforts to restore the functionality and connectivity of floodplains (Waltham et al., 2019). Building or reinstating more coastal wetlands in the coastal plain, in low lying marginal land areas, is one way to improve water quality while providing habitat for local species (Waltham et al., 2021). In summary, fish are likely to inhabit areas with elevated pesticide concentrations, and their populations may be under pressure from other stressors. As this risk hypothesis test has now been met (Figure 1), we must examine whether there is a mechanism by which toxicity may occur.

MECHANISM OF IMPACTS FOR PAIs

Pesticide AI monitoring in GBR wetlands and catchments has demonstrated that concentrations regularly exceed ETVs, and/or the combined concentrations of PAI mixtures are likely to adversely affect populations of some aquatic species, but not at concentrations that would be expected to cause acute toxicity in fish (Table 1; Negri, Flores, Kroon, et al., 2015; Negri, Flores, Mercurio, et al., 2015; Smith et al., 2012; Vandergragt et al., 2020; Warne, Neelamraju, Strauss, et al., 2020; Warne et al., 2022; Waterhouse, Brodie, et al., 2017). As discussed above, a variety of life stages of fish inhabit these waterways, and the time of year when exposure is most likely is a critical period in their life

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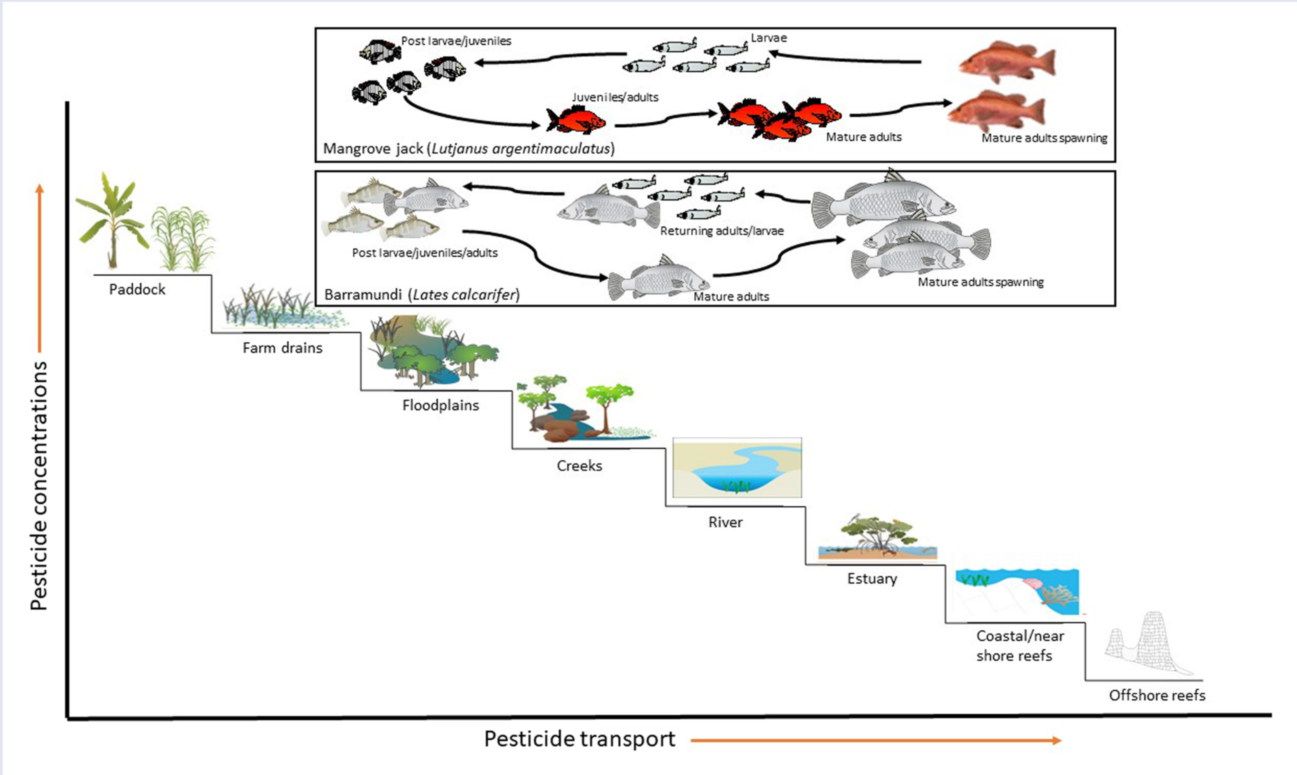

FIGURE 5 A conceptual diagram of the transport and decrease in pesticide concentrations (vertical axis) moving from agricultural land (paddock) to the offshore marine zone (horizontal axis) overlaid with the life history of barramundi and mangrove jack indicating where each life-stage lives. Although pesticide concentrations decrease through dilution as water is transported from the farm drains to the offshore, the number of PAIs would be expected to increase with inputs from different land uses

history. The next step in our risk evaluation is to determine whether these PAIs are likely to cause adverse outcomes in fish and other organisms, either directly or indirectly, and either alone or in concert with other stressors. Typically, risk assessments compare monitored PAI concentrations with laboratory-based ecotoxicity data and ecological thresholds of the most sensitive type of species (e.g., phototrophs for herbicides), the premise being that protecting the most sensitive species will also protect those that are less vulnerable to direct effects, but which may rely on the ecosystem functions provided by the more sensitive species. The organisms generally considered to be at greatest risk in GBR catchments (Table 1) are phototrophs to herbicide AIs, arthropods to insecticide AIs, and fungi to fungicides, based on the PAIs modes of action (reviewed in Butcherine et al., 2019; Wood et al., 2016). Fish species are considered relatively insensitive to these types of PAIs compared, for instance, with their sensitivity to organophosphate PAIs (e.g., chlorpyrifos and fipronil) that are detected only occasionally in GBR catchments (Table 1; Devlin et al., 2015).

The approach of focusing on the most sensitive species identified in standardized laboratory tests is scientifically logical; however, it does not specifically address the impacts that might be occurring to species that GBRCA residents value the most. Rather, providing residents with information on impacts on the ecosystems and species they value highly could help promote environmental stewardship leading to greater improvements in water quality. Whereas fish in GBR ecosystems are not likely to experience direct mortality after PAI exposure (compared with more sensitive species), it possible that sublethal impacts will occur with unidentified consequences (reviewed in Hook et al., 2014). For example, the PAIs more commonly detected in GBRCA waterways have been shown to affect fish at the metabolic level, for example, affecting circulating hormone levels and causing endocrine disruption (Eni et al., 2019; Tillit et al., 2010). Sublethal impacts causing stress on an organism could affect their resilience to other co-occurring stressors such as other water-quality pollutants. Indirectly, PAIs could also affect the organisms and habitats that less sensitive species depend on for food, shelter, oxygen, and nutrient cycling.

We reviewed the literature to identify mechanistic studies (i.e., those that have eco-physiological or biomarker type endpoints, as described in Hook et al., 2014) that describe potential sublethal impacts that may occur because of ongoing exposure to PAIs. We also identified studies that used a "systems biology" type approach—where the abundance of all gene transcripts, proteins, or metabolites are measured to demonstrate differences between individuals that can be linked to stressors to demonstrate real-world consequences of PAI exposures in the GBRCA. Taken together, this information can identify plausible pathways to harm from exposure to sublethal concentrations of PAIs. The mechanistic information for all these taxa was used to

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TABLE 1 Reported toxic concentrations of pesticide active ingredients detected in Great Barrier Reef catchments compared with ecotoxicity threshold values

Active ingredient	Detection	PC99 to PC80 values (µg/L)	Fish acute toxicity values (µg/L)	Fish sublethal toxicity values (µg/L)	Crustacean acute toxicity values (µg/L)	Crustacean sublethal toxicity values (µg/L)
Atrazine (H)	Common	1.3–2.1	30–95	0.15–555[a]	94–54 000	0.1–12.5[a]
Diuron (H)	Common	0.29–2.1	24.6–5900		160–15 500	10–7700[b]
Metsulfuron-methyl (H)	Occasional	0.0047–0.28	4500–8000	450–6800[c]	43 100[c]	3130[c]
Chlorothalonil (F)	Occasional	0.24–1.3	3–6.5	0.96–40[d]	0.17–125[d]	0.4–720[d]
Imidacloprid (I)	Common	0.04–0.38	480–24 000	1200–362 000[e]	2–175[f]	0.1–12.9[g]
Fipronil (I)	Rare	0.0034–0.033	0.2–365	0.061–0.33[h]	0.2–1.5[i]	0.001–0.2[j]
Chlorpyrifos (I)	Rare	0.00004–0.01	0.57–1018	0.625–11.6[k]	0.035–6.00	0.035–693[h]

Note: Acute toxicity values were obtained from ANZG (2018) or Williams et al. (2017). Sublethal toxicity values were obtained from these sources and the scientific literature to facilitate the inclusion of molecular responses.
Abbreviations: F, fungicide; H, herbicide; I, insecticide.
[a]Tillit et al. (2010), Shelley et al. (2012). https://comptox.epa.gov/dashboard/chemical/hazard/DTXSID9020112.
[b]https://comptox.epa.gov/dashboard/chemical/hazard/DTXSID0020446.
[c]https://comptox.epa.gov/dashboard/chemical/hazard/DTXSID6023864.
[d]https://comptox.epa.gov/dashboard/chemical/hazard/DTXSID0020319.
[e]https://comptox.epa.gov/dashboard/chemical/hazard/DTXSID5032442.
[f]Hook, Doan, et al. (2018); Hook, Mondon, et al. (2018); Anderson et al. (2015).
[g]Anderson et al. (2015).
[h]Beggel et al. (2012), Baird et al. (2013); Stehr et al. (2006).
[i]Data from USEPA OPP ecotoxicology pesticide database, http://www.ipmcenters.org/ecotox/DataAccess.cfm.
[j]Xing et al. (2012); reviewed in Tierney et al. (2010).
[k]Reviewed in Zhao and Chen (2016).

develop a conceptual model of ecosystem impacts. Sublethal toxicity of pesticide AIs to fish.

Mechanisms of impacts of PAIs to fish in controlled laboratory exposure

Water quality criteria are derived using the results of standardized laboratory toxicity tests (ANZG, 2018); however, the impacts of field-borne PAI exposure to fish may be more subtle and affect reproduction, metabolism, or foraging behavior via unrelated modes of action (reviewed in Hook et al., 2014). A review of the literature indicates that these sublethal impacts are plausible after PAI exposure. Although the literature is inconsistent (e.g., van der Kraak et al., 2014), there is evidence from studies conducted on fish in the laboratory that atrazine and diuron may act as reproductive endocrine disruptors (Kroon et al., 2015; Rohr & McCoy, 2010; Tillitt et al., 2010). A recent meta-analysis indicated that an atrazine predicted no effects concentration (PNEC) for reproductive endpoints of 0.044 µg/L, which is much lower than PNECs based on other endpoints (Zheng et al., 2017). Egg production decreased in fathead minnow (*Pimephales promelas*) exposed to environmentally relevant concentrations of atrazine, and gonad abnormalities were observed in both male and female fish (Tillitt et al., 2010). High exposure concentrations (e.g., those that exceed environmental concentrations) have also been shown to change circulating steroids and tissue structure in the testes of male goldfish (Spano et al., 2004). Exposure to environmentally realistic concentrations of atrazine caused changes in the abundance of transcripts for genes with a neuroendocrine function (Wirbisky et al., 2016). Some studies have also reported transgenerational impacts of atrazine exposure (Cleary et al., 2019). When the parental generation of medaka, *Oryzias latipes*, a laboratory model fish, are exposed to 5 µg/L atrazine, the offspring experience reproductive dysfunction (as decreased fertilization rates) and altered transcriptomic profiles, including for steroidogenesis and DNA methylation pathways (Cleary et al., 2019).

There is also evidence from the mammalian literature that these compounds may act as metabolic endocrine disruptors. Metabolic endocrine disruptors change the organisms' sensitivity to insulin, leading to altered lipid storage and use of carbohydrates (Nadal et al., 2017). Many of these compounds activate peroxisome proliferator-activated receptors (PPARs; Adeogun et al., 2016; Ibor et al., 2019). This family of receptors regulates lipid homeostasis and plays a role in the regulation of energy homeostasis and adipose tissue (Ibor et al., 2019). Transcriptomic patterns of PPARs were altered profoundly in barramundi from agriculturally affected catchments (Hook, Kroon, Greenfield, et al., 2017; Hook, Kroon, Metcalfe, et al., 2017; Hook, Mondon, et al., 2018). It is also possible that these compounds cause mitochondrial toxicity. The thylakoid membrane that is the target of photosystem II herbicides is structurally similar to

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the mitochondrial membrane (Lim et al., 2009), and studies performed on rodents reveal altered mitochondrial function (Lim et al., 2009; Simoes et al., 2017).

Exposure to PAIs such as atrazine may be causing additional sublethal impacts. Several studies have reported changes in immune-related transcript levels after exposure to atrazine in the laboratory (Shelley et al., 2012; Wang et al., 2011) or to PAI mixtures in the environment (Hook, Doan, et al., 2018; Hook, Kroon, Greenfield, et al., 2017; Hook, Kroon, Metcalfe, et al., 2017; Hook, Mondon, et al., 2018). Changes in the abundance of transcripts associated with the mitochondrial respiratory chain have been noted in zebrafish (*Danio rerio*) exposed to atrazine at concentrations as low as 1 μg/L in the laboratory (Jin et al., 2010). Atrazine exposure also disrupts smoltification (migrating from freshwater to marine) in salmon (Moore et al., 2003; Nieves-Puigdoller et al., 2007). Atrazine changes the activity of sodium–potassium pumps in the gill, which play important roles in ion regulation, at concentrations as low as 0.1 μg/L (Moore et al., 2003). Changes in the ion composition of smolts exposed to high concentrations of atrazine in the laboratory have also been noted (Nieves-Puigdoller et al., 2007). Atrazine exposure also interferes with olfaction, which fish use in navigation, detection of prey and predators, and mate selection (Moore et al., 2007). These exposure responses have important implications for migratory fish in GBR catchments.

The herbicide 2,4-D may also affect recruitment of larval fish. Dehnert et al. (2018) found that 0.05 ppm 2,4-D impairs survival of fathead minnow larvae. The adults and juveniles are seemingly unaffected; only larvae are affected. The mode of action is thought to occur via activation of oxidation stress pathways. The impact occurs regardless of the formulation used, suggesting that it is the AI causing toxicity (Dehnert et al., 2018). Other insecticides may also be affecting fish in the GBRCA. For example, pyrethroid insecticides, commonly used for mosquito control, may act as endocrine-active compounds in fish. In laboratory exposure, fish exposed to environmentally realistic concentrations of these compounds exhibited changes in gonad morphology, decreased testosterone, and increased estrogen (Eni et al., 2019). The study's authors also recorded changes in blood enzyme levels that indicate tissue damage as well as changes in liver gonad histopathology (Eni et al., 2019). Taken together, the data from the studies reviewed in the preceding paragraphs suggest that exposure to environmentally realistic concentrations of PAIs may cause impacts that would not be detected in standardized laboratory tests but would nonetheless affect their ability to grow, reproduce, and survive in contaminated environments.

Indicators of impacts on fish in the GBRCA

Several studies indicate that these impacts may be occurring in fish from the GBRCA. Using a systems biology approach, we identified changes in the transcriptomic profiles of barramundi (*Lates calcarifer*) collected from waterways that receive agricultural runoff (Hook, Kroon, Metcalfe, et al., 2017). Some of these altered transcripts suggested physiological changes, including altered patterns of lipid processing and altered immune response. These changes were only apparent if the fish were collected at a time of year when water quality was compromised (Hook, Kroon, Greenfield, et al., 2017). Other studies of fish exposed to atrazine under environmentally realistic laboratory conditions have found similar changes in transcriptomic profiles (Shelley et al., 2012). Follow-up studies in different GBRCA rivers but with the same land use patterns and contaminant loading revealed the same transcriptomic changes in barramundi (Hook, Mondon, et al., 2018). Similar transcriptomic changes have been observed in fish from rivers exposed to the same types of contaminants in North American river systems (Jeffries et al., 2015). Our previous work also indicated changes to lipid levels in fish and swelling (hyperplasia) of the gills (Hook, Mondon, et al., 2018). This gill hyperplasia may make fish more susceptible to hypoxia.

Kroon et al. (2015) examined barramundi and coral trout in GBR catchments and the GBR lagoon along 600 and 1200 km of the GBR, respectively. They found altered transcription levels for liver vitellogenin transcript abundance that was significantly related to the percentage of land used for sugarcane in the catchments adjacent to where the barramundi were collected. The liver vitellogenin transcript abundances were also significantly related to the aqueous concentrations of four sugarcane PAIs, namely ametryn, diuron, hexazinone, and imidacloprid, as well as with simazine. The pattern of liver vitellogenin activity in the ocean trout was consistent with that of the barramundi.

Impacts on arthropods

Pesticide AI concentrations in the GBR catchments may affect crustacean populations. Arthropods, similar to fish, are generally much less sensitive to the harmful effects of herbicide AIs than phototrophs. However, impacts may occur at concentrations lower than those predicted in laboratory studies. Orlinskiy et al. (2015) found that measurable declines in sensitive freshwater insects occurred in field mesocosms at PAI concentrations three to four orders of magnitude lower than the acute LC50 toxicity values (the concentration that causes mortality in half of the population) for *Daphnia* sp. and *Chironomus* sp. from standard laboratory toxicity tests. Thus, population declines could be occurring at concentrations well below 1 μg/L. In addition, some impacts may be predicted based on the results of laboratory studies alone. Exposure to mg/L concentrations of atrazine decreased the growth rate of crayfish (Mac Loughlin et al., 2016). Mud crabs (*Scylla serrata*) exposed to atrazine concentrations greater than 30 μg/L displayed decreases in muscle glycogen and a decrease in ovarian growth and vitellogenesis (Silveyra et al., 2017). Similar reproductive changes were measured in crayfish (*Procambarus clarkia*) exposed for extended periods to atrazine, as well as changes in lactate metabolism and circulating glutathione (Silveyra et al., 2018).

Imidacloprid is the most abundant neonicotinoid insecticide measured in the GBRCA; it was detected in 54% of

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6493 water samples from the GBRCA between 2009 and 2017 (Warne et al., 2022), but its presence is highly variable, spatially occurring in between 0 and 99.7% of samples from individual waterways (Warne et al., 2022). Neonicotinoid PAIs are specifically designed to bind to the arthropod GABA receptor, so insects and crustaceans are much more sensitive than algae, fish, and other types of invertebrates (Anderson et al., 2015). Numerous laboratory studies have confirmed the potential for neonicotinoid PAIs to exert harmful effects on nontarget crustaceans (e.g., Brodie & Landos, 2019; Butcherine et al., 2019). A risk assessment (Pathiratne & Kroon, 2016) determined that imidacloprid could be having ecosystem-level impacts as the upper 95th percentile values of concentration in GBRCA waterways exceeded a PC95 value of 0.18 µg/L. A more recent study examined the spatial and temporal variation in the concentration of and risk by imidacloprid in 14 GBRCA waterways between 2009 and 2017 (Warne et al., 2022). They found that imidacloprid concentrations and risk had increased during the period in six waterways. They also found that, across the 14 waterways, imidacloprid posed a small risk with 74% of samples protecting at least 99% of species, but in one waterway, up to 42% of aquatic species would experience harmful chronic effects. Imidacloprid has been shown to cause feeding inhibition in native larval prawns at 0.5 µg/L, concentrations that are routinely measured in Queensland rivers (Hook, Doan, et al., 2018). Adult prawns exposed to imidacloprid have decreased lipid content and body mass (Butcherine et al., 2020), demonstrating the potential for ecosystem-wide effects caused by decreased nutritional content of crustacean prey. Studies of blue crabs (*Callinectes sapidus*) in the southern USA found that imidacloprid exposure increased molting frequency and increased molting-related mortality (Osterberg et al., 2012).

Impacts of exposure to neonicotinoid insecticides have also been measured in microcrustaceans, which has implications for trophic transfer and biogeochemical cycling. Exposure to thiacloprid has been shown to cause feeding inhibition in copepods (Arican et al., 2017). In a mesocosm experiment where organisms were exposed to a single concentration of imidacloprid, copepods, chironomids, and mayflies were all found to be sensitive to exposure, with NOECs (or concentrations with no toxic impacts) below 0.2 µg/L (Rico et al., 2018). Effects were greatest 14–28 days after exposure, and the invertebrate community recovered after eight weeks. The authors suggested that larval life stages of the community may be especially sensitive and that the Mediterranean temperatures used in their study may enhance sensitivity (Rico et al., 2018). As the GBRCA is tropical, a similar range of temperatures as were recorded in the Mediterranean may occur. Other mesocosm studies using imidacloprid have found similar results and that copepods were among the most sensitive of the species studied (Sumon et al., 2018). Chara-Serna et al. (2019) found that simultaneous exposure to combinations of sediments, nutrients, and imidacloprid significantly enhanced declines in zooplankton density and richness. These results are directly relevant to the GBR because these three stressors often co-occur. Intriguingly, exposure to thiamethoxam, which has a shorter half-life than other neonicotinoid insecticides (Rico et al., 2018), did not alter zooplankton community structure in mesocosm experiments eight weeks after a single pulsed exposure (Finnegan et al., 2018; Lobson et al., 2018).

Pesticide AIs that reduce the abundance of zooplankton and other fish prey items may affect fish populations via bottom–up effects. A recent example of such bottom–up effects is the work by Yamamuro et al. (2019) who found that the commencement of using imidacloprid in rice paddies in the Shimane Prefecture, Japan (1993), was followed one year later by zooplankton biomass decreasing by 83% in Lake Shinji and that the biomass had not recovered by 2004. They also found that mean annual harvested yields of two zooplanktivorous fish (*Hypomesus nipponensis* and *Anguilla japonica)* had large decreases whereas the yields of a third diatom eating fish (*Salangichthys microdon*) did not change. No equivalent studies have been conducted into the effects of PAIs on food webs in freshwater, estuarine, or marine ecosystems associated with the GBR. Despite this, indirect evidence suggests that imidacloprid could be causing harmful effects on fish populations in waterways of the GBRCA. It is not clear what neonicotinoid concentrations caused the decline in zooplankton and fish abundance in Lake Shinji, because Yamamuro et al. (2019) did not measure neonicotinoid analyses until 2018, 15 years after neonicotinoids use began. The highest measured concentration of total neonicotinoids in 2018 was 0.072 µg/L (Yamamuro et al., 2019). This was measured when total neonicotinoid use in the Shimane Prefecture was several thousand times greater than when the fish population declines occurred (Yamamuro et al., 2019). Therefore, the maximum neonicotinoid concentrations in Lake Shinji in 1993 would have been markedly lower than 0.072 µg/L. Nine of 14 GBRCA waterways examined by Warne et al. (2022) had maximum concentrations between 2009/2010 and 2015/2016 that were greater than the maximum reported imidacloprid concentration in Lake Shinji in 2018. Therefore, Warne et al. (2022) argue it is plausible that imidacloprid is exerting harmful effects on aquatic zooplankton and indirectly on fish in GBR waterways.

Organic matter (including leaves) sprayed with imidacloprid are also a potential source of imidacloprid that could affect aquatic ecosystems. Kreutzweiser et al. (2008) examined the impact of introducing sugar maple tree leaves that had been sprayed with imidacloprid into aquatic microcosms in Canada. They found that mortality of leaf-shredding insects was not affected but feeding rates were reduced, leaf decomposition decreased, and concluded that natural decomposition processes could be harmed. Decreased food availability, which is effectively the same as decreased feeding rates, has been shown to decrease: the number of young, the net reproductive rate and population growth rate in other crustaceans (e.g., Rose et al., 2002), and insects (Giberson & Rosenberg, 1992). Such effects could

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have flow-on effects to insectivorous fish. This potential source of imidacloprid in GBRCA waterways and its potential impacts have not been investigated.

Although not directly relevant to this assessment, it is also possible that aqueous concentrations of imidacloprid in GBRCA waterways could be exerting effects on terrestrial species. Hallmann et al. (2014) found that an annual average imidacloprid concentration of as low as 0.02 μg/L in Dutch rivers led to an annual decrease in insectivorous bird populations of 3.5%. They argued that the imidacloprid killed or reduced the number of aquatic insects that emerged from Dutch rivers, reducing the food available to insectivorous birds with subsequent negative effects on their populations. The annual average concentration of imidacloprid in the Mulgrave, Russell, North Johnstone, Tully, O'Connell, and Pioneer Rivers and both Barratta and Sandy Creeks for 2009/2010 to 2016/2017 were all equal to or greater than 0.02 μg/L (Warne et al., 2022). Also, the multiyear average concentration of imidacloprid (based on approximately 6500 samples from 14 GBRCA waterways) was 0.051 μg/L (Warne et al., 2022). As GBRCA waterways annual average concentration is 2.5 times higher than the threshold found by Hallman et al. (2014), Warne et al. (2022) argued it is quite plausible that insectivorous bird populations in the GBRCA might be declining. If imidacloprid concentrations of 0.02 μg/L in rivers are sufficient to decrease insectivorous bird populations, when many insects they feed on would be of terrestrial origin, then it is highly likely that populations of insectivorous fish would simultaneously suffer declines. No such investigations have been conducted in GBRCA catchments.

Impacts on algae

It is plausible that PAIs are affecting fish populations via indirect effects mediated through the food web (e.g., Fleeger et al., 2003). Algae are likely to be the most sensitive species to herbicide exposure. Environmentally realistic concentrations of diuron have been shown to change community composition of benthic microalgae in microcosm exposures (Magnusson et al., 2012). Ongoing exposure to herbicides in rivers in the GBRCA has been shown to change the species composition of benthic diatoms (Wood et al., 2019). Wood and colleagues (2019) developed a benthic diatom indicator profile to determine the fraction of a community in each watershed that was sensitive to herbicides. The index could be correlated with overall herbicide toxicity and was reduced in wet season samples from agriculturally affected catchments. Many of the diatoms isolated from affected rivers are known to be highly tolerant of organic pollutants (Wood et al., 2019). The impacts of the changes in algal species composition on the organisms that consume plankton are unknown. More recently, Van de Perre et al. (2021) demonstrated that imidacloprid concentrations as low as 0.03 μg/L in subtropical mesocosms led to major changes in the composition of phytoplankton and zooplankton and indirectly led to cyanobacteria blooms with subsequent potential impacts on ecosystems and human health. In addition, they found that the cyanobacteria blooms reduced light penetration into the water column and subsequently decreased photolysis of imidacloprid. They further postulated that the combined presence of *Microcystis aeruginosa* and imidacloprid could be synergistic as Cerbin et al. (2010) found that carbaryl and *M. aeruginosa* interacted synergistically.

ECOLOGICAL IMPACTS FROM OTHER STRESSORS

Nutrients are applied predominantly to agricultural land as fertilizers and, like water soluble PAIs, would enter the GBRCA via surface or groundwater. Local impacts of nutrient runoff can include hypoxia, eutrophication, and ammonia toxicity (Davis et al., 2017). Although nutrients are toxic at sufficiently high concentrations (e.g., LC_{50} of 0.045 mg/L for ammonia and 1.5 g/L for nitrate [Tilak et al., 2002]), they are more likely to affect fish and crustacean populations indirectly. Algal growth is typically limited by nitrogen and phosphorus and, in many cases, increasing nutrient concentrations causes algal blooms (Glibert et al., 2016). When the algae decompose, it can cause localized hypoxia and fish kills. Even under scenarios where elevated dissolved nutrients are not measured because it is rapidly sequestered by plants, there can be an increased incidence of hypoxic events (Davis et al., 2017). Nutrient runoff can also contribute to the proliferation of invasive aquatic weeds (Davis et al., 2017), which can change fish habitat (Waltham, Coleman, et al., 2020b).

It is not only that changing the concentrations of nutrients can cause increased growth of phytoplankton, but changing nutrient concentrations can also change phytoplankton community composition (Caron et al., 2017; Glibert et al., 2016). The transporters that phytoplankton use to concentrate nutrients in their cells perform optimally at either low or high concentrations (Rogato et al., 2015). Algae (including photosynthetic cyanobacteria) typically have optimal nutrient ranges as a consequence. The optimum N:P ratio also differs for different algal subclasses, with dinoflagellates and cyanobacteria thriving under nutrient regimens with higher N:P ratios than the typical 16:1 Redfield ratio (Bouwman et al., 2011; Glibert et al., 2016). Modern fertilizers more commonly use ammonia or urea than nitrate (Glibert et al., 2016). Different classes of algae specialize in taking up each form of nitrogen, so changing the form of nutrients will further change the community composition (Glibert et al., 2018). Because of selective grazing in the zooplankton community and, in some cases, toxin production by the algal community, changing the phytoplankton community composition will have bottom–up impacts on the rest of the ecosystem.

Floodplains in the GBRCA are also susceptible to algal blooms, excessive aquatic weed growth, and turbidity (e.g., irrigation tailwater on the Burdekin floodplain), along with periodic and persistent hypoxic conditions, which each vary over complex spatial and temporal patterns (Perna et al., 2012; Waltham & Fixler, 2017). Arthington et al. (2015) found that richness in exotic aquatic plants was one of the main correlates for differences in fish assemblages in wet

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tropics floodplain lagoons, which outcompetes native vegetation cover, reducing fish habitat and can also cause hypoxia.

The use of herbicides to control aquatic weeds on floodplains is common on the Burdekin floodplain, which assists in flood control and delivery of irrigation water across the network (Davis et al., 2014). However, an important consequence of this spraying is that it contributes to secondary problems, for example, when the aquatic plants decompose, the available oxygen is consumed to levels well below critical thresholds for fish. If fish are not able to activate some compensatory response (e.g., surface gulping of oxygen), they will die (Butler et al., 2007). Although the hypoxia exposure risk is generally greatest during summer under warm conditions and high rainfall, which transports turbid, nutrient rich water to floodplain wetlands (Waltham, Coleman, et al., 2020b), direct impact of the herbicides on fish condition has not been investigated and requires further targeted research.

Although only a few of the studies summarized in the section above were conducted in the GBRCA, the summarized literature demonstrates the plausibility that pesticide exposure is causing sublethal toxicity, meeting the criteria for the third risk hypothesis test. The few studies that examine metrics of fish health have found transcriptomic and other molecular alterations with putative links to pesticide exposure (Hook, Kroon, Greenfield, et al., 2017; Hook, Kroon, Metcalfe, et al., 2017; Hook, Mondon, et al., 2018), providing initial evidence of the fourth risk hypothesis (Figure 1) that there are physiological indicators of changed health.

CHANGES IN FISH COMMUNITIES

A conceptual model of ecosystem changes: Determining a pathway to harm

Most of the PAIs that have so far been detected in the catchments of the GBRCA pose the greatest risk to organisms that are typically toward the bottom of food webs. For example, herbicides such as atrazine and diuron are most toxic to algae, and insecticides are most toxic to insects and crustaceans. Therefore, it might be expected that, if such PAIs were to exert effects on fish, they would be bottom–up (indirect) effects.

Changes in fish physiology induced by PAIs may not cause mortality in the exposed fish outright. However, by affecting their energy stores, their ability to migrate for spawning, their susceptibility to hypoxia, or their fecundity, native fish (such as barramundi or mangrove jack) may be less resilient to other stressors and replaced with invasives, such as tilapia, which do not need to migrate. These physiological changes related to PAI exposure may be exacerbated by hypoxic events or fragmentation of river habitat by physical changes such as damming.

Figure 6 illustrates how these PAI stressors could interact to cause a decline in the fitness of fishery species and potentially create opportunities for the expansion of opportunistic or invasive species. Although these ideas remain hypothetical, as outlined above, there is evidence to suggest they are plausible. For example, exposure to insecticides would cause feeding inhibition in crustaceans (e.g., Hook, Doan, et al., 2018), which could reduce their abundance and lipid stores, resulting in lessened prey quantity and quality for foraging fish. These changes may be exacerbated by the metabolic changes measured in fish exposed to herbicides (Hook, Kroon, Greenfield, et al., 2017; Hook, Kroon, Metcalfe, et al., 2017; Shelley et al., 2012). Decreases in prey quality and quantity could lead to reduced recruitment. Similarly, exposure to herbicides has been shown to cause inflammation of the gills (Hook, Mondon, et al., 2018), which would lead to an increased susceptibility to hypoxia. Because increased concentrations of nutrients would be expected to increase the frequency of algal blooms and exotic aquatic plant species, hypoxic events would also be likely (Arthington et al., 2015; Glibert et al., 2016). Consequently, fish kills may increase in severity and frequency. Decreased recruitment and increased mortality may result in the replacement of species. Although evidence exists for the plausibility of these outcomes, additional evidence would need to be collected to determine if this is happening in the GBRCA.

Observed changes in fish communities in the GBRCA

Despite ample evidence of the spatial and temporal overlap of high PAI concentrations (i.e., that exceed ETVs) with fish habitation and the plausible links between sublethal exposure to these PAIs and changes to organism health, there are very few studies or programs that have evaluated whether exposure to PAIs has affected fish populations in the GBRCA.

Arthington et al. (2015) looked for evidence that changes in water quality and fish habitat from agricultural land use (including PAIs) affected fish assemblages in the GBRCA. The authors examined fish assemblages in 10 wetlands (Tully–Murray catchment) surrounded by sugarcane and other agricultural land uses, finding negative relationships between species richness and hexazinone, chlorophyll-a, dissolved oxygen, and dissolved organic nitrogen concentrations. However, diuron and atrazine were also examined with no significant relationships observed. In this case, impacts of agricultural land use does seem to play a role in changes in fish assemblages, but the influencing role that PAIs have, among other agricultural stressors, is not clear.

At first glance, results from the annual Mackay–Whitsunday–Isaac water-quality Report Cards (Mackay-Whitsunday-Issac Healthy Rivers to Reef Partnership, 2021) seem inconsistent with the hypothesis that PAIs affect fish communities; for example, catchments with "good" to "very good" grades for fish species richness have "very poor" grades for PAIs. In addition to the Catchment Loads Water Quality Monitoring Program (mentioned in earlier sections), a fish monitoring program also operates in some areas of the Mackay–Whitsunday, where both sets of results are reported in annual waterway report cards. However, robust

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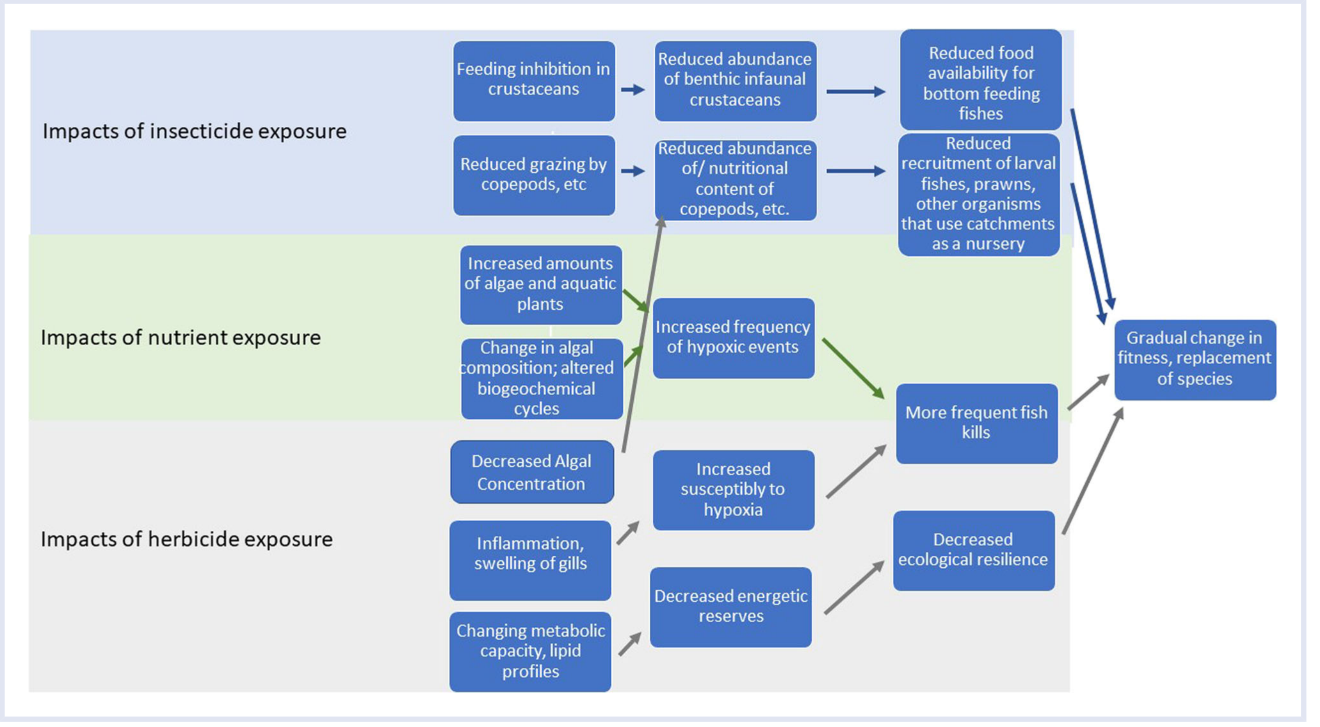

FIGURE 6 Conceptual model showing how stressors could interact to lead to replacement of species in the Great Barrier Reef catchment area

comparisons between their outputs is difficult because the two monitoring programs were historically not designed to be scientifically aligned, that is, sampling areas are not paired and results are not reported in a chronological order to make cause–effect links (i.e., the fish are sampled before the water quality). This has not prevented some stakeholders from making their own comparisons in the media, leading to questions about the validity of the results (e.g., https://healthyriverstoreef.org.au/news/answering-your-questions-on-freshwater-fish-pesticides-and-waterway-health/). Ideally, to measure if PAIs are having any effect on fish populations, aligning the timing of monitoring and site selection would be required—although fish sampling has logistical limitations in these areas that overlap with saltwater crocodile habitat toward the end-of-catchments.

In areas outside the GBRCA, albeit with different contaminants and fish, previous studies have demonstrated that sublethal concentrations of contaminants have been sufficient to affect fish at the population level. For instance, in the Pacific Northwest of the USA, studies have revealed that ongoing pollution of Portland Harbor is preventing restoration of salmon populations in the area, even after habitats were restored and connectivity was improved (Lundin et al., 2019). Fish with longer residence times in contaminated areas are expected to be most affected. The models used predict that the population will increase by as much as 20% after Portland Harbor is remediated (Lundin et al., 2019). In summary, of the risk hypotheses presented in Figure 1, there is the least evidence to either support or refute the hypothesis that PAIs are affecting fish populations. Despite the lack of evidence of PAI exposure to be causing population-level impacts in fish, there is evidence that these exposures are causing changes in the species composition at lower trophic levels.

PERSISTENCE AND MITIGATION OF THE ECOLOGICAL EFFECTS OF PAIs

Several factors could mitigate (reduce) the potential effects of pesticides on fish, including undisturbed sections upstream of exposed habitats, riparian and native aquatic vegetation, and frequent flushing of exposed habitats. The presence of "undisturbed stream sections" (also referred to as upstream forested reaches) decreases the duration and magnitude of impacts on macroinvertebrate community composition by PAIs (Bunzel et al., 2014; Liess & Von der Ohe, 2005; von der Ohe & Goedkeep, 2013; Schäfer et al., 2007) for up to 11 km downstream (Orlinskiy et al., 2015) and decreases the duration of the impacts (Liess & Von der Ohe, 2005; Orlinskiy et al., 2015). These undisturbed stream sections act as sources for recolonizing organisms and/or of allochthonous material (Webster, 2007) that aid recovery (Bond et al., 2006) of downstream macroinvertebrate communities. Orlinskiy et al. (2015) found that pesticide mixture toxicity and the length of the undisturbed stream sections could explain 78% of the variation in macroinvertebrate community composition. The minimum and optimal length of undisturbed stream sections required to improve the community structure of other fast-reproducing species is likely to be similar to that for macroinvertebrates, whereas it is likely that improving fish community structure would take longer.

Ameliorative effects of naturally vegetated sections downstream of agriculture are likely to be smaller than upstream

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undisturbed sections not exposed to PAIs (Orlinskiy et al., 2015), although Arthington et al. (2015) concluded that the Tully–Murray floodplain lagoons (surrounded by intensive agriculture) were in good ecological condition, which was likely the result of the retention of some riparian vegetation. Orlinskiy et al. (2015) concluded that "uniform agricultural landscapes devoid of refuge habitats are a precondition for the local extinction of vulnerable species of aquatic invertebrates." Schriever et al. (2007) states that the ameliorative effects of undisturbed stream sections suggest that "landscape management options may exist that would allow relatively intensive agriculture to coexist with reasonable levels of aquatic invertebrate biodiversity." Also considering the findings of Arthington et al. (2015), similar relationships likely exist between the biodiversity of any type of organism (including fish) and undisturbed stream sections.

Rasmussen et al. (2013) stated that organisms with short life cycles and strong migration abilities have great recovery potential. Thus, algae and aquatic insects might be expected to recover relatively quickly from the exposure to PAIs during the wet season but species with long life cycles (e.g., some fish) would be expected to recover more slowly. This is consistent with the findings of Liess and von der Ohe (2005), Orlinskiy et al. (2015), and Wood et al. (2019) who studied organisms with a high recovery potential.

The percentage of land devoted to conservation in 141 GBR catchments ranges from 0 to 100%, with 75% and 50% of catchments having at least 20% and 40%, respectively, of land devoted to conservation (Al-Ghafri, 2021). Thus, there is considerable potential for conservation land to reduce the impacts of PAIs or to increase the rate of recovery from the adverse effects of PAIs in GBR catchments. The proportion of conservation land is also a source of diluent, that is, runoff free of pesticides, which acts to reduce PAI concentrations and therefore their risk to aquatic ecosystems. Arthington et al. (2015) noted that the frequent flushing in the Tully–Murray catchments were likely another reason for the good ecological condition of the floodplain wetlands they assessed. In comparison, the Herbert and Burdekin floodplains have less frequent flushing to dilute poor water quality that has resulted from sugarcane runoff (Arthington et al., 2015, and references therein).

In a major review of the effect of co-occurrence of suspended solids and PAIs that included some Australian studies (Phyu et al., 2004, 2005a, 2005b, 2005c, 2006, 2013), Knauer et al. (2016) concluded that only the toxicity of pyrethroids with log K_{ow} values greater than 5 decreased in the presence of suspended solids. Given the log K_{ow} values of most PAIs detected in GBR catchments are less than 5, the co-occurrence of suspended solids and PAIs is unlikely to modify PAI bioavailability and toxicity.

NEEDS FOR IN SITU ASSESSMENTS

Thus far, we have documented the plausibility that PAIs could affect the health of freshwater ecosystems. The concentrations of PAIs measured in the GBRCA would pose an environmental hazard but, as of yet, evidence is lacking that these changes are actually occurring (e.g., Chapman, 1999), in that they exceed those that cause toxicity in laboratory studies. Drawing inferences from the initial hazard assessment to ecologically relevant endpoints, such as recruitment of commercially important species, cannot be done with the existing data. As detailed above, only a handful of studies have revealed the impact of changes in water quality on individual fish health and fitness (Hook, Kroon, Greenfield, et al., 2017; Hook, Kroon, Metcalfe, et al., 2017; Hook, Mondon, et al., 2018), and there is insufficient evidence to determine what impact, if any, these changes in water quality are having on populations of fish, crustaceans, and other species with high social values.

The potential ameliorative effects of undisturbed or naturally vegetated stream sections on the effects of PAIs in GBRCA waterways warrant investigation. In addition, it would also be important to investigate the impacts of herbicide AIs on native aquatic plant species where reduced riparian vegetation cover, and therefore reduced cooling and shading, also occurs. Aquatic plants exposed to higher light intensities often have a greater susceptibility to photosystem II herbicides as a result of the increased formation of reactive oxygen species that cause photodamage (Jones, 2005). Similarly, the combined impacts of photosystem II herbicides with higher temperatures demonstrated that water quality guideline values for herbicides would need to be reduced to protect an equal number of species at higher water temperatures (Negri et al., 2020).

To better assess the consequences of the hazard presented by elevated PAI levels, and to provide the evidence needed to change land management practices, the focus of the current monitoring work should shift to conducting in situ impact assessment. Typically, impact assessments are conducted using several lines of evidence, including pressure information, chemical analysis, toxicity testing, bioaccumulation, biomarkers, and population level changes (Hook et al., 2014; Lehtonen et al., 2019; Regoli et al., 2019). The lines of evidence accumulated to date indicate the potential for impact, e.g., there are several changes associated with the declines in water quality. The plausibility of impacts has been established in this review. However, as the studies conducted to date have been opportunistic, have been conducted with only a few taxa, and have investigated each line of evidence independently (e.g., Regoli et al., 2019), a conclusive picture of the impact of PAI concentrations on the health of socioeconomically valuable species in GBR catchments, such as barramundi or mud crabs, cannot be determined. A more thorough impact assessment (typically conducted by measuring ecological community structure and/or organism health metrics in concert with assessments of the stressor—in this case the PAI concentrations) is needed before the true impacts of changes in water quality of the health of the catchments can be determined. Integrating many lines of evidence would be required to avoid spurious conclusions. For impacts on fish populations, because changes in species richness can

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happen for myriad reasons (competition from invasive species, changes in food resources, hypoxia, temperature shocks, as well as changes in fitness caused by toxicant exposure), it would be difficult to make a specific link between exposure and population level declines without specific linking information (such as contaminant body burdens or linkages made with the assistance of physiological indicators or biomarkers).

Some work that may address these gaps is currently underway. Some of the current authors have a citizen science project collecting water and eDNA samples at approximately 40 sites in the Mackay–Whitsunday and Wet Tropics NRM regions (https://barrierreef.org/news/news/10-citizen-science-projects-get-all-hands-on-deck-to-boost-reef-protection). This study aims to determine if concentrations of nutrients, sediments, or pesticides are correlated with the species present at the time of sample collection. Despite the limitations of eDNA sampling, in particular because it does not provide information about abundance or health of the organisms present, we expect that this may provide a valuable line of evidence as to the potential for impacts of changing water quality on freshwater organisms.

Another potential that warrants investigation is whether sediment deposition areas in waterways may have elevated concentrations of more hydrophobic PAIs and whether these could cause locally significant impacts by entering food chains.

CONCLUSIONS AND RECOMMENDATIONS FOR MANAGEMENT AND ADDRESSING KNOWLEDGE GAPS

This study demonstrates that the first three of the five key attributes to proving causality (Figure 1) have been met, and there is some evidence of the fourth. First, the concentrations of PAIs in waterways discharging to the GBR lagoon are sufficiently elevated to cause harmful effects (section entitled "Temporal variation in pesticide AI concentrations") as they frequently exceed the ETVs. Second, PAIs occur in the same areas that are important to fish i.e., in the nurseries (section entitled "Co-occurrence of fishery habitats and pesticide AIs?"). Third, there are physiological mechanisms by which PAIs could cause harm to fish or their prey (section entitled "Mechanism of impacts for pesticide AIs"). Fourth, there are a few studies suggesting that PAI exposure could be harming individual fish (section entitled "Mechanism of impacts for pesticide AIs). However, for the GBRCA, there is no direct evidence that PAIs have caused measurable changes in fish populations (section on "Changes in fish communities"). In summary, we have demonstrated there is a plausible pathway to harm for PAIs to cause indirect harmful effects on freshwater fish in the GBRCA as a consequence of frequent exposure to elevated and persistent concentrations of PAIs in some waterways.

Although there has been some in situ monitoring undertaken to correlate fish species richness and PAI exposure, the monitoring assessments have not been specifically designed to test for this. A study design needs to consider the timing of PAI exposure and ensure the PAI monitoring provides a spatial perspective of fish exposure and also consider how PAIs may be affecting fish through indirect impacts, that is, habitat, food, and multiple stressor interactions. In addition, more work using indicators of health and fitness should be conducted to determine whether other species are being affected by changing water quality and exposure to PAIs and to better delineate cause and effect type response between PAI exposure and organism health.

Linking deteriorating water quality to adverse outcomes for freshwater ecosystems could lead to better outcomes for the GBR system as a whole, (i.e. both the freshwater and marine components). As summarized in the section on "Observed pesticide AIs in waterways of the GBRCA," declines in water quality are a concern for the GBR. Stakeholders who have the ability to make water quality improvements frequently value the freshwater systems more because they interact with them more regularly. Linking declines in water quality to changes in freshwater systems could inspire more change and foster greater environmental stewardship, so we advocate additional research into the health of freshwater systems, which in turn are an important and obvious ecosystem supporting the health and resilience of the GBR. As mentioned previously, we hope to start this process using eDNA-based approaches to examine links between changing water quality and species use.

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AUTHOR CONTRIBUTION

Sharon E. Hook: Conceptualization, Data curation, formal analysis, visualization, writing—original draft, writing—review and editing. **Rachael A. Smith and Nathan Waltham**: Conceptualization, formal analysis, investigation, visualization, writing—original draft, writing—review and editing. **Michael St.J. Warne**: Conceptualization, formal analysis, visualization, writing—original draft, writing—review and editing.

DATA AVAILABILITY STATEMENT

Data are publicly available from Queensland Department of Water Quality Investigations. https://environment.des.qld.gov.au/management/water/quality-data-assessments.

SUPPORTING INFORMATION

Supplementary table of water quality guideline values. Supplementary figures showing concentrations and seasonal trends of less frequently detected pesticides.

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