2022 Scientific Consensus Statement

Question 5.1 What is the spatial and temporal distribution of pesticides across Great Barrier Reef ecosystems? What are the (potential or observed) ecological impacts in these ecosystems? What evidence is there for pesticide risk?

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Explanatory Notes for readers of the 2022 SCS Syntheses of Evidence

These explanatory notes were produced by the SCS Coordination Team and apply to all evidence syntheses in the 2022 SCS.

What is the Scientific Consensus Statement?

The Scientific Consensus Statement (SCS) on land use impacts on Great Barrier Reef (GBR) water quality and ecosystem condition brings together scientific evidence to understand how land-based activities can influence water quality in the GBR, and how these influences can be managed. The SCS is used as a key evidence-based document by policymakers when they are making decisions about managing GBR water quality. In particular, the SCS provides supporting information for the design, delivery and implementation of the Reef 2050 Water Quality Improvement Plan (Reef 2050 WQIP) which is a joint commitment of the Australian and Queensland governments. The Reef 2050 WQIP describes actions for improving the quality of the water that enters the GBR from the adjacent catchments. The SCS is updated periodically with the latest peer reviewed science.

C_2O Consulting was contracted by the Australian and Queensland governments to coordinate and deliver the 2022 SCS. The team at C_2O Consulting has many years of experience working on the water quality of the GBR and its catchment area and has been involved in the coordination and production of multiple iterations of the SCS since 2008.

The 2022 SCS addresses 30 priority questions that examine the influence of land-based runoff on the water quality of the GBR. The questions were developed in consultation with scientific experts, policy and management teams and other key stakeholders (e.g., representatives from agricultural, tourism, conservation, research and Traditional Owner groups). Authors were then appointed to each question via a formal Expression of Interest and a rigorous selection process. The 30 questions are organised into eight themes: values and threats, sediments and particulate nutrients, dissolved nutrients, pesticides, other pollutants, human dimensions, and future directions, that cover topics ranging from ecological processes, delivery and source, through to management options. Some questions are closely related, and as such readers are directed to Section 1.3 (Links to other questions) in this synthesis of evidence which identifies other 2022 SCS questions that might be of interest.

The geographic scope of interest is the GBR and its adjacent catchment area which contains 35 major river basins and six Natural Resource Management regions. The GBR ecosystems included in the scope of the reviews include coral reefs, seagrass meadows, pelagic, benthic and plankton communities, estuaries, mangroves, saltmarshes, freshwater wetlands and floodplain wetlands. In terms of marine extent, while the greatest areas of influence of land-based runoff are largely in the inshore and to a lesser extent, the midshelf areas of the GBR, the reviews have not been spatially constrained and scientific evidence from anywhere in the GBR is included where relevant for answering the question.

Method used to address the 2022 SCS Questions

Formal evidence review and synthesis methodologies are increasingly being used where science is needed to inform decision making, and have become a recognised international standard for accessing, appraising and synthesising scientific information. More specifically, 'evidence synthesis' is the process of identifying, compiling and combining relevant knowledge from multiple sources so it is readily available for decision makers[1]. The world's highest standard of evidence synthesis is a Systematic Review, which uses a highly prescriptive methodology to define the question and evidence needs, search for and appraise the quality of the evidence, and draw conclusions from the synthesis of this evidence.

In recent years there has been an emergence of evidence synthesis methods that involve some modifications of Systematic Reviews so that they can be conducted in a more timely and cost-effective

[1] Pullin A, Frampton G, Jongman R, Kohl C, Livoreil B, Lux A, ... & Wittmer, H. (2016) Selecting appropriate methods of knowledge synthesis to inform biodiversity policy. *Biodiversity and Conservation*, 25: 1285-1300. https://doi.org/10.1007/s10531-016-1131-9

manner. This suite of evidence synthesis products are referred to as **'Rapid Reviews'**[2]. These methods typically involve a reduced number of steps such as constraining the search effort, adjusting the extent of the quality assessment, and/or modifying the detail for data extraction, while still applying methods to minimise author bias in the searches, evidence appraisal and synthesis methods.

To accommodate the needs of GBR water quality policy and management, tailormade methods based on Rapid Review approaches were developed for the 2022 SCS by an independent expert in evidence-based syntheses for decision-making. The methods were initially reviewed by a small expert group with experience in GBR water quality science, then externally peer reviewed by three independent evidence synthesis experts.

Two methods were developed for the 2022 SCS:

- The **SCS Evidence Review** was used for questions that policy and management indicated were high priority and needed the highest confidence in the conclusions drawn from the evidence. The method includes an assessment of the reliability of all individual evidence items as an additional quality assurance step.
- The **SCS Evidence Summary** was used for all other questions, and while still providing a high level of confidence in the conclusions drawn, the method involves a less comprehensive quality assessment of individual evidence items.

Authors were asked to follow the methods, complete a standard template (this 'Synthesis of Evidence'), and extract data from literature in a standardised way to maximise transparency and ensure that a consistent approach was applied to all questions. Authors were provided with a Methods document, *'2022 Scientific Consensus Statement: Methods for the synthesis of evidence'*[3], containing detailed guidance and requirements for every step of the synthesis process. This was complemented by support from the SCS Coordination Team (led by C_2O Consulting) and the evidence synthesis expert to provide guidance throughout the drafting process including provision of step-by-step online training sessions for Authors, regular meetings to coordinate Authors within the Themes, and fortnightly or monthly question and answer sessions to clarify methods, discuss and address common issues.

The major steps of the Method are described below to assist readers in understanding the process used, structure and outputs of the synthesis of evidence:

1. **Describe the final interpretation of the question.** A description of the interpretation of the scope and intent of the question, including consultation with policy and management representatives where necessary, to ensure alignment with policy intentions. The description is supported by a conceptual diagram representing the major relationships relevant to the question, and definitions.
2. **Develop a search strategy**. The Method recommended that Authors used a S/PICO framework (Subject/Population, Exposure/Intervention, Comparator, Outcome), which could be used to break down the different elements of the question and helps to define and refine the search process. The S/PICO structure is the most commonly used structure in formal evidence synthesis methods[4].
3. **Define the criteria for the eligibility of evidence for the synthesis and conduct searches.** Authors were asked to establish **inclusion and exclusion criteria to define the eligibility of evidence** prior to starting the literature search. The Method recommended conducting a **systematic literature search** in at least **two online academic databases**. Searches were typically restricted to 1990 onwards (unless specified otherwise) following a review of the evidence for the previous (2017) SCS which indicated that this would encompass the majority of the evidence

[2] Collins A, Coughlin D, Miller J, & Kirk S (2015) The production of quick scoping reviews and rapid evidence assessments: A how to guide. UK Government. https://www.gov.uk/government/publications/the-production-of-quick-scoping-reviews-and-rapid-evidence-assessments

[3] Richards R, Pineda MC, Sambrook K, Waterhouse J (2023) 2022 Scientific Consensus Statement: Methods for the synthesis of evidence. C_2O Consulting, Townsville, pp. 59.

[4] https://libguides.jcu.edu.au/systematic-review/define

base, and due to available resources. In addition, the geographic **scope of the search for evidence** depended on the nature of the question. For some questions, it was more appropriate only to focus on studies derived from the GBR region (e.g., the GBR context was essential to answer the question); for other questions, it was important to search for studies outside of the GBR (e.g., the question related to a research theme where there was little information available from the GBR). Authors were asked to provide a rationale for that decision in the synthesis. Results from the literature searches were screened against **inclusion and exclusion** criteria at the title and abstract review stage (**initial screening**). Literature that passed this initial screening was then read in full to determine the eligibility for use in the synthesis of evidence (**second screening**). Importantly, all literature had to be **peer reviewed and publicly available.** As well as journal articles, this meant that grey literature (e.g., technical reports) that had been externally peer reviewed (e.g., outside of organisation) and was publicly available, could be assessed as part of the synthesis of evidence.

4. **Extract data and information from the literature**. To compile the data and information that were used to address the question, **Authors were asked to complete a standard data extraction and appraisal spreadsheet**. Authors were assisted in tailoring this spreadsheet to meet the needs of their specific question.
5. **Undertake systematic appraisal of the evidence base**. Appraisal of the evidence is an important aspect of the synthesis of evidence as it provides the reader and/or decision-makers with valuable insights about the underlying evidence base. Each evidence item was assessed for its spatial, temporal and overall relevance to the question being addressed, and allocated a relative score. The body of evidence was then evaluated for overall relevance, the size of the evidence base (i.e., is it a well-researched topic or not), the diversity of studies (e.g., does it contain a mix of experimental, observational, reviews and modelling studies), and consistency of the findings (e.g., is there agreement or debate within the scientific literature). Collectively, these assessments were used to obtain an overall measure of the level of confidence of the evidence base, specifically using the overall relevance and consistency ratings. For example, a high confidence rating was allocated where there was high overall relevance and high consistency in the findings across a range of study types (e.g., modelling, observational and experimental). Questions using the **SCS Evidence Review Method** had an **additional quality assurance step**, through the assessment of reliability of all individual studies. This allowed Authors to identify where potential biases in the study design or the process used to draw conclusions might exist and offer insight into how reliable the scientific findings are for answering the priority SCS questions. This assessment considered the reliability of the study itself and enabled authors to place more or less emphasis on selected studies.
6. **Undertake a synthesis of the evidence and complete the evidence synthesis template** to address the question. Based on the previous steps, a narrative synthesis approach was used by authors to derive and summarise findings from the evidence.

Guidance for using the synthesis of evidence

Each synthesis of evidence contains three different levels of detail to present the process used and the findings of the evidence:

1. **Executive Summary**: This section brings together the evidence and findings reported in the main body of the document to provide a high-level overview of the question.
2. **Synthesis of Evidence:** This section contains the detailed identification, extraction and examination of evidence used to address the question.
    - ***Background***: Provides the context about why this question is important and explains how the Lead Author interpreted the question.
    - ***Method:*** Outlines the search terms used by Authors to find relevant literature (evidence items), which databases were used, and the inclusion and exclusion criteria.
    - ***Search Results:*** Contains details about the number of evidence items identified, sources, screening and the final number of evidence items used in the synthesis of evidence.
    - ***Key Findings:*** The **main body of the synthesis**. It includes a summary of the study characteristics (e.g., how many, when, where, how), a deep dive into the body of evidence

covering key findings, trends or patterns, consistency of findings among studies, uncertainties and limitations of the evidence, significance of the findings to policy, practice and research, knowledge gaps, Indigenous engagement, conclusions and the evidence appraisal.

3. **Evidence Statement:** Provides a succinct, high-level overview of the main findings for the question with supporting points. The Evidence Statement for each Question was provided as input to the 2022 Scientific Consensus Statement Summary and Conclusions.

While the Executive Summary and Evidence Statement provide a high-level overview of the question, it is **critical that any policy or management decisions are based on consideration of the full synthesis of evidence.** The GBR and its catchment area is large, with many different land uses, climates and habitats which result in considerable heterogeneity across its extent. Regional differences can be significant, and from a management perspective will therefore often need to be treated as separate entities to make the most effective decisions to support and protect GBR ecosystems. Evidence from this spatial variability is captured in the reviews as much as possible to enable this level of management decision to occur. Areas where there is high agreement or disagreement of findings in the body of evidence are also highlighted by authors in describing the consistency of the evidence. In many cases authors also offer an explanation for this consistency.

Peer Review and Quality Assurance

Each synthesis of evidence was peer reviewed, following a similar process to indexed scientific journals. An Editorial Board, endorsed by the Australian Chief Scientist, managed the process. The Australian Chief Scientist also provided oversight and assurance about the design of the peer review process. The Editorial Board consisted of an Editor-in-Chief and six Editors with editorial expertise in indexed scientific journals. Each question had a Lead and Second Editor. Reviewers were approached based on skills and knowledge relevant to each question and appointed following a strict conflict of interest process. Each question had a minimum of two reviewers, one with GBR-relevant expertise, and a second 'external' reviewer (i.e., international or from elsewhere in Australia). Reviewers completed a peer review template which included a series of standard questions about the quality, rigour and content of the synthesis, and provided a recommendation (i.e., accept, minor revisions, major revisions). Authors were required to respond to all comments made by reviewers and Editors, revise the synthesis and provide evidence of changes. The Lead and Second Editors had the authority to endorse the synthesis following peer review or request further review/iterations.

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Executive Summary

Question

Question 5.1 What is the spatial and temporal distribution of pesticides across Great Barrier Reef ecosystems? What are the (potential or observed) ecological impacts in these ecosystems? What evidence is there for pesticide risk?

Background

Pesticides, primarily sourced from agriculture in catchments of the Great Barrier Reef (GBR) have been detected in GBR waters, sediments and biota since the 1990s. Early research found that pesticides have the potential to negatively affect important GBR species, including seagrass, corals and fish. Water quality guideline values (GVs) have been applied to indicate concentrations of potential harm to GBR ecosystems, and risk assessments conducted based on observed (or predicted) exceedances of GVs by pesticides in GBR waters. Pesticide targets have been set by Government agencies towards the ultimate objective of improving water quality of water flowing from the catchments adjacent to the GBR[5]. Improvements in land management practices to meet the Reef 2050 Water Quality Improvement Plan (WQIP) targets for pesticide risk are guided by our understanding of the temporal and spatial distribution of pesticides and their potential impacts on GBR ecosystems. This understanding is underpinned by large-scale monitoring programs to assess the concentrations of pesticides in catchment and marine waters of the GBR and supported by studies that estimate the concentrations of pesticides that can adversely affect GBR species. Toxicity studies can be used to develop and/or validate GVs applied in GBR ecosystems. Assessing the potential risks posed by pesticides to GBR ecosystems requires an understanding of the likelihood that aquatic species of the GBR are exposed to harmful concentrations of pesticides. This review addresses the question in three parts:

1) An assessment of the spatial and temporal distribution of pesticide concentrations in freshwater, estuaries, wetlands and marine ecosystems.
2) Identification of toxicity thresholds for pesticides detected in GBR waters to aquatic species of the GBR (potential consequence of exposure), including a comparison with recent water quality GVs applied in GBR ecosystems.
3) An assessment of risks to aquatic ecosystems of the GBR based on recent exceedances of pesticide GVs.

Methods

- A formal Rapid Review approach was used for the 2022 Scientific Consensus Statement (SCS) synthesis of evidence. Rapid reviews are a systematic review with a simplification or omission of some steps to accommodate the time and resources available[6]. For the SCS, this applies to the search effort, quality appraisal of evidence and the amount of data extracted. The process has well-defined steps enabling fit-for-purpose evidence to be searched, retrieved, assessed and synthesised into final products to inform policy. For this question, an Evidence Review method was used.
- Search locations included Scopus, Web of Science (WoS), Google Scholar and other publications found by the Authors.
- Main source of evidence: overwhelmingly publications directly relevant to GBR waters.
- The total search (Scopus, WoS, Google Scholar and manual searches) revealed 1,045 evidence items, of which 231 met the eligibility criteria and were used in the synthesis.

[5] Reef 2050 Water Quality Improvement Plan. https://www.reefplan.qld.gov.au/

[6] Cook CN, Nichols SJ, Webb JA, Fuller RA, Richards RM (2017) Simplifying the selection of evidence synthesis methods to inform environmental decisions: A guide for decision makers and scientists. *Biological Conservation* 213: 135-145

Method limitations and caveats to using this Evidence Review

For this Evidence Review, the following caveats or limitations should be noted when applying the findings for policy or management purposes:

- Only studies written in English were included (although no reports in other languages directly relevant to the GBR were detected in the searches).
- Only two academic databases were searched.
- With a few exceptions, only GBR and Queensland studies were included.
- Only studies published after 1990 were included.

Key Findings

Summary of evidence to 2022

A total of 231 eligible studies were found to address the primary question. The question addressed is highly quantitative; therefore, quantitative assessments were made on the distribution of-, effects of- and risks posed by pesticides since the 2017 Scientific Consensus Statement (SCS).

What is the spatial and temporal distribution of pesticides across GBR ecosystems?

- Pesticides are ubiquitous across monitored GBR ecosystems including end-of-catchment waterways, palustrine wetlands and in estuarine and nearshore marine habitats. Detection of pesticides in seagrass, mangroves and marine sediments demonstrates exposure; however, most contemporary pesticides partition strongly into water (i.e., they have high aqueous solubility). Therefore, the spatial and temporal distribution of pesticides have been assessed based on the data from extensive water quality monitoring programs from 2016/17 onwards.
- Over 70 pesticides and their transformation products were identified in GBR waters: 74 at the end-of-catchment, 59 in palustrine wetlands and 22 in marine waters (fewer pesticides were monitored in marine samples).
- The most frequently quantified pesticides across the GBR from 2016/17 to 2021/22 were the herbicides atrazine, diuron, hexazinone, metolachlor and imazapic and the insecticide imidacloprid.
- The vast majority of pesticides across all GBR habitats were found in mixtures. For example, in 72% and 96% of all end-of-catchment and marine samples, respectively and in all palustrine wetlands samples (with an average of 15 pesticides per sample).
- It was not practical to assess the distribution of 20+ pesticides across 37 freshwater sites, so this review focused on 12 pesticides at 12 end-of-catchment freshwater and estuarine sites and 11 marine sites. The 12 focus pesticides, when combined, typically accounted for at least 99% of the total toxicity of pesticide mixtures in GBR waterways. Estuarine habitats were not assessed separately due to a lack of consistent monitoring data.
- Sites in the Mackay Whitsunday region, along with Barratta Creek in the Burdekin region which featured intense cropping and lower discharge (related to rainfall), recorded consistently higher concentrations of pesticides than other locations. Sites in the Fitzroy and Burnett Mary region as well as the Daintree River (northern Wet Tropics) had the lowest maximum annual concentrations across all years.
- A diuron dispersal simulation exercise for 2016/2018 indicated concentrations were greatest near river mouths and were transported northwards within plumes, with high concentrations typically not extending far into the GBR. Rapid changes in diuron concentrations (e.g., <0.1 $\mu g\ L^{-1}$ to > 1 $\mu g\ L^{-1}$) within hours highlighted the dynamic exposure of nearshore marine organisms. Not all 11 sites in the MMP, for the period studied, reliably captured flood plumes, and therefore, the results may have underestimated marine pesticide concentrations nearby.
- Pesticide concentrations were typically higher in fresh and marine waters during wet seasons compared to dry seasons, with rapid increases at the start of the wet season followed by a gradual decrease.
- There are generally insufficient observations to identify annual pesticide trends for all 12 focus pesticides since 2016/17; however, recent studies report significant increases in imidacloprid in

some freshwater sites (2009/10 to 2015/16) in the Burdekin, Mackay Whitsunday and Wet Tropics regions and in PSII herbicide concentrations over 14 years of MMP monitoring, primarily in the Mackay Whitsunday and Burdekin regions.

What are the (potential or observed) ecological impacts in these ecosystems?

- Pesticides are designed to control agricultural pest species and virtually all tested pesticides were reported as harmful to non-target aquatic species of the GBR. For example, PSII herbicides, consistently impact all photosynthetic marine organisms of the GBR that have been tested, including corals and seagrass.
- Pesticides, or their mixtures, pose a risk if they occur at concentrations greater than a relevant toxicity threshold or GV. A review of the GVs indicated that the most up to date and reliable are those developed for application in the Pesticide Risk Metric (PRM). The PRM GVs were developed in accordance with the Australian and New Zealand guidelines, are applicable to both freshwater and marine ecosystems, and can be applied to assess the combined effects of 22 pesticides in mixtures - an essential criteria for application to assess risk in the GBR. An extensive review demonstrated that PRM GVs are protective of the vast majority of GBR species and are therefore applicable to assess the risk of pesticides (and pesticide mixtures) in the GBR.
- Experimental studies with GBR species demonstrated that the effects of mixtures of herbicides are generally additive and that low concentrations of individual pesticides add to the overall effect of the mixture. These results, along with international evidence, validate the application of the PRM to assess risk to GBR ecosystems posed by simultaneous exposure to multiple pesticides. To date, there is little evidence that additives in pesticide formulations contribute to toxicity to GBR species.
- Other simultaneous pressures, including heatwave conditions and variation in light were shown to increase the sensitivity of GBR species to pesticides, indicating GVs applied under some conditions in the field are likely to underestimate the risk to aquatic ecosystems.

What evidence is there for pesticide risk?

- The Reef 2050 WQIP pesticide target of protecting 99% of species has consistently not been met at numerous end-of-catchment sites (e.g., ~87% of end-of-catchment (or freshwater) focus sites between 2016/17 and 2021/22). There have also been substantial shortfalls in protection recorded in palustrine wetland ecosystems and sometimes coastal marine ecosystems of the GBR.
- While the risk assessments were able to account for the presence of more than one pesticide (found in the vast majority of water samples), the reported risks are likely to be underestimated by not accounting for: all pesticides present (only 22); other pressures such as heat (climate change) and light stress; the conservative nature of the model used to predict mixture toxicity; adverse biological effects occurring below the Protective Concentration 99 (PC99) and likely cumulative sublethal effects of very prolonged exposures to pesticides in some habitats.
- The greatest risk posed by pesticides was closest to the source in palustrine wetlands, followed by freshwater and coastal marine ecosystems, with sites in the Mackay Whitsunday region and Barratta Creek in the Burdekin region estimated as being the most affected by exposure to pesticide mixtures between 2016/17 and 2021/22.
- A diuron dispersal simulation (three-dimensional (3D) hydrodynamic model) showed broad spatial risk patterns across the entire GBR similar to those generated from the GBR Catchment Loads Monitoring Program (GBRCLMP) and Marine Monitoring Program (MMP) data. It also showed regular periods when less than 99% of species were protected from diuron across >1,400 km^2 of the GBR.
- There were increased contributions of non-PSII herbicides to risk at some sites; however, trends in risk due to all pesticides across GBR ecosystems will only be apparent when longer data series are assessed with a consistent metric.

Recent findings 2016-2022

The review had a strong focus on recent studies and the Summary of Evidence (above) describes all important findings from 2016–2022. This Recent Findings section instead highlights the key studies since 2016. Approximately 44 studies were found for the period 2016–2023, including studies on pesticide concentration in the GBR (n=15), pesticide effects/toxicity (n=27) and pesticide risk (n=16). Most studies that assessed pesticide distribution also assessed risk as exceedances of GVs.

What is the spatial and temporal distribution of pesticides across GBR ecosystems?

- Information on the spatial and temporal distribution of pesticides since 2016 was primarily drawn from GBRCLMP data published in the Pesticide Reporting Portal and MMP data. GBRCLMP data are also summarised in five reports, while MMP data are summarised in three reports.
- Of great relevance was a recent analysis of spatial and temporal trends of PSII herbicides based on 14 years of MMP data. One prominent modelling exercise simulated the spatial and temporal distribution of the PSII herbicide diuron in the GBR.
- Information on the spatial and temporal distribution of pesticides in the wetland ecosystems of the GBR since 2016 was available in only two studies. Only palustrine wetlands were considered in this report and estuaries were not assessed separately due to a paucity of data.

What are the (potential or observed) ecological impacts in these ecosystems?

Approximately 27 studies published information on the observed or potential effects of pesticides on GBR species since 2016.

- Five assessed indications of toxicity in the field, while 22 studies quantified toxicity thresholds for pesticides to GBR species in laboratory studies (4 freshwater and 18 marine).
- There were ten studies that reported evolving GVs for pesticides that could be applied in GBR waters.
- The combined effects of pesticide mixtures on GBR species were assessed in one publication, while the influence of other simultaneous pressures (e.g., heatwave conditions) were assessed in seven publications.

What evidence is there for pesticide risk?

- Studies that assessed the risk of pesticides to the freshwater, estuarine, wetlands, and marine ecosystems of the GBR since 2016 included 16 that compared monitored or modelled pesticide concentrations (often as mixtures) against pesticide GVs.
- The 2020 publication of the PRM provided the basis to assess the risk posed by multiple pesticides (up to 22) alone or in mixtures across freshwater, wetland and marine ecosystems.
- A diuron dispersal simulation (3D hydrodynamic model) revealed spatial risk patterns across the entire GBR consistent with those generated from GBRCLMP and MMP data. It also showed regular periods when less than 99% of species were protected from diuron across >1,400 km^2 of the GBR.
- Long-term trend analyses suggest an increase in the concentrations of imidacloprid in freshwaters and PSII herbicides in marine waters that may indicate increasing risk, but this needs to be assessed further by applying the PRM.

Significance for policy, practice, and research

What is the spatial and temporal distribution of pesticides across GBR ecosystems?

- There have been significant increases in imidacloprid concentrations in freshwater sites and in PSII herbicide concentrations at several marine sites, indicating pesticide exposure may not be decreasing in GBR waters in accordance with targets set by the Reef 2050 WQIP.
- The first comprehensive survey of wetlands found very high concentrations of pesticides across many locations. This study represents an important first step in addressing a large data gap in long-term monitoring to assess pesticide distribution in an important GBR habitat.

- A sophisticated modelling exercise revealed a larger spatial extent of diuron dispersal in the GBR than previously reported and indicated that diuron exposure is likely underestimated by current MMP monitoring.

What are the (potential or observed) ecological impacts in these ecosystems?

- This Evidence Review found the pesticide GVs developed for application in the PRM can be applied with confidence in risk assessments. They were generated from the most comprehensive toxicity datasets available, are protective of GBR species (freshwater and marine) and effectively account for the total toxicity of pesticide mixtures.
- The review also found that simultaneous pressures such as heatwaves and reduced light conditions can increase species sensitivity to pesticides and that future developments of the PRM approach might account for the effects of additional stressors.

What evidence is there for pesticide risk?

- Publishing of the Pesticide Reporting Portal means the potential risk of exposure to all pesticides identified can now be readily accessed across the GBRCLMP and MMP sites. This is the first time a consistent metric for risk has been applied to freshwater and marine ecosystems of the GBR to assess progress towards meeting the GBR pesticide target of 99% species protection.
- By revealing locations at highest relative risk from pesticides, the assessment in this Evidence Review provides information to focus investment and guide improvements in land management practices required to meet the pesticide target in the future.
- The risk assessment also identified the individual pesticides contributing most to risk in freshwater, estuarine and marine ecosystems, providing further opportunities to manage risk through substitution of pesticides with lower toxicity to non-target species.
- Recent studies revealed increasing trends in subsets of some pesticides over long periods. The application of the PRM to assess the total risk of a wider range of pesticides (22 so far) provides an excellent opportunity for future studies to improve our understanding of long-term trends and whether pesticide risk is changing.
- The MMP is an effective program to assess long-term trends of pesticide concentrations and risk to marine ecosystems of the GBR; however, it includes only a limited number of sites. The recent diuron simulation model (using the eReefs marine model) offers the most promising approach to predict pesticide exposure of seagrass and coral habitats of the GBR, and further development and validation, incorporating all pesticides in PRM and supported by *in situ* monitoring, would present a step-change in our appreciation of pesticide risk across the entire GBR.

Key uncertainties and/or limitations

What is the spatial and temporal distribution of pesticides across GBR ecosystems?

- The catchment monitoring of pesticides (GBRCLMP) used grab samples which may underestimate or overestimate concentrations over ecologically relevant exposure periods. There has been limited sampling of small coastal waterways that drain intensively farmed catchments that may experience substantial pesticide exposures.
- The most comprehensive study of pesticides in wetlands is limited to 22 palustrine wetlands over two years and may not have been representative of the range of wetland types.
- The monitoring of pesticides in the GBR (MMP) was limited to 11 sites and has not been reported since 2018/19 (recommencing in 2022/23). Sampling is not adequate to inform risk to marine habitats of the GBR, given the scale of the GBR and the likelihood that some fixed sites are not located to reliably sample pesticide dispersal in plumes (resulting in underestimates).
- The large amount of GBRCLMP data meant that a full quantitative assessment was not possible within the scope of the review and some important findings may have been missed.

- Insufficient research has been conducted on the temporal trends in pesticide concentrations accounting for all pesticides detected in GBR surveys. No research has been conducted on the temporal variation in risk posed by pesticide mixtures.
- There are too few surveys of biota and sediments to meaningfully contribute to an understanding of the GBR-wide spatial and temporal distribution of pesticides in these compartments.

What are the (potential or observed) ecological impacts in these ecosystems?

- Links between organism response (mortality and biomarkers of sublethal responses) and pesticide exposure in the field are uncertain due to the possibility that other environmental factors confound responses. More validation is required.
- While there have been many experimental studies that identify toxicity thresholds for pesticides for freshwater and marine taxa of the GBR, most of these have tested only a small subset of pesticides; therefore, the sensitivity of GBR taxa to many pesticides remains largely unknown. However, the sensitivity of related international species is much better known.
- Guideline values (GVs) applied in the PRM are generally protective of GBR species; however, this has not been validated for all 22 pesticides in the PRM.
- While additivity is the most common response of GBR organisms exposed to multiple pesticides or pesticides and other stressors, not all combinations have been tested, nor is this possible. The effects of pesticide formulation additives such as surfactants are also largely unknown. International literature has far more of these kinds of data and must be relied upon to guide estimates of the responses of GBR organisms.

What evidence is there for pesticide risk?

- The risks posed by pesticides to GBR species were primarily calculated by assessing measured pesticide concentrations against GVs of the PRM. Therefore, uncertainties in assigning risk primarily result from uncertainties contributed by monitoring programs and the PRM (see above).
- The PRM does not include GVs for all pesticides detected in the GBR (22 of 74), and therefore, pesticide risk is likely to be underestimated.
- The PRM does not account for non-pesticide stressors (e.g., heatwave conditions) which can increase pesticide toxicity; therefore, total risk is likely to be underestimated in many circumstances.
- The PRM does not account for very long-term exposures to low concentrations of pesticides often observed in GBR waters due to the long persistence of many pesticides. Therefore, total risk is likely to be underestimated in many circumstances.
- Although a recent risk assessment which applied a 3D-hydrodyamic model represents a major advance over previous modelling exercises, the simulated diuron concentration relied on multiple assumptions (end-of-catchment loads, half-lives, conservative mixing etc.) and these require further assessment to improve certainty in absolute diuron concentrations. The estimated areas of seagrass and coral habitats at risk of harm are likely to be underestimated as the simulation only accounted for a single pesticide. There are limited field measurements of the effects of pesticides on GBR species, but the available studies are consistent with the comparison of pesticide concentrations to GVs.

Evidence appraisal

A total of 231 studies were used for the synthesis. The overall relevance of the body of evidence to the question was rated as being High. The relevance of each individual indicator was: High for the relevance of the study approach and reporting of results to the question, High for spatial relevance, and High for temporal relevance. Of the 231 articles included in the review, 68% (158 of 231) were given a High score for overall relevance to the question, while 60% (130 of 218) had a High spatial relevance score, and 67% (143 of 214) had a High temporal relevance score. This was due to a number of factors described below.

- Consistency for the overall body of evidence was considered High across the sub-group analysis. Virtually all 93 studies that analysed pesticides in the GBR were able to identify pesticides in waters, sediments and/or biota. There was very high consistency in the types and concentrations of pesticides detected at individual sites in the GBRCLMP or MMP reports. Since consistent methodologies were used in these monitoring programs over time, differences in pesticides reported are likely due to actual differences in pesticide occurrence in fresh and marine waters.
- Experimental studies (72 in total) generally applied standard techniques to assess the effects of pesticides on GBR species. The sensitivity of GBR species reported in these studies were consistent with each other and with previous datasets used to generate recent guideline values for application in risk assessments.
- The sites/regions reported as being at highest risk from pesticides were consistent over a decade of studies, even when applying different approaches.
- From our assessment of the internal validity of studies used, it was determined that most studies (95%) had a low risk of bias. The findings of those studies that were rated as having some potential risk of bias were generally consistent with the findings from the larger body of evidence or included other information that was not considered biased.
- The Confidence rating was High since both the Consistency and Relevance for the overall body of evidence was High. The High confidence rating was also influenced by the large number of eligible studies and that, with few exceptions, generally resulted in consistent findings from observational, experimental, modelled and secondary studies.
- The 231 studies used represents a High sample of studies from the total number of potentially available studies on the topic; a more comprehensive search is likely to uncover few additional highly relevant studies.

1. Background

Contemporary pesticides, defined here as the active chemicals in herbicide, insecticide and fungicide formulations, have been detected in waters, sediments and biota of the Great Barrier Reef (GBR) since the 1990s (Haynes et al., 2000a; Haynes & Michalek-Wagner, 2000). Their recognition as a potentially widespread risk to GBR ecosystems precipitated extensive pesticide monitoring programs in the GBR and associated catchments, as well as a series of studies to assess the potential hazard posed by pesticides to aquatic species of the GBR (Devlin et al., 2015).

While pesticides are applied in industrial and urban settings of north Queensland, large quantities are used to control pests in agriculture in catchments adjacent to the GBR. The sources and transport of pesticides to the end-of-catchments and GBR have been reviewed (Bartley et al., 2017; Devlin et al., 2015; Haynes et al., 2007; Kroon et al., 2013) and are dealt with in detail in Question 5.2 (Templeman & McDonald, this Scientific Consensus Statement (SCS)). Pesticides, by design, are very toxic to target species and, although some have relatively selective modes of action (**Table P1**)[7], most pesticides can also be harmful to non-target aquatic species. For example, the Photosystem II inhibiting (PSII) herbicides such as diuron, which are used to control broadleaf weeds and some annual grasses in sugarcane and other crops (APVMA, 2011a) can also reduce photosynthesis and growth in most aquatic phototrophs, including microalgae and seagrass (Magnusson et al., 2008; Negri et al., 2015).

Assessing the potential risks posed by pesticides to GBR ecosystems (freshwater, wetlands and marine) requires an understanding of the likelihood that aquatic species of the GBR are exposed to harmful concentrations of pesticides. This approach follows recommendations in the National Water Quality Guidelines (ANZG, 2018) and is consistent with approaches taken in previous Scientific Consensus Statement (SCS) reports (Brodie et al., 2013; Waterhouse et al., 2017).

The question this review addresses can be broken down into three parts as illustrated in the conceptual model (Figure 1):

1. An assessment of the spatial and temporal distribution of pesticides in freshwater, wetlands and marine ecosystems (likelihood of exposure expressed as concentrations).
2. Identification of toxicity thresholds for pesticides detected in GBR waters to aquatic species of the GBR (potential consequence of exposure), including a comparison with recent water quality guideline values (GVs) applied in GBR ecosystems.
3. An assessment of risks to aquatic ecosystems of the GBR based on recent exceedances of pesticide GVs.

The question addressed in this review is highly quantitative; therefore, quantitative assessments were made on the distribution of-, effects of- and risks posed by pesticides since the 2017 SCS. Data summaries can be found in separate Excel spreadsheets referred to in the text and listed in Table 2 of Section 4.1 Narrative Synthesis.

Previous risk assessments have identified freshwater and wetland ecosystems downstream of intensive agriculture in GBR catchments as being at greatest risk to pesticides, with a primary focus on the risks posed by select PSII herbicides (e.g., Waterhouse et al., 2017) . However, there is now more data on the distribution and toxicity of a broader suite of pesticides to GBR species and a refinement of GVs based on this and other recent data. There have also been recent studies to assess pesticide distribution in selected palustrine wetlands, long-term trends in pesticide distribution and modelling to illustrate pesticide concentrations at greater spatial and temporal resolution across the GBR.

This question presents the most recent (2016 – 2022) regionally specific information on pesticide distribution, effects and risk, informing the Reef 2050 Water Quality Improvement Plan[8] (Reef 2050 WQIP) on its objective of improving the quality of water flowing from the adjacent catchments to the GBR. The review will also contribute to the ongoing development of the Pesticide Risk Metric (PRM), a risk assessment tool that can be used to communicate the risk to aquatic ecosystems associated with

[7] Appendices Tables available to download as a zip file from the 2022 SCS website.
[8] Reef 2050 Water Quality Improvement Plan. https://www.reefplan.qld.gov.au/

mixtures of multiple chemicals and the preferred method to describe pesticide risk in the Australian and Queensland Governments' Reef Report Card.

1.1 Question

Primary question	**Q5.1** What is the spatial and temporal distribution of pesticides across Great Barrier Reef ecosystems? What are the (potential or observed) ecological impacts in these ecosystems? What evidence is there for pesticide risk?

Element	Author's interpretation
What is the spatial and temporal distribution of pesticides across GBR ecosystems?	What are the types, concentrations and combinations of pesticides (herbicides, insecticides and fungicides) measured in water, sediments and biota across the marine, estuarine, wetland and freshwater habitats of the GBR? Do pesticide concentrations differ across regions and habitats and how do they change over time?
What are the (potential or observed) ecological impacts in these ecosystems?	Focus on the concentrations of pesticides at which ecologically relevant adverse effects (as defined in Warne et al., 2018a) commence and what these effects are. Where available report on the concentrations of pesticides at which subcellular effects (which are currently not defined as ecologically relevant effects) commence and what these effects are.
What evidence is there for pesticide risk?	What evidence is there that concentrations of individual pesticides (or mixtures of more than one pesticide) measured in water, sediments or biota of the GBR reach concentrations that: 1) are potentially harmful to biota relevant to the GBR (based on laboratory, microcosm and mesocosm-based toxicity data); or 2) exceed GBR-relevant water quality guideline values.

1.2 Conceptual diagram

Figure 1 provides a conceptual representation of the question. The blue boxes below represent the three parts of the primary question 5.1:
1) What is the spatial and temporal distribution of pesticides across GBR ecosystems?
2) What are the (potential or observed) ecological impacts in these ecosystems?
3) What evidence is there for pesticide risk?

Issues outside the scope of Question 5.1 are indicated in boxes with green dashed lines and are addressed by other questions (as indicated).

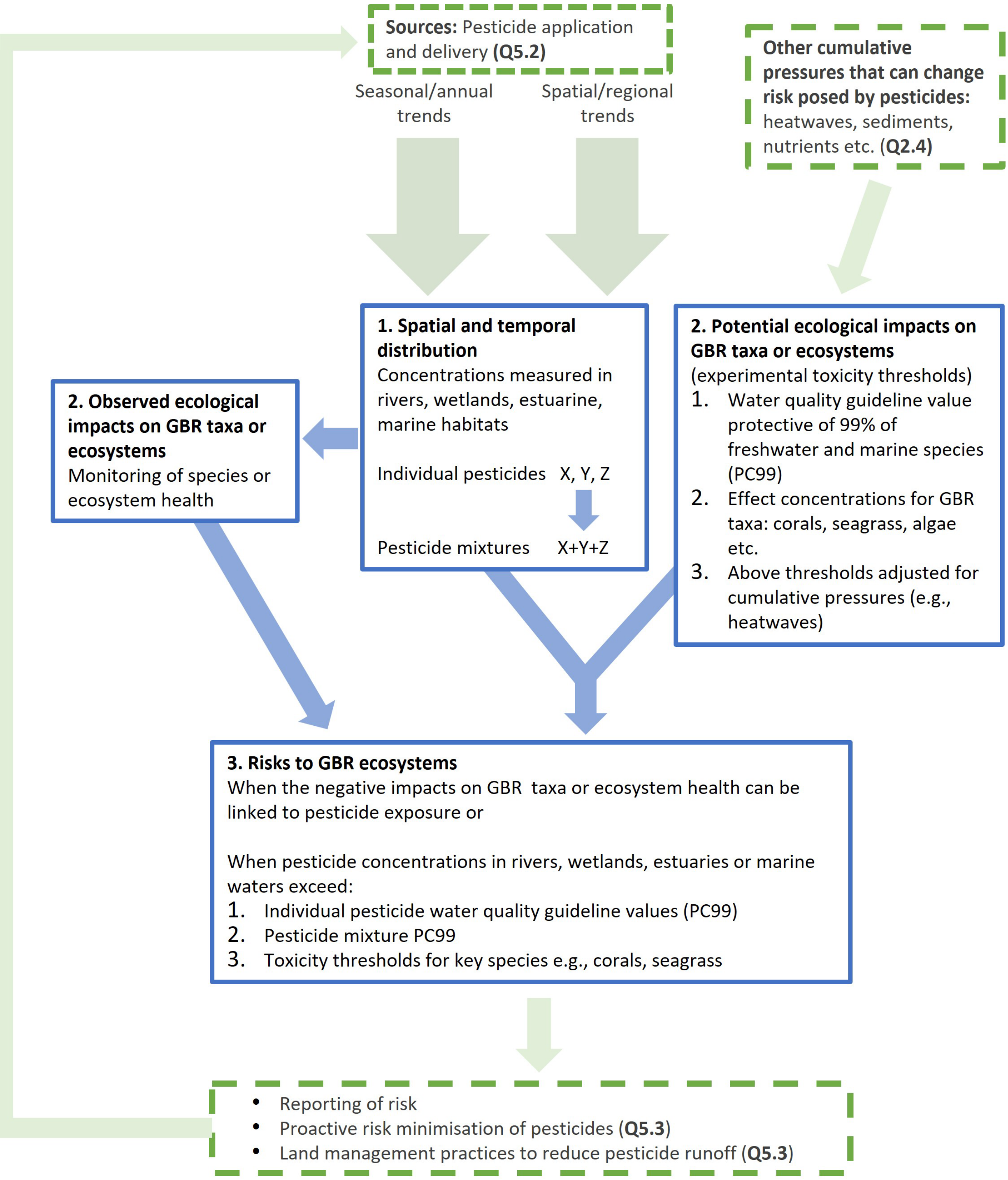


Figure 1. Conceptual diagram demonstrating how an understanding of 1) the spatial and temporal distribution (likely exposure) of pesticides, and 2) potential ecological impacts on GBR taxa or ecosystems (hazard) informs 3) risks posed by pesticides to GBR ecosystems. Blue boxes represent the three parts of the Question 5.1. Linked issues outside the scope of Question 5.1 are indicated in boxes with green dashed lines.

1.3 Links to other questions

This synthesis of evidence addresses one of 30 questions that are being addressed as part of the 2022 SCS. The questions are organised into eight themes: values and threats, sediments and particulate nutrients, dissolved nutrients, pesticides, other pollutants, human dimensions, and future directions, that cover topics ranging from ecological processes, delivery and source, through to management options. As a result, many questions are closely linked, and the evidence presented may be directly relevant to parts of other questions. The relevant linkages for this question are identified in the text where applicable. The primary question linkages for this question are listed below.

Links to other related questions	**Links are shown in the conceptual diagram** **Q5.2** What are the key factors that influence pesticide delivery from the Great Barrier Reef catchments, and where are these factors most significant? Secondary question **5.2.1**: What types, levels and combinations of pesticides are delivered to the Great Barrier Reef, and what are the primary sources of pesticides? **Q5.3** What are the most effective management practices for reducing pesticide risk (all land uses) from the Great Barrier Reef catchments, and do these vary spatially or in different climatic conditions? What are the costs of the practices, and cost-effectiveness of these practices, and does this vary spatially or in different climatic conditions? What are the production outcomes of these practices? **Q2.4** How do water quality and climate change interact to influence the health and resilience of Great Barrier Reef ecosystems? Secondary question **2.4.1**: How are the combined impacts of multiple stressors (including water quality) affecting the health and resilience of Great Barrier Reef coastal and inshore ecosystems? Secondary question **2.4.2**: Would improved water quality help ecosystems cope with multiple stressors including climate change impacts, and if so, in what way?

2. Method

A formal Rapid Review approach was used for the 2022 SCS synthesis of evidence. Rapid reviews are a systematic review with a simplification or omission of some steps to accommodate the time and resources available[9]. For the SCS, this applies to the search effort, quality appraisal of evidence and the amount of data extracted. The process has well-defined steps enabling fit-for-purpose evidence to be searched, retrieved, assessed and synthesised into final products to inform policy. For this question, an Evidence Review method was used.

2.1 Primary question elements and description

The primary question is: ***What is the spatial and temporal distribution of pesticides across Great Barrier Reef ecosystems? What are the (potential or observed) ecological impacts in these ecosystems? What evidence is there for pesticide risk?***

S/PICO frameworks (Subject/Population, Exposure/Intervention, Comparator, Outcome) can be used to break down the different elements of a question and help to define and refine the search process. The S/PICO structure is the most commonly used structure in formal evidence synthesis methods[10] but other variations are also available.

- **Subject/Population:** Who or what is being studied or what is the problem?
- **Intervention/exposure:** Proposed management regime, policy, action or the environmental variable to which the subject populations are exposed.
- **Comparator**: What is the intervention/exposure compared to (e.g., other interventions, no intervention, etc.)? This could also include a time comparator as in 'before or after' treatment or exposure. If no comparison was applicable, this component did not need to be addressed.
- **Outcome:** What are the outcomes relevant to the question resulting from the intervention or exposure?

Table 1. Description of primary question elements for Question 5.1.

Question S/PICO elements	Question term	Description
Subject/Population	Pesticides	Herbicide, insecticide, fungicide
Intervention, exposure & qualifiers	GBR ecosystems	Including: seawater, freshwater, sediments, biota, marine, estuarine, freshwater, river, wetland, seagrass meadow, coral reef, mangrove forest
	Spatial and temporal distribution	What are the types, concentrations and combinations of pesticides measured in water, sediments and biota across the marine, estuarine, wetland and freshwater habitats of the GBR? Do pesticide concentrations differ across regions and habitats and how have they changed over time?
Comparator	Thresholds values, ecotoxicity threshold values or water quality guidelines	Concentrations of pesticides at which ecologically-relevant adverse effects (as defined in Warne et al., 2018b) commence and what these effects are. Threshold values are usually described for individual species, while guideline values (refer to Table 3),

[9] Cook CN, Nichols SJ, Webb JA, Fuller RA, Richards RM (2017) Simplifying the selection of evidence synthesis methods to inform environmental decisions: A guide for decision makers and scientists. *Biological Conservation* 213: 135-145

[10] https://libguides.jcu.edu.au/systematic-review/define and https://guides.library.cornell.edu/evidence-synthesis/research-question

Question S/PICO elements	Question term	Description
		including the Australian Water Quality Guideline Values have been developed from the toxicity thresholds of multiple species.
Outcome & outcome qualifiers	Evidence of pesticide risk	What evidence is there that concentrations of individual pesticides (or mixtures of more than one pesticide) measured in water, sediments or biota of the GBR reach concentrations that: 1) are potentially harmful to biota relevant to the GBR (based on laboratory, microcosm and mesocosm-based toxicity data); or 2) exceed current or proposed national water or sediment quality guideline values and ecotoxicity threshold values.

Table 2. Definitions for terms used in Question 5.1.

Definitions	
Pesticide	Includes the land-sourced chemicals used to control pest species including herbicides, insecticides and fungicides. For the purposes of this review pesticides refer to active ingredients and not commercial pest control formulations.
GBR ecosystems	Marine (coral, seagrass, pelagic, benthic + plankton communities), estuarine (estuaries, mangroves, saltmarsh), freshwater (rivers, natural or wetlands).
Spatial distribution	Includes GBR ecosystem. Comparisons among Natural Resource Management (NRM) regions (possibly summary tables) and catchments consistent with the Marine Monitoring Program (MMP). Ecosystems include reef, seagrass meadow, river mouth, wetlands).
Estuary	Semi-enclosed bodies of water that open to the sea and are supplied with freshwater draining from the land via rivers and streams.
Wetland	Natural and near natural wetlands only, including estuarine, marshes and floodplain lakes (excluding rivers).
Palustrine wetlands	Vegetated, non-riverine or non-channel wetlands excluding lakes and estuaries. All wetland pesticide monitoring reported was in palustrine wetlands.
End-of-catchment	Located at the lowest point in a river or creek where the volume of water passing that point can be accurately measured by a gauging station and typically is not subject to tidal influence close to the upper limit of the tide.
Temporal distribution	Strong focus on describing long-term MMP pesticide trends. In marine (coral, seagrass, pelagic, benthic + plankton communities), estuarine (estuaries, mangroves, saltmarsh), freshwater (freshwater wetlands – see specific wetland types below, floodplain wetlands) ecosystems. Update from the 2017 SCS. Seasonal and pulses included. Other data on grab samples, interstitial water, sediments and biota to be included but mostly for context.
Risk	Defined as Exposure x Consequences. There is a risk of harm to biota when measured concentrations of pesticides in aquatic systems exceed toxicity thresholds including water quality guideline values. Risk can also be expressed as the estimated % of species affected by a given pesticide exposure.
Consequences	Negative effect on biota due to pesticide exposure.

Definitions	
Toxicity threshold	Concentration of a pesticide above which there is a measurable or defined (i.e., 10%) effect on survival or sublethal responses.
Ecological impact	Ecologically relevant effects of pesticides on biota, including reduced survival, growth, reproductive success. Can be observed in controlled laboratory experiments or in the field following exposure.
Tropical regions	Tropical regions of the world are located between the Tropic of Cancer and the Tropic of Capricorn between latitudes of about 23°05′ north and south of the equator.

Table 3. Acronyms used in Question 5.1.

Acronyms	
ANZECC & ARMCANZ	Australian and New Zealand Environment and Conservation Council and the Agriculture and Resource Management Council of Australia and New Zealand
ANZG	Australian and New Zealand governments
APVMA	Australian Pesticides and Veterinary Medicines Authority
CA	Concentration Addition: a model of joint action to predict the total toxic effect of two or more pesticides that have similar modes of action and do not interact with each other. CA yields slightly larger estimates of risk than by Independent Action (IA, see below).
DGV	The nationally endorsed limits for pollutants in waterbodies in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZG, 2018) are referred to as Default Guideline Values (DGVs). These are calculated using the nationally endorsed methods (Warne et al., 2018a).
EC10	10% effect concentration
ETV	Ecotoxicity Threshold Values: the equivalent of DGVs (see above) that have been derived using the nationally endorsed method for deriving water quality guidelines (Warne et al., 2018b) but the limits have not been submitted for national endorsement.
GBR	Great Barrier Reef
GBRCLMP	Great Barrier Reef Catchment Loads Monitoring Program
GBRMPA	Great Barrier Reef Marine Park Authority
GVs	Guideline Values: a generic term that includes ecotoxicity threshold values, current and proposed default guideline values
IA	Independent Action: a model of joint action to predict the total toxic effect of two or more pesticides that have do not have similar modes of action but do not interact with each other. The IA yields slightly lower estimates of risk than concentration addition (CA, see above).
LC10	10% lethal concentrations
MMP	Marine Monitoring Program
msPAF	multi-substance Potentially Affected Fraction: estimates the % of species affected (or conversely protected) by mixtures of pesticides.
NEC	No Effect Concentration: highest concentration of a pesticide that has no effect on a species.

Acronyms	
NOEC	No Observed Effect Concentration: the highest concentration that statistically has no effect on a species.
NRM	Natural Resource Management region
PCx	Protective Concentrations (e.g., PC99, PC95). GVs are usually presented as PCx, which if not exceeded should protect x% of species in an aquatic ecosystem.
PDGVs	Proposed Default Guideline Values: the equivalent of ETVs (see above).
PRM	Pesticide Risk Metric: a method that incorporates the msPAF method and is used to estimate the total toxicity of up to 22 different pesticides simultaneously present in water samples.
PSII	Photosystem II inhibiting herbicide
PSII-HEQ	Photosystem II-Herbicide Equivalent concentration: a toxicity metric that presents the potency of PSII herbicides relative to diuron.
SPEAR	Species At Risk: a pesticide bioassessment index
SSD	Species Sensitivity Distribution. A cumulative distribution of toxicity values for diverse species.
Teq	Toxicity equivalent. Also referred to as Toxic Equivalence Quotient (TEQ): a toxicity metric that presents the potency of PSII herbicides relative to atrazine.
TV	Threshold values - the highest concentration of a pesticide that has either no effect (NEC) or a low effect (EC10) on a species.
WQG	Water Quality Guideline(s). The WQG value applied in GBR waters is PC99. This is the guideline applied in waters of high ecological value. Concentrations of pesticides below the PC99 should not negatively affect 99% of species in an aquatic ecosystem. The nationally endorsed limits for pollutants in waterbodies in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZG, 2018) are referred to as Default Guideline Values (DGVs). These are calculated using the nationally endorsed methods (Warne et al., 2018a). Other limits for pollutants that are calculated using but have not been submitted for national endorsement are referred to by a variety of names including Ecotoxicity Threshold Values (ETVs) and Proposed Default Guideline Values (PDGVs). In this review, the term 'guideline value' will be used as the generic term for all pollutant limits.
WQIP	Reef 2050 Water Quality Improvement Plan

2.2 Search and eligibility

The Method includes a systematic literature search with well-defined inclusion and exclusion criteria.

Identifying eligible literature for use in the synthesis was a two-step process:

1. Results from the literature searches were screened against strict inclusion and exclusion criteria at the title and abstract review stage (initial screening). Literature that passed this initial screening step were then read in full to determine their eligibility for use in the synthesis of evidence.
2. Information was extracted from each of the eligible papers using a data extraction spreadsheet template. This included information that would enable the relevance (including spatial and temporal), consistency, quantity, and diversity of the studies to be assessed.

a) Search locations

Searches were performed in:

- Web of Science and Scopus
- Google Scholar
- Sources referred to in publications assessed by the Authors during data extraction.

b) Search terms

Table 4 shows a list of the search terms used to conduct the online searches. Terms in Bold were used as other potential search terms limited the number of returns.

Table 4. Search terms for S/PICO elements of Question 5.1.

Question element	Search terms
Subject/Population	**pesticide(s), herbicide(s), insecticide(s), fungicide(s)**
Exposure or Intervention	**Great Barrier Reef, GBR,** seawater, sediments, biota, inshore, offshore marine habitat, estuarine habitat, freshwater, river, seagrass meadow, wetlands, coral, mangrove, distribution, accumulation, monitoring, concentration, bioaccumulation, biomagnification, spatial distribution, temporal distribution
Comparator (if relevant)	**guideline, ANZECC**, water quality, WQGV, toxicity, threshold
Outcome	ecological impacts, risk, harm

c) Search strings

Table 5 shows a list of the search strings used to conduct the online searches.

Table 5. Search strings used for electronic searches.

Search strings
(pesticide* OR herbicide* OR insecticide* OR fungicide*) AND (“Great Barrier Reef” OR “GBR”)
(pesticide* OR herbicide* OR insecticide* OR fungicide*) AND (guideline* OR ANZECC) AND (Australia* OR tropical)

d) Inclusion and exclusion criteria

Table 6 shows a list of the inclusion and exclusion criteria used for accepting or rejecting evidence items.

Table 6. Inclusion and exclusion criteria for Question 5.1 applied to the search returns.

Question element	Inclusion	Exclusion
Subject/Population	**Pesticides:** chemicals used to control pest species including herbicides, insecticides and fungicides	Poisons that control mammals, biological pesticides
Exposure or Intervention	**GBR ecosystems** include: marine, estuarine and wetlands within the Great Barrier Reef Marine Park. **Spatial and temporal distribution Include:** Comparisons of pesticide concentrations among NRM regions and catchments consistent with the MMP. Ecosystems include (reef, seagrass meadow, river mouth, wetlands). Natural and near-natural wetlands only, including estuarine, marshes and floodplain lakes. The detection of pesticides in aquatic biota of the GBR provides evidence of exposure.	Artificial wetlands, channels, dams, farms, groundwater. Other areas not linked to Great Barrier Reef Ecosystems

Question element	Inclusion	Exclusion
Comparator (if relevant)	Guideline, ANZECC, water quality, WQGV, toxicity, threshold. **Water quality guideline values** guide aquatic ecosystem protection. We will consider current and proposed (updated with improved data) Australian and New Zealand default guideline values (DGVs, including ANZECC & ARMCANZ 2000 and those developed for GBR waters). **Threshold values:** Concentration of a pesticide (or pesticide mixtures) above which there is a measurable or defined (i.e., 10%) effect on survival or sublethal responses. **Ecotoxicity threshold values**: the equivalent of DGVs (see above) that have been derived using the nationally endorsed method for deriving water quality guidelines (Warne et al., 2018a) but the limits have not been submitted for national endorsement.	
Outcome	**Ecological impact:** Ecologically relevant effects of pesticides on biota, including reduced survival, growth, reproductive success. Can be observed in controlled laboratory experiments or in the field following exposure. **Risk:** There is a risk of harm to biota when measured concentrations of pesticides in aquatic systems exceed toxicity thresholds including WQG values.	Effects on or risks to non-aquatic organisms.
Language	English	Non-English language
Study type	Journal articles, reviews, reports Studies published during or after 1990	Non peer reviewed studies, reviews or position papers with little quantitative evidence

Eligibility criteria used in screening to exclude literature:

1) Not geographically in the GBR.
2) Relevant to artificial wetlands, channels, dams, farms, groundwater.
3) More relevant to SCS question 5.2 sources transport - outside scope.
4) More relevant to SCS question 5.3 management - outside scope.
5) Did not refer to aquatic organisms.
6) Reviews or position pieces – which contain little primary evidence.
7) Non-peer reviewed literature.
8) Non-English language.
9) A lack of information on pesticides.
10) A lack of information on pesticides since 1990.
11) Using pesticide loads which has been superseded.
12) Reports were superseded in later peer-reviewed articles.
13) Methods not being designed to identify effect thresholds or very insensitive monitoring method.
14) Error in Mendeley.

3. Search Results

A total of 953 studies were identified through online searches for peer reviewed and published literature. An additional 92 studies were identified manually through expert contact and personal collections, which represented 9% of the total evidence considered. Following full-text screening, 231 studies were eligible for inclusion in the synthesis of evidence (Table 7, Figure 2).

*Table 7. Search results table, separated by A) Academic databases, B) Search engine (i.e., Google Scholar) and C) Manual searches. * first refers to highest similarity (not by year).*

Date (d/m/y)	Search strings	Source	
A) Academic databases		Web of Science	Scopus
Search string 1	*(pesticide* OR herbicide* OR insecticide* OR fungicide*) AND ("Great Barrier Reef" OR "GBR")*	*267 total* *146 eligible*	*190 total* *104 eligible*
Search string 2	*(pesticide* OR herbicide* OR insecticide* OR fungicide*) AND (guideline* OR ANZECC) AND (Australia* OR tropical)*	*159* *41 eligible*	*209* *43 eligible*
B) Search engines (e.g., Google Scholar)			
Search string 1	*(pesticide* OR herbicide* OR insecticide* OR fungicide*) AND ("Great Barrier Reef" OR "GBR")*	*first 200* (of 18,400)* *114 eligible*	
Search string 2	*(pesticide* OR herbicide* OR insecticide* OR fungicide*) AND (guideline* OR ANZECC) AND (Australia* OR tropical)*	*first 200* (of 20,000)* *21 eligible*	
	Total items online searches	***953 total, 276 relevant initial screening (91%)***	
C) Manual search			
Date	Source	Number of items added	
	Referenced in King et al., 2017	*40*	
	Author's personal collection	*52*	
	Total items manual searches	***92 (9%)***	

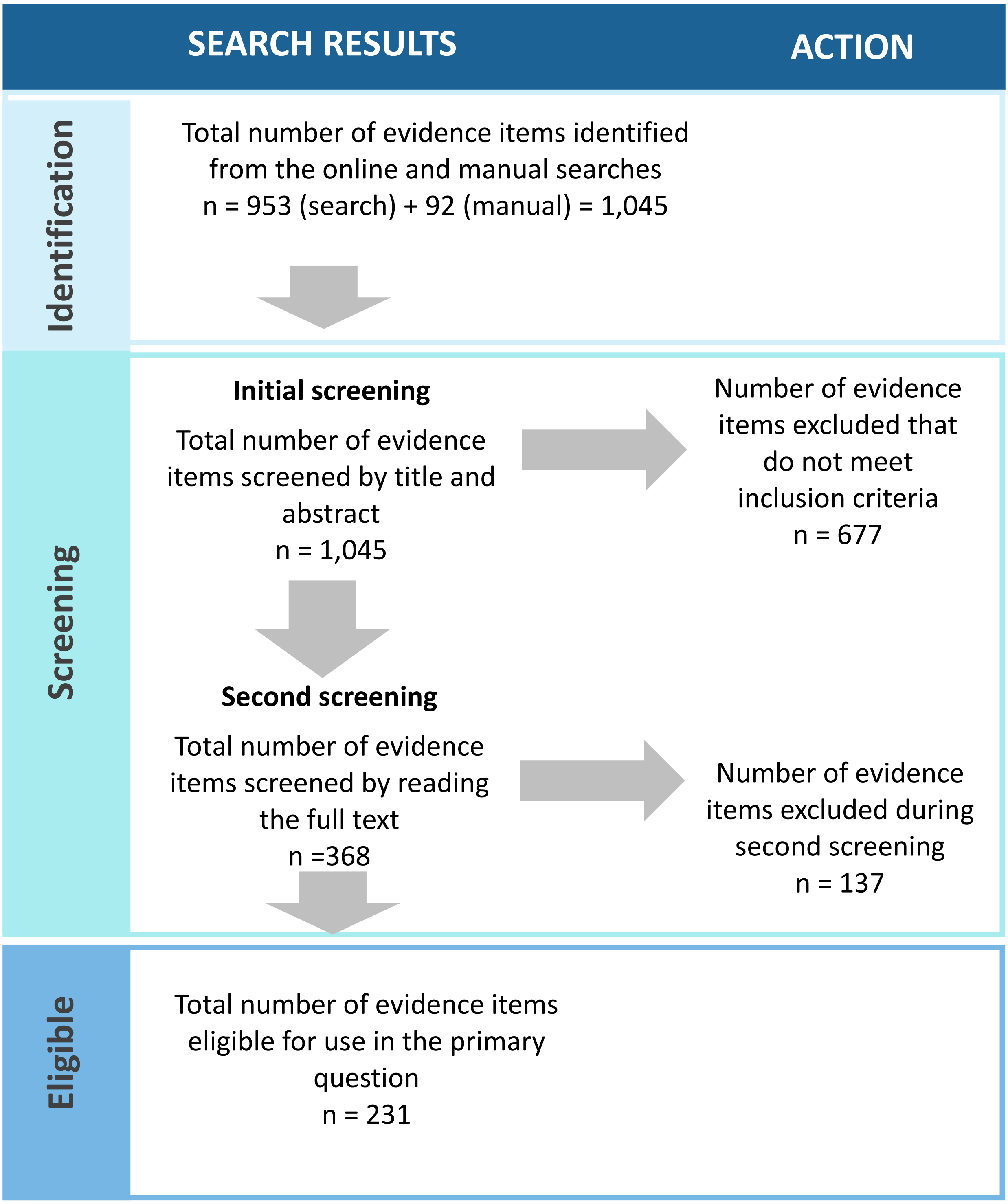


Figure 2. Flow chart of results of screening and assessing all search results for Question 5.1.

4. Key Findings

4.1 Narrative synthesis

4.1.0 Summary of study characteristics

A total of 231 eligible studies were found to address the primary question, the vast majority (80%) of studies were Australian, and most of those were directly related to the GBR. The characteristics of these studies are summarised in Table 8. The studies included were classed as primary (observational, modelled or experimental) and secondary (reviews, systematic reviews or meta-analysis).

Table 8. Summary of the primary characteristics evaluated, and the study approach used. Some publications covered more than one question characteristic so the grand total (286) > eligible studies (231).

	Spatial and temporal pesticide distribution	Observed or potential effects of pesticides to GBR ecosystems	Pesticide risk	Total
Primary (observational, modelled or experimental)	79	103	58	240
Secondary (reviews etc.)	14	15	17	46
Total	93	118	75	286

The most relevant studies on spatial and temporal pesticide distribution were from two large, multi-year monitoring programs: 1) the Great Barrier Reef Catchment Loads Monitoring Program (GBRCLMP, 6 years freshwater); and 2) the Marine Monitoring Program (MMP, 3 years marine). Recent pesticide data (2016/17 onwards) were summarised and compared to data from earlier programs and other studies. An emphasis was also placed on pesticide concentrations rather than loads, since concentrations are directly related to ecosystem risk. Many earlier studies had a strong focus on Photosystem II inhibiting (PSII) herbicides, while the current review focused on the 12 pesticides that contribute >99% of risk to freshwater and marine habitats. For freshwater ecosystems, the current review concentrated on 12 waterways with end-of-system monitoring sites, which were sampled for most of the six-year period, included five of the six Natural Resource Management (NRM) regions in the GBR catchment area (the exception being Cape York NRM), and represented the full range of total pesticide mixture risk values (from very low risk (<1% of aquatic species likely to be affected) to very high risk (>20% of aquatic species likely to be affected). For marine ecosystems, the review included all 11 fixed monitoring sites located along the inshore zone of the GBR.

Studies on the observed or potential effects of pesticides on GBR ecosystems represented two broad approaches: 1) studies that linked pesticides detected in GBR ecosystems to observed impacts on GBR species (in the field); and 2) experimental identification of pesticide concentrations that have negative effects on GBR organisms (e.g., toxicity thresholds). The review summarises:

1) Studies on the effects of pesticides on GBR species in the field.
2) Observed effects of pesticides on GBR species (experimental studies).
3) Pesticide guidelines values (GVs) that have been applied in GBR ecosystems.
4) The sensitivity of GBR species (experimental) to pesticides in comparison to the most recent GVs.
5) The assessment of total toxicity of pesticide mixtures to GBR species.
6) The influence of other environmental factors on pesticide toxicity to GBR species.

The potential risk of pesticides to GBR ecosystems was assessed by documenting the percentage of species that may be affected by pesticides (based on guideline values) detected across the selected 12 freshwater monitoring sites and all 11 marine monitoring sites. While most previous assessments of risk have concentrated on PSII herbicides, the current review accounted for the potential contribution of all pesticides that were able to be quantified in the monitoring programs.

The question addressed in this review is highly quantitative; therefore, quantitative assessments were made on the distribution of-, effects of- and risks posed by pesticides since the 2017 SCS. Data summaries can be found in separate Excel spreadsheets referred to in the text and listed in Table 9.

Table 9. Quantitative summary spreadsheets on the distribution of-, effects of- and risks posed by pesticides since the 2017 SCS, and included as Appendices (available to download as a zip file from the 2022 SCS website).

Table name	Description
Table P1	Pesticide mode of action and identification in monitoring programs
Table F1	Freshwater sites (all): Number of samples, detection frequency, minimum and maximum concentration of all pesticides
Table F2	Freshwater sites (all): Detection frequency (%) for all pesticides over all years
Table F3	Freshwater sites (all): Percent mixtures for all years
Table F4	Freshwater sites (12 focus): Annual detection frequency (%) of the 12 focus pesticides
Table F5	Freshwater sites (12 focus): Median wet season concentrations ($\mu g\ L^{-1}$) of the 12 focus pesticides sites
Table F6	Freshwater sites (12 focus): Median dry season concentrations ($\mu g\ L^{-1}$) of the 12 focus pesticides
Table F7	Freshwater sites (12 focus): Wet to dry ratio for the 12 focus pesticides
Table F8	Freshwater sites (12 focus): Maximum annual concentration ($\mu g\ L^{-1}$) for 12 focus pesticides
Table F9	Freshwater sites (12 focus): Minimum annual concentration ($\mu g\ L^{-1}$) for 12 focus pesticides
Table M1	Marine sites: Number of samples, detection frequency, minimum and maximum concentration of all pesticides across all sites and years
Table M2	Marine sites: Number of samples and percentage mixtures at each monitoring site
Table M3	Marine sites: Monitoring period detection frequency (%) of the focus pesticides
Table M4	Marine sites: Wet to dry ratio for the 12 focus pesticides for 12
Table M5	Marine sites: Minimum, maximum concentration, number of samples, and detection frequency of the 12 focus pesticides
Table M6	Marine sites: Total number of samples by year and monitoring site.
Table M7	Marine sites: Number of grab samples, detection frequencies, minimum and maximum concentration of all pesticides
Table M8	Marine sites: Percentage mixtures at all monitoring sites
Table T1	Toxicity threshold data freshwater species
Table T2	Toxicity threshold data marine species

4.1.1 Summary of key evidence to 2022

This review assessed (1) the spatial and temporal distribution of pesticides and (2) the potential effects of pesticides on GBR relevant species. The potential risks that pesticides pose to GBR ecosystems (3) were primarily assessed by comparing concentrations measured in the GBR (likelihood of exposure) against recently developed water quality guidelines (potential consequences) as shown in the conceptual diagram (Figure 1). There was a strong focus on assessing palustrine wetlands, end-of-catchment and marine pesticide concentrations (dissolved) from 2016/17. Estuaries were not independently assessed as there was little consistent monitoring from 2016/2017. Earlier studies have assessed pesticides in estuarine habitats of the GBR (Bainbridge et al., 2009; Davis et al., 2012; Mitchell et al., 2005; Packett et al., 2009; Smith et al., 2012), suggesting concentrations and exposure times are lower than those at the end-of-catchment due to dilution. The guideline values for pesticides were compared to toxicity thresholds derived exclusively for GBR species to test their validity for application in risk assessments.

Spatial and temporal distribution of pesticides across GBR ecosystems: end-of-catchment

The potential risk of widespread contamination of GBR ecosystems by agricultural chemicals including pesticides was recognised over two decades ago (Haynes et al., 2000a; Haynes & Johnson, 2000; Haynes & Michalek-Wagner, 2000). Long-term monitoring of pesticides was initiated to assess the spatial and temporal patterns and changes in pesticides over time and inform land management practices to help mitigate any identified risk. Pesticides have been detected in water, sediments, and biota of freshwater GBR ecosystems; however, most contemporary pesticides are relatively water soluble and preferentially partition into the dissolved phase (Davis et al., 2012; Devlin et al., 2015). Hence, pesticide monitoring programs have focused on dissolved pesticides (e.g., Thai et al., 2020; Water Quality & Investigations, 2023a).

Water quality surveys conducted in the mid-1990s reported the presence of herbicides in the Johnstone River including atrazine, 2,4-D, 2,4,5-T, trifluralin and 2-methyl-4-chlorophenoxyacetic acid (MCPA) (Hunter et al., 2001). Later monitoring of wet season flow events in catchments in the Wet Tropics, Burdekin and Mackay Whitsunday regions (Davis et al., 2008; Faithful et al., 2008; Lewis et al., 2009; Mitchell et al., 2005; Packett et al., 2009) demonstrated the presence of multiple pesticides in waterways. Prominent among the chemicals detected were the PSII inhibiting herbicides ametryn, atrazine, diuron, hexazinone, simazine and tebuthiuron, environmental breakdown products of diuron and atrazine, and to a lesser extent other pesticides like the auxin mimic 2,4-D and the insecticide imidacloprid. The conclusion from these studies was that pesticides emanating from agriculture in the freshwater catchment may present a toxicity risk to GBR ecosystems (Lewis et al., 2009).

In 2009, in response to the reports on the presence of pesticides in waterways that flowed into the Great Barrier Reef, the Reef Water Quality Protection Plan (Queensland Government, 2009) was expanded to include pesticides. Five PSII inhibiting pesticides (ametryn, atrazine, diuron, hexazinone, tebuthiuron) were introduced as an element of the GBR Catchment Loads Monitoring Program (GBRCLMP) (e.g., Garzon-Garcia et al., 2016; Turner et al., 2012; 2013a; Wallace et al., 2014) and reported as loads (i.e., total masses) potentially delivered to GBR ecosystems. In 2014, the scope of monitoring was expanded to report on a much wider variety of pesticides (Huggins et al., 2017; Wallace et al., 2016) and the loads of the five PSII herbicides were reported as diuron toxicity equivalent (TEq) loads (Smith et al., 2017a; 2017b). More recently, a wider suite of 22 pesticides, including nine PSII inhibiting pesticides, ten other herbicides with varying modes of action and three insecticides (imidacloprid, chlorpyrifos, fipronil) have been reported in terms of their combined toxicity to aquatic ecosystems (Ten Napel et al., 2019a; 2019b; Water Quality & Investigations, 2020a). The full history of concentrations for all 22 pesticides and a further two (bromacil and diazinon) detected at a total of 51 sites across five NRM regions is provided in the Pesticide Reporting Portal (Water Quality & Investigations, 2020b).

Although it is widely recognised that pesticides enter waterways downstream of multiple land uses, including grazing, grains, sugarcane cropping and horticultural crops (Bartley et al., 2017; Kroon et al., 2013; Lewis et al., 2009) and that concentrations of pesticides will be higher closer to the source

(Donaldson & Rohde, 2022; Rohde et al., 2013; Wallace et al., 2017), monitoring has concentrated on end-of-system sites in order to, initially estimate the loads of PSII herbicides to GBR ecosystems, and more recently to estimate the potential risks to GBR ecosystems from all pesticides.

The focus of this section of the review was to assess the spatial and temporal distribution of dissolved pesticide concentrations as these are most relevant for understanding risk to aquatic biota (Warne et al., 2020a). The most extensive data on pesticides in GBR catchments has been generated by the GBR Catchment Loads Monitoring Program (GBRCLMP), which has applied standardised and consistent monitoring and analytical methodologies to pesticides since 2009. In this program, pesticides are analysed from "grab" samples, which provide representative (instantaneous) concentrations of pesticides in water passing the monitoring site at an instant in time. Annual loads (mass) of individual pesticides at the end of a catchment can then be calculated by combining pesticide concentrations from grab samples with the time and date matched discharge of waterways over a year (e.g., Huggins et al., 2017). More recently the concentration data for mixtures of pesticides have been used to calculate the estimated risk to GBR ecosystems (Ten Napel et al., 2019a; 2019b; Water Quality & Investigations, 2020a; 2021; 2023a). The current review assesses spatial and temporal trends in pesticide distribution at the end-of-catchment from 2016/17 to 2021/22 GBRCLMP data.

Total number of pesticides and their frequency of detection in freshwater systems

Pesticides are ubiquitous in GBR freshwater ecosystems. The GBRCLMP began monitoring for pesticides in 2009 and 72 sites in 54 waterways have been monitored since 2016. With the exception of one site, Fig Tree Creek, that was specifically selected as a reference site upstream of potential chemical inputs, pesticides have been detected at every site and waterway. All publications from other pesticide monitoring projects in GBR freshwater ecosystems reported measuring pesticides. Although analytical methods have improved, the 74 pesticides detected during the last 6 years of the GBRCLMP (Table 10) are broadly similar in identity and number to those detected in previous monitoring programs (see individual reports for target analytes and limits of reporting). More than 90 pesticides and their transformation products are currently monitored as part of the GBRCLMP; however, only 24 pesticides are quantitatively reported in the GBRCLMP—including all 22 pesticides in the Pesticide Risk Metric (PRM) for determining the toxicity of pesticide mixtures (Warne et al., 2020a; Water Quality & Investigations, 2020b).

- Approximately 79% of grab samples collected over the six monitoring seasons (2016/17 to 2021/22) contained quantifiable concentrations of pesticides (Table 10) which is similar to the preceding four years (2011/12 to 2014/15) where 90% of 2,600 samples contained quantifiable pesticide concentrations (Warne et al., 2020b). The frequency of pesticide mixtures in samples during these two periods were also similar at 82% and 72% in 2011/12 to 2014/15 (Warne et al., 2020b) and 2016/17 to 2021/22, respectively.
- The pesticides identified at end-of-catchment sites were similar to those identified previously. A comprehensive review in 2015 (Smith et al., 2015) that included other (non GBRCLMP) monitoring results reported 56 pesticides and transformation products had been identified in waterways across all NRM regions. The increase in the number of pesticides identified from 56 to 74 is most likely due to the expansion of the number of pesticides analysed by the GBRCLMP and the program's inclusion of non-targeted analysis, but it is possible that the number of pesticides being applied within the GBR catchment area has increased.
- The most frequently identified pesticides in 2011/12 to 2014/15 (Spilsbury et al., 2020; Warne et al., 2020b) and 2016/17 to 2021/22 were very similar, although the order of frequency among these pesticides varied. The most frequently identified pesticides that were common to both periods were (in alphabetical order) 2,4-D, ametryn, atrazine, diuron, desethyl atrazine, desisopropyl atrazine, fluroxypyr, hexazinone, imidacloprid, isoxaflutole, MCPA, metolachlor, metribuzin and tebuthiuron.

Table 10. Key findings on pesticide frequency of quantification and mixtures for all pesticides and sites from six GBRCLMP seasons: 2016/17 to 2021/22 GBRCLMP (Water Quality & Investigations, 2020b).

Pesticide data	Key findings: all sites, pesticides and years	Data location
Number of samples collected	• 10,309 grab samples collected from between 34 (2016/17) and 51 (2017/18) sites across 6 NRM regions. A total of 72 unique sites were monitored across all years.	**Table F1**
Frequency of pesticides detection	• Agricultural pesticides and their transformation products were quantified in 8,162 of 10,309 samples (79%) across all sites and years.	**Table F1**
Total number of pesticides	• 90 contemporary pesticides and transformation (breakdown) products were monitored in freshwater, with 74 detected at least once.	**Table P1**
Most frequently detected PSII herbicides	• Diuron and atrazine were both in 54% of all samples. • Atrazine 2-hydroxy, desthyl atrazine and desisopropyl atrazine (all degradation products of atrazine) were in 53%, 44% and 22% of samples, respectively. • Hexazinone was in 47% of samples. • Tebuthiuron was in 22% of samples.	**Table F2**
Most frequently detected non-PSII pesticides	• Metolachlor (a non-PSII herbicide) was in 43% of samples. • Imidacloprid (an insecticide) was in 43% of samples. • 2,4-D (a non-PSII herbicide) was in 42% of samples. • Imazapic (a non-PSII herbicide) and DCPMU (a degradation product of diuron) were both in 37% of samples. • 4-hydroxy chlorothalonil (a fungicide transformation product) was in 34% of samples (based on 1 year of monitoring data).	**Table F2**
Mixtures	• Pesticides rarely occur in isolation: 72% of all samples contained mixtures (7,380 of 10,309 samples).	**Table F3**

Note: Appendices Tables available to download as a zip file from the 2022 SCS website.

Spatial and temporal distribution of the selected pesticides at end-of-catchment

The concentrations of 24 pesticides at a total of 51 sites representing 27 basins and all six NRM regions are provided in the Pesticide Reporting Portal (Water Quality & Investigations, 2020b). For the six years examined by this Evidence Review (i.e., 2016/17 to 2021/22) pesticide data were available from 37 sites. This readily accessible dataset was used to compare the spatial and temporal distributions of pesticides in GBR catchments. It is not practical to summarise the spatial and temporal distribution of 24 pesticides across 37 sites here, so this review focused on 12 pesticides at 12 waterways (the focus pesticides and sites) between 2016/17 and 2021/22. The 12 focus pesticides (ametryn, atrazine, diuron, fipronil, hexazinone, imazapic, imidacloprid, isoxaflutole, metolachlor, MCPA, metsulfuron-methyl and triclopyr) were selected, as combined, they typically account for at least 99% of the total toxicity of pesticide mixtures in GBR waterways (Spilsbury et al., 2020; Warne et al., 2020b; Water Quality & Investigations, 2023a; see risk section below). The criteria used to select the 12 focus sites (Table 11) were: they should be located at the end-of-catchments, be sampled for most of the six-year period, represent the NRM regions in the GBR catchment area, and represent the full range of total pesticide mixture risk values (i.e., from ≤1% (very low risk) to >20% (very high risk)). The main findings and data for the selected pesticides and sites are summarised in a series of figures and tables here and in the Appendix 2, while the summary data for all pesticides and sites can be found in separate spreadsheets (Table 12).

Table 11. The twelve focus waterways selected to represent the monitored Great Barrier Reef waterways (freshwater) and their characteristics. Risk classes summarised from Water Quality and Investigations (2023b).

	GBR waterway	Characteristics (NRM region/risk classes)	Years sampled
1	Daintree River	Wet Tropics / Very Low risk	17/18 – 21/22
2	Russell River	Wet Tropics / Low to Moderate risk	16/17 – 21/22
3	Tully River	Wet Tropics / Low to Moderate risk	16/17 – 21/22
4	Haughton River at Powerline	Burdekin / Moderate risk	16/17 – 17/18
	Haughton River at Giru Weir	Burdekin / Low risk	17/18 – 21/22
5	Barratta Creek	Burdekin / High to Very High risk	16/17 – 21/22
6	Burdekin River	Burdekin / Very Low risk	16/17 – 21/22
7	Sandy Creek	Mackay Whitsunday / Very High risk	16/17 – 21/22
8	Plane River	Mackay Whitsunday / Low to Moderate risk	16/17 – 21/22
9	O'Connell River	Mackay Whitsunday / Moderate to High risk	16/17 – 21/22
10	Fitzroy River at Fitzroy River Water	Fitzroy / Low risk	16/17 – 21/22
11	Burnett River at Anderson Bridge	Burnett Mary / Low risk	16/17 – 17/18
	Burnett River at Quay Street Bridge	Burnett Mary / Very Low to Low risk	17/18 – 21/22
12	Mary River at Home Park	Burnett Mary / Low risk	16/17 – 17/18
	Mary River at Churchill Street	Burnett Mary / Low to Moderate risk	17/18 – 21/22

*Table 12. Summary findings of the spatial and temporal distribution of the focus pesticides and focus waterways from the 2016/17 to 2021/22 GBRCLMP monitoring. Summary tables in the Appendices cover the 12 focus pesticides and waterways (**Tables F4 to F9**), and summary data for all quantified pesticides and sites over the same period (**Tables F1, F2, F3**). Wet season was 182 days from the start of summer rainfall, while the dry season represents the 182 days prior to the start of the wet season.*

Pesticide data	Key findings: Spatial and temporal variation of the focus sites and pesticides	Data
Frequency of detection	• The five most frequently quantified pesticides in the 12 focus waterways were atrazine (56%), hexazinone (50%), diuron (48%), metolachlor (42%) and imazapic (33%). • Sandy Creek (68%), followed by Barratta Creek (48%) had the highest average quantification frequency across all years. • While quantification frequency varied between years for the different pesticides, the average quantification frequency for all sites was slightly higher in 2016/17 and 2021/22.	**Table F4**
Median wet season concentrations	• Sandy Creek had the highest median wet season concentrations across all years, followed by the O'Connell River and Barratta Creek. • At Sandy Creek, diuron had the highest median wet season concentration followed by atrazine, hexazinone and imazapic. • The median wet season concentrations of each pesticide varied between years for the different sites. At Sandy Creek the median concentrations of atrazine ranged from 0.54 to 1.9 µg L^{-1}, diuron ranged from 0.64 to 1.4 µg L^{-1}, hexazinone ranged from 0.2 to 0.6 µg L^{-1} while imazapic ranged from 0.24 to 0.38 µg L^{-1}. • At Sandy Creek the highest median concentrations were detected in 2016/17.	Figure 3, **Table F5**
Median dry season concentrations	• The median dry season concentration of atrazine at Barratta Creek (which is irrigated) was 90-times higher than the median dry season concentration across all other sites and years. • The median dry season concentration of diuron at Barratta Creek was ten-times higher than the corresponding median dry season concentration across all other sites and years. • Generally, there was little variation in the median dry season concentrations of individual pesticides across years at each site.	**Table F6**

	• At Barratta Creek the highest median dry season concentrations of atrazine (9 µg L^{-1}), diuron (2.5 µg L^{-1}), imazapic (0.05 µg L^{-1}) and isoxaflutole (0.18 µg L^{-1}) were detected in 2019/20.	
Ratio of median wet/dry season concentrations	• Pesticides concentrations were higher in the wet season three times more often than they were higher in the dry season (average of all pesticides, sites, years). • The ratio of median wet/dry season concentrations ranged from 0.04 to 40 over all years and all sites. For example, ranges at Sandy Creek included the following ratios: atrazine 0.97 to 37, diuron 2.5 to 40 and metolachlor 0.30 to 30. The highest ratios for many pesticides at Sandy Creek were in 2020/21. • The ratio of median wet/dry season concentrations was ≥1 in 76% of all samples. • The Daintree, Russell and O'Connell rivers were the only sites with all values ≥1.	**Table F7**
Maximum annual concentrations	• Barratta Creek followed by Sandy Creek and O'Connell River had the highest maximum annual concentrations across all years, with atrazine (maximum 59 µg L^{-1}) and diuron (maximum 13 µg L^{-1}) found at the highest concentrations. • Fitzroy River, Mary River, Burnett River and Daintree River had the lowest maximum annual concentrations across all years. • The maximum annual concentrations of each pesticide varied between years for the different sites. For example, at Barratta Creek, the maximum annual concentrations of atrazine and diuron were highest in 2021/22, while the maximum annual concentrations of isoxaflutole and MCPA were highest in 2020/21.	**Table F8**

Note: Appendices Tables available to download as a zip file from the 2022 SCS website.

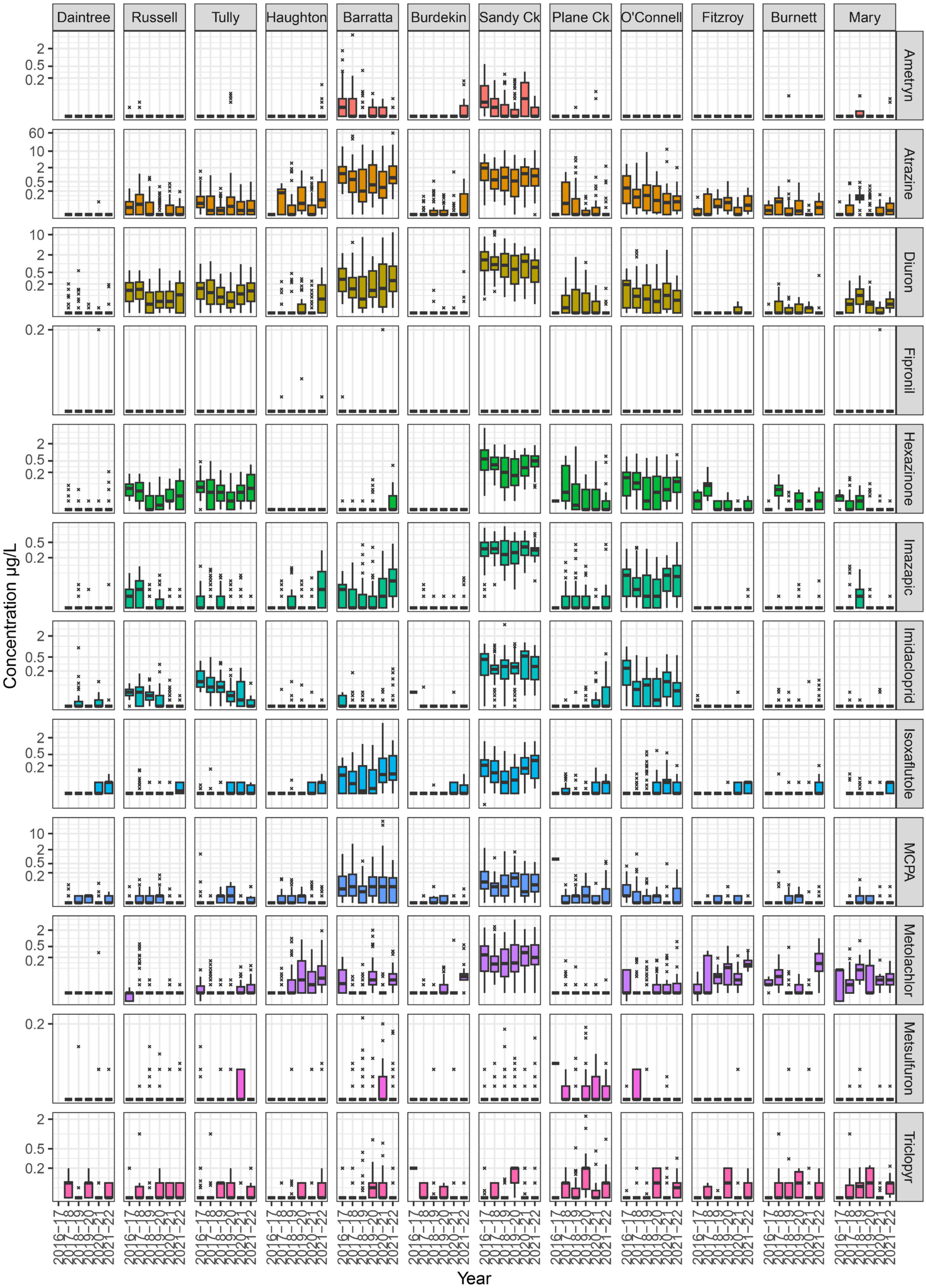


Figure 3. Median wet season pesticide concentrations for the 12 focus pesticides across 12 freshwater focus waterways. See ***Table F4*** *(*[*Appendices*]*) for the detection frequency of each pesticide at each focus site.*

The frequency of quantification of pesticides across the 12 focus sites over the six years is shown in **Table F4**, with atrazine quantified in over half the samples (56%). Hexazinone (50%), diuron (48%) and metolachlor (42%) were also frequently quantified. Fipronil was the least frequently quantified focus pesticide (0.26%) and was predominantly quantified in samples from the Burdekin region.

There were limited pesticide concentration data available for the Cape York region and it was not collected in a systematic manner like the GBRCLMP. The following spatial analysis is based on the focus waterways and pesticides. The Burdekin region has the highest maximum annual pesticide concentration (59 µg L^{-1}, atrazine), followed in decreasing order by the Mackay Whitsunday (13 µg L^{-1}, diuron), the Wet Tropics (1.4 µg L^{-1} atrazine), Burnett Mary (1 µg L^{-1}, metolachlor) and the Fitzroy (0.6 µg L^{-1}, metolachlor) regions. However, this ranking could be biased by atypically high concentrations. A better ranking comes from comparing regions based on their median pesticide concentrations (Figure 3). On this basis Mackay Whitsunday has the highest pesticide concentrations (1.9 µg L^{-1}, atrazine), followed by the Burdekin (1.1 µg L^{-1}, atrazine), Wet Tropics (0.14 µg L^{-1}, diuron), Burnett Mary (0.12 µg L^{-1}, metolachlor) and Fitzroy (0.11 µg L^{-1}, metolachlor). These findings are consistent with earlier studies (e.g., Waterhouse et al., 2017). A more detailed description of the spatial variation within each region is provided below.

Wet Tropics region: The Daintree River had the lowest median pesticide concentrations of the three Wet Tropic region sites (Figure 3). It also had a low average pesticide quantification frequency (3%) compared to the Russell and Tully rivers (average pesticide quantification frequencies of 27 and 32%, respectively) (**Table F4**). The PSII herbicides diuron and hexazinone and insecticide imidacloprid were among the most frequently quantified pesticides in the Russell and Tully rivers, with diuron having the highest median wet season concentration at both sites (**Table F5**).

Burdekin region: Barratta Creek had the highest average quantification frequency (48%) compared to the other sites in the Burdekin region (Haughton River, 17% and Burdekin River, 6%). Atrazine was quantified in 99.7% of samples collected from Barratta Creek, with diuron (94%), MCPA (75%) and imazapic (64%) also frequently quantified (**Table F4**). Atrazine was found at the highest concentrations in Barratta Creek, with a maximum concentration of 59 µg L^{-1} (**Table F8**). From the Burdekin region, 40% of samples had a wet to dry season ratio <1 (**Table F7**, compared to 24% for all sites in Table 4) and the dry season medians for atrazine and diuron at Barratta Creek were 90- and 10-times higher, respectively, than the median dry season concentration for all sites (**Table F6**).

Mackay Whitsunday region: Sandy Creek had the highest average quantification frequency (68%) compared to the other sites in the Mackay Whitsunday region (Plane Creek, 24% and O'Connell River, 37%). Hexazinone was quantified in 100% of samples collected from Sandy Creek, with atrazine and diuron quantified in 99% of samples and imazapic quantified in 98% of samples (**Table F4**). Hexazinone was also the most quantified pesticide at Plane Creek (61% of samples) and O'Connell River (85% of samples). Atrazine and diuron were found at the highest concentrations at Sandy Creek and O'Connell River (**Table F8**). Median pesticide concentrations at Sandy Creek were, on average, 9-times higher in the wet season than in the dry season (ratio of median wet/dry season ratio ranged from 0.3 to 40) (**Table F7**).

Fitzroy region: Only one site, Fitzroy River, was included for the Fitzroy region. Metolachlor was quantified in 83% of samples, followed by atrazine (72%) and hexazinone (57%) (**Table F4**). All other pesticides were quantified in <5% of samples. Metolachlor (maximum concentration 0.6 µg L^{-1}) and atrazine (maximum concentration 0.53 µg L^{-1}) were present at the highest concentrations in the Fitzroy River (**Table F8**).

Burnett Mary region: Both sites in this region, the Burnett and Mary rivers, had similar average quantification frequencies (19% and 21%, respectively) (**Table F4**). Hexazinone was quantified in 72% of samples collected from the Burnett River, with metolachlor (49%) and atrazine (42%) also frequently quantified. The order of commonly quantified pesticide at Mary River was different, with metolachlor quantified in 57% of samples, followed by diuron (50%) and hexazinone (42%). At both sites, triclopyr and hexazinone were present at the highest concentration (**Table F8**).

The above analysis reveals there is considerable spatial variation in the number and types of pesticides measured in monitoring studies. In agriculture each crop has a number of pesticides that can legally be applied to them. Therefore, in catchments dominated by agriculture, the crops grown will determine the pesticides likely to be measured in waterways (Bainbridge et al., 2009; Lewis et al., 2009). Also, as the relative amount of land used for a crop increases in a catchment, higher aqueous pesticide concentrations are likely to occur. For example, concentrations of the insecticide imidacloprid were found to increase as the proportion of the upstream catchments used for bananas, sugarcane and urban land uses increased (Warne et al., 2022b). Warne et al., (2020b) analysing over 2,500 water samples from GBR catchments also found that the number of pesticides differed spatially with land use. Typically, catchments dominated by conservation and/or forestry land uses had the lowest number of pesticides measured, but as the amount of grazing increased so did the number of pesticides measured, and irrespective of other land uses the addition of sugarcane increased the number of pesticides measured (Warne et al., 2020b). The only statistically significant relationship between the number of pesticides present and land use in these GBR waterways was with the percentage of sugarcane in the catchment, which was able to explain 65% of the variation in the number of pesticides present (Warne et al., 2020b). Vandergragt et al. (2020) examining GBR palustrine wetlands also found that the percent of catchment used for sugarcane and intensive agriculture within 1 km of wetlands was significantly related to the number of pesticides measured ($r^2 \sim 0.5$). Also earlier work by Bainbridge et al. (2009) found good quality linear relationships ($r^2 = 0.71$) between aqueous diuron concentrations and the proportion of a catchment used for sugarcane. Relationships between land use and the number of pesticides present in rivers in Germany and the USA were also reported by Schreiner et al. (2016).

Along with land use in the catchments, the pesticide transport and detection at the end-of-catchment t is also highly dependent on the magnitude of river discharge which in turn is related to rainfall (Mitchell et al., 2005; O'Brien et al., 2014a; Packett et al., 2009). Two waterways, the Tully River in the Wet Tropics region and the Pioneer River in the Mackay Whitsunday region, with similar upstream catchment areas, illustrate the impact of these two factors on measured concentrations of two frequently detected herbicides (atrazine and diuron) and an insecticide (imidacloprid) (Table 13). This clearly shows that all summary measures of pesticide concentrations, except the median values for imidacloprid, are markedly larger in the Pioneer River (higher sugarcane land use and less discharge) than in the Tully River.

*Table 13. The concentrations of three frequently detected pesticides (atrazine, diuron, imidacloprid) in two waterways of similar catchment size but with differing rainfall (Bureau of Meteorology), river discharge (Water Quality & Investigations, 2020b) and land use (i.e., area of sugarcane and mixed horticulture) (State of Queensland, 2020) between 2016/17 and 2021/22. Concentration data sourced from (Water Quality & Investigations, 2020b). * Tully Sugar Mill gauge 20042 ** Mackay gauge 33119*

Region	Catchment /Monitoring Site	Catch-ment area (km^2)	Mean annual Rainfall (mm)	Long-term mean annual discharge (GL)	Area pesticide-intensive agriculture above monitoring site (ha)	No. pesticide samples 2016 / 2022	Atrazine ($\mu g\ L^{-1}$)		Diuron ($\mu g\ L^{-1}$)		Imidacloprid ($\mu g\ L^{-1}$)	
							50^{th} %ile	95^{th} %ile	50^{th} %ile	95^{th} %ile	50^{th} %ile	95^{th} %ile
Wet Tropics	Tully River at Euramo	1,532	4,085*	3,100	15,342	516	0.03	0.34	0.07	0.46	0.05	0.22
Mackay Whit-sunday	Pioneer River at Dumbleton Weir	1,575	1,560**	780	27,949	398	0.15	1.92	0.2	1.8	0.06	0.54

The above relationship for diuron concentrations across all 12 focus waterways is presented in Figure 4. Similar relationships for other pesticides could explain the spatial distribution of individual pesticides in the GBR catchments.

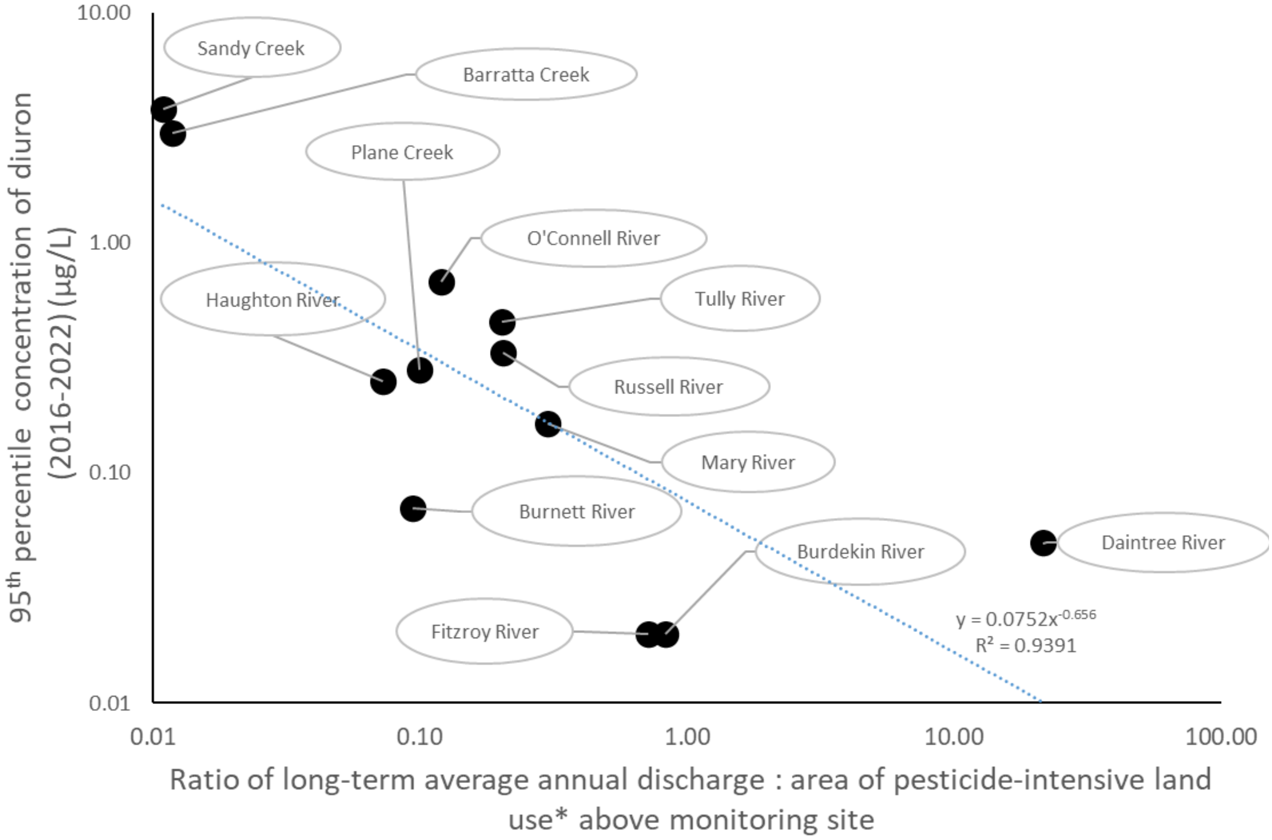


*Figure 4. Diuron concentration (95th percentile) as a function of the ratio of average annual discharge: area of pesticide-intensive agriculture above monitoring sites between 2016/17 and 2021/22. Data extracted from Water Quality and Investigations (2020) * Pesticide Intensive agriculture includes the areas under sugarcane and horticultural crops (State of Queensland, 2020).*

Temporal variation in pesticides can be both intra-annual and inter-annual as illustrated in Figure 5 for diuron concentrations over a six-year period at Sandy Creek. Intra-annual variation is caused by variation in rainfall. Pesticides generally occur in waterways when runoff from adjacent agriculture occurs, and the majority of runoff occurs during the wet season. Pesticide concentrations seen in waterways are generally higher at the beginning of the wet season and reduce substantially as the wet season progresses; i.e., there is exhaustion and/or degradation of available pesticides during the wet season (Figure 5) (Davis et al., 2008; Smith et al., 2011). The exception among the 12 focus waterways is Barratta Creek, where high concentrations of multiple pesticides are often present before the wet season commences (Water Quality & Investigations, 2020b). This occurs because the sugarcane in the Lower Burdekin is predominantly irrigated and runoff occurs outside the wet season (Davis et al., 2013; O'Brien et al., 2016). Another exception to the general intra-annual variation occurs when pesticides are re-applied through the wet season. This leads to one or more rapid increases in pesticide concentrations followed by the typical exhaustion pattern – the resulting pesticide trend line is a downward curve with one or more spikes like teeth on a saw (as in 2017/18 and 2020/21 in Figure 5).

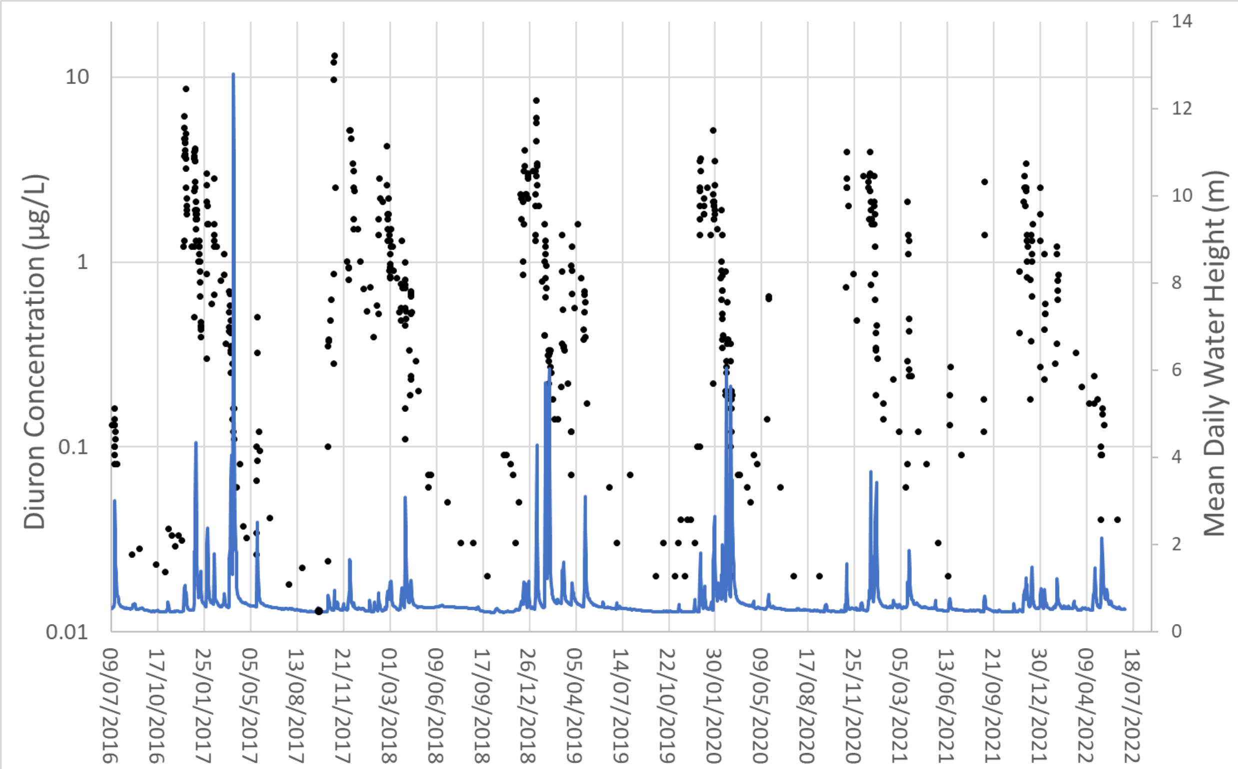


Figure 5. Intra- and inter-annual temporal variation of diuron concentrations at Sandy Creek in the Mackay Whitsunday region between 1 July 2016 and 30 June 2022 and the creeks height (blue line) which acts as a surrogate for river discharge. Data extracted from Water Quality & Investigations (2020).

Based on the six years of monitoring for the focus waterways and pesticides, it was difficult to determine any clear annual trends over time. Focusing on the most frequently quantified pesticides across the 12 focus sites, atrazine, hexazinone and diuron (Table 12), higher median wet season concentrations were detected in 2016/17 for some waterways (e.g., Tully River, Barratta Creek, Sandy Creek, O'Connell River) (Figure 3, **Table F5**). However, for other waterways, there was no change in median wet season concentration over time for atrazine, hexazinone and diuron (e.g., Daintree and Burdekin rivers).

There were large differences in the ratio of median wet/dry season concentrations for the focus pesticides, with the ratio ranging from 0.04 to 40 (**Table F7**). Taking the example of Sandy Creek, the ratio of median wet/dry season concentration ranged from 0.97 to 37 for atrazine, 2.5 to 40 for diuron, 0.3 to 30 for metolachlor and 1.3 to 27 for imazapic. The highest median wet/dry season concentration for atrazine, diuron, metolachlor, imidacloprid and hexazinone at Sandy Creek occurred in 2020/21, while the lowest ratio for the same pesticides was in 2021/22. Overall, 76% of samples had a median wet/dry season concentration ratio ≥1, with all samples from Daintree, Russell and O'Connell rivers ≥1.

Detailed analysis of temporal variation of pesticides in GBR waterways has been limited to a single study (Warne et al., 2022b) which examined changes in the aqueous concentrations of imidacloprid in 14 GBR waterways between 2009/10 to 2015/16. Imidacloprid concentrations significantly increased in 6 of the 14 waterways studied (i.e., the Herbert, Pioneer, Russell and Tully rivers and Barratta and Sandy creeks), and the increase was marginally significant ($p = 0.072$) in the O'Connell River. In these waterways the imidacloprid concentrations either (a) increased continuously (e.g., Herbert River and Sandy Creek) or b) increased and then decreased (i.e., Barratta Creek). Potential causes of imidacloprid concentration trends were examined (Warne et al., 2022b). The only factor that could explain the trends was increased use of imidacloprid and in the case of Barratta Creek, education activities to reduce imidacloprid use. Now that pesticide concentration data are available at many sites for approximately 10 years, trend analysis should be a high research priority to determine if the concentrations are increasing, decreasing or staying the same. This would allow a direct assessment of the success or otherwise of the Reef 2050 WQIP, as opposed to using modelling to determine progress. Currently, the temporal variation of imidacloprid and five PSII herbicides (ametryn, atrazine, diuron, hexazinone and tebuthiuron) over a 13-year period from 2009/10 to 2021/22 is being examined (Warne, M. *in prep.*). Visual inspection of imidacloprid data (Water Quality & Investigations, 2020b; 2023a) suggest there have been no changes between 2015/16 and 2021/22.

Main findings:

- Pesticides are ubiquitous at end-of-catchment monitoring sites of GBR waterways.
- 74 different pesticides and their transformation products were identified over the monitoring periods 2016/17 to 2021/22.
- The pesticides most frequently quantified in the 12 focus waterways between 2016/17 and 2021/22 were atrazine, hexazinone, diuron, metolachlor and imazapic in decreasing order.
- Consistent with Spilsbury et al. (2020) and Warne et al. (2020b), the vast majority of pesticides occurred as mixtures.
- Sites in the Mackay Whitsunday region along with Barratta Creek in the Burdekin region recorded consistently higher median and maximum concentrations of pesticides, while the Fitzroy River, Mary River, Burnett River and Daintree River had the lowest maximum annual concentrations across all years. The highest concentrations of pesticides were detected in catchments with intense cropping and lower discharge (related to rainfall).
- Pesticide concentrations were typically higher in wet seasons compared to dry seasons by a factor of three across all pesticides, sites and years.
- There was a strong intra-annual trend with rapid increases in pesticide concentration at the start of the wet season followed by a gradual decrease.
- Significant increases in imidacloprid concentrations between 2009/10 and 2015/16 have occurred in some waterways.
- Insufficient research has been conducted on the inter-annual temporal trends in pesticide concentrations in GBR waterways. This should be an area of high research priority.

Spatial and temporal distribution of pesticides across GBR wetlands

There have only been two unpublished and two published studies on pesticides and their degradation products in freshwater lacustrine and palustrine wetlands in the GBR. The unpublished studies were discussed in Devlin et al. (2015). The first of the unpublished reports examined two palustrine wetlands and detected 19 pesticides, while the second study detected a maximum of two pesticides in sediments from seven of eleven monitored wetlands. Allan et al. (2017) measured pesticides in seven sugarcane drains and wetlands near Mon Repos, a turtle breeding area located near Bundaberg, in the Burnett Mary region and detected 20 herbicides and 4 herbicide degradates and 2 insecticides. Concentrations ranged from below the limit of detection (i.e., 0.1 µg L^{-1}) to 856 µg L^{-1} for 2,4-D, 322 µg L^{-1} for imazapic, 131 µg L^{-1} for metolachlor. The concentrations of insecticides were considerably smaller (i.e., a maximum of 7.29 µg L^{-1} fenamiphos and 2.46 µg L^{-1} imidacloprid). Vandergragt et al. (2020) examined 22 palustrine wetlands located from the Wet Tropics to the Burnett Mary regions over two seasons and found pesticides and degradation products were "ubiquitous", being detected in every wetland. A total of 59 pesticides and degradates were detected across all wetlands (**Table P1**). The suite of pesticides analysed in Vandergragt et al. (2020) was similar but not identical to that in the GBRCLMP. Seven of the 12 focus pesticides were present in at least 68% of the wetlands over the two years (atrazine and metolachlor were present in 100% of samples, hexazinone 91%, diuron 88%, imidacloprid 82%, ametryn 71% and metsulfuron-methyl 68%). All wetlands contained mixtures of pesticides – the number present in each wetland ranged from 7 to 19 with a mean of 15 pesticides per wetland. Vandergragt et al. (2020) stated that coastal wetlands contained more pesticides at higher concentrations than in waterways monitored by the GBRCLMP. The spatial variation across the 22 sites was moderate with the total number of pesticides per wetland over the two years ranging from 19 to 30. There was little spatial variation in the number of pesticides and degradates measured at the regional scale – with the average number in each region ranging from 22 in the Wet Tropics and Mackay Whitsunday regions to 27 in the Burdekin region (Vandergragt et al., 2020). The wetlands in Vandergragt et al. (2020) were selected so that moderate to high-intensity land use was dominant within a radius of 1 km of each wetland.

Therefore, the selected wetlands may overestimate the exposure to pesticides of wetlands surrounded by less intensive land uses.

Of the 22 wetlands sampled only 12 were analysed in both years and for these there was little overall variation in the number of pesticides and degradation measured with a mean of 18 and 21 chemicals measured in the first and second years, respectively (Vandergragt et al., 2020). In the second year there were on average four extra herbicides and one fungicide measured but a decrease of one insecticide. They also reported that the types of contaminants detected and their relative abundance varied between regions and sites in the two years (Vandergragt et al., 2020). With only two years data for 12 common sites, the certainty of these above estimates of temporal variability is low. Further, work is required to assess the spatial and temporal variation of pesticides in GBR palustrine wetlands.

Main findings:

- Pesticides are ubiquitous in the 22 palustrine wetlands studied.
- 59 different pesticides and their transformation products were identified between 2016/17 and 2017/18.
- Pesticides always occurred as mixtures that contained an average of 15 pesticides.
- The pesticides detected and their frequency was similar to that for GBR rivers and creeks.
- More pesticides at higher concentrations occurred in wetlands than GBR rivers and creeks.
- There was little temporal variation in the total number of pesticides detected in the two years, but the pesticides present did vary.
- Further research into the spatial and temporal variation in pesticides in wetlands is required.

Spatial and temporal distribution of pesticides across GBR ecosystems: marine

Pesticides have been identified in water, sediments, and biota of marine and estuarine ecosystems. The spatial and temporal distribution of pesticides in these ecosystems are best assessed from water samples as most contemporary pesticides are relatively water soluble and less likely to be associated with sediments and biota than legacy organochlorine pesticides such as DDT or dieldrin (Davis et al., 2012; Negri et al., 2009). The most extensive long-term data on pesticide distribution in the GBR is associated with the MMP which has applied standardised and consistent monitoring and analysis methodologies since 2005 (e.g., Bartkow et al., 2008; Taucare et al., 2022; Thai et al., 2020). In assessing the spatial and temporal distribution of pesticides in marine ecosystems of the GBR, this review considered:

- Pesticides in biota which provides evidence of exposure.
- Pesticides in marine and estuarine sediments.
- Pesticides in flood plume events assessed by grab samples. Although not spatially or temporally consistent, these *snapshot* surveys provide important information on identity, instantaneous concentrations and fate of pesticides during flood plumes.
- The spatial and temporal distribution of pesticides from 11 fixed monitoring sites (long-term) over the three most recent MMP pesticide surveys (Gallen et al., 2019b; Grant et al., 2018; Thai et al., 2020). The review focused on results from passive samplers which sorb and accumulate pesticides from the water over (typically) one-month long deployment periods by passive diffusion, allowing time-averaged exposures to be calculated (Thai et al., 2020).
- Studies which combined end-of-catchment pesticide concentrations (measured or calculated from loads) with freshwater dispersal estimates (from satellite imagery or hydrodynamic models) to predict the distribution of pesticides in the GBR (Devlin et al., 2012; Lewis et al., 2013; Skerratt et al., 2023).

Pesticides in GBR biota and sediments

Over 40 studies have reported agricultural pesticides in marine biota, sediments and water of the GBR since 1990. Several studies prior to 1990 reported organochlorine pesticides such as DDT and dieldrin in crown-of-thorns starfish, hard corals, molluscs, fish and dugongs of the GBR (Haynes & Johnson, 2000). These now-banned insecticides are highly persistent and readily accumulate in biota, with low concentrations identified across most GBR regions in estuarine and marine fish (Von Westernhagen &

Klumpp, 1995), crabs (Mortimer, 2000; Negri et al., 2009) and dolphins (Cagnazzi et al., 2013). Concentrations of these legacy pesticides should continue to decrease and were not detected in seagrass (Haynes et al., 2000a) or more recent surveys which screened turtles across several GBR regions (Heffernan et al., 2017; Vijayasarathy et al., 2019). While a carbamate insecticide metabolite was identified in ~10% of turtles from Cleveland Bay (Burdekin Region) (Heffernan et al., 2017), few other contemporary pesticides have been identified in GBR organisms, since most are less persistent and less likely to bioaccumulate than organochlorines (Negri et al., 2009). However, studies have identified low concentrations of the PSII herbicide diuron in seagrass from Townsville to Cairns (Haynes et al., 2000a) and mangrove leaves from the Pioneer River estuary (Mackay Whitsunday region) (Duke, 2005).

Organochlorines such as DDT and dieldrin have been identified at low concentrations in marine sediments south of the Daintree River (Haynes et al., 2000a); however, there have been no reported identifications in marine sediments since 2000 (Davis et al., 2012; Negri et al., 2009). Although up to 30% of contemporary pesticides can be particulate bound when transported to the GBR (Davis et al., 2012), few studies have reported pesticides such as PSII herbicides in marine sediments of the GBR. Low concentrations of diuron and atrazine have been identified in marine sediment samples from the Mackay Whitsunday to the Wet Tropics (Davis et al., 2012; Duke, 2005; Haynes et al., 2000a); however, there are too few samples to reveal meaningful temporal or spatial distributions. Other reports include elevated concentrations of mercury in sediment from marine sediments near the Herbert River (Burdekin), Missionary and Upstart bays (Walker & Brunskill, 1996) and sediment and water samples from the Tully River (Wet Tropics), which may be linked to mercuric fungicide use (Cavanagh et al., 1999; Turull et al., 2018). Low concentrations of the herbicide metolachlor have also been reported in the sediments of turtle habitats of the Burdekin and Cape York regions (Gallen et al., 2019a).

Main findings:

- Some of the more persistent legacy pesticides can still be detected across a range of GBR taxa.
- There are too few surveys of biota and sediments to meaningfully contribute to an understanding of the GBR-wide spatial and temporal distribution of pesticides.
- However, identification of PSII herbicides in seagrass and mangroves confirms the exposure of these keystone species.

Discharge of pesticides during flood events into the GBR (grab samples)

Discharge of pesticides into the GBR during flood events has been assessed by the analysis of grab samples since the mid-2000s and several pre-2016 publications revealed important findings and are included here for context. Grab sampling has focused on contemporary pesticides since many legacy pesticides partition strongly into sediments and biota. The sampling site locations and timings have not been consistent among years; therefore, long-term spatial and temporal pesticide trends are difficult to assess. However, grab sampling of flood plumes has identified and quantified pesticides present and examined their fate as summarised below:

- Over 26 pesticides have been identified in marine grab samples (**Table M7**). These have been consistently dominated in terms of frequency and concentration by PSII herbicides ametryn, atrazine, diuron, hexazinone, tebuthiuron, PSII transformation products desethyl atrazine (DEA) desisopropyl atrazine (DIA), the dinitroaniline herbicide metolachlor and the insecticide imidacloprid (but all differ among sites) (Bartkow et al., 2008; Bentley et al., 2012; Davis et al., 2008; 2012; Gallen et al., 2013; 2014; 2016; 2019b; Grant et al., 2017; 2018; Kennedy et al., 2010a; 2010b; 2011; 2012a; Lewis et al., 2009; Shaw et al., 2012; Thai et al., 2020).
- The concentrations measured in grab samples from flood plumes represent short-term acute exposures and can be one to two orders of magnitude higher than concentrations reported from passive samplers which are deployed for longer periods of approximately one month over the wet season (Lewis et al., 2012; Thai et al., 2020). Concentrations of pesticides in flood plume grab samples have been reported up to 1.7 µg L^{-1} diuron and 0.73 µg L^{-1} atrazine at inshore sites close to the Pioneer River (Lewis et al., 2009).

- Pesticide concentrations are highest near the freshwater discharge points and decrease in concentration with distance inversely with salinity (Davis et al., 2008; Kennedy et al., 2012b; Lewis et al., 2009; Shaw et al., 2012; Thai et al., 2020). Some sampling indicates highest concentrations of pesticides at intermediate salinities before reducing further offshore; an observation consistent with the timing of sampling capturing high concentrations from "first flush" plume events, where pesticide concentrations are greatest at the start during the first rainfall of the wet season (Davis et al., 2008; Lewis et al., 2009).
- The inverse relationship of pesticides with salinity in flood plumes indicates conservative mixing, and the accord between pesticides identified in flood plumes and land use practices in adjacent catchments confirm the source of most pesticides in the GBR is from agricultural application in adjacent catchments (Kennedy et al., 2012a; 2012b; Lewis et al., 2009). Importantly, the relationship between salinity and pesticide concentration in flood plumes enables spatial and temporal models (from simple interpolation to satellite and hydrodynamic) to predict pesticide concentrations in the GBR from end-of-catchment concentrations and/or loads (Devlin et al., 2012; Kennedy et al., 2012b; Lewis et al., 2013; Petus et al., 2016; Skerratt et al., 2023; Waterhouse et al., 2017).
- Pesticides can be identified at low concentrations in plumes (Lewis et al., 2009) up to 240 km from its likely source in the Fitzroy River (Kennedy et al., 2012b). The very long persistence of pesticides in seawater (diuron lowest half-life $t_{½}$ =139 d; atrazine $t_{½}$ =107 d; hexazinone $t_{½}$ =201; tebuthiuron $t_{½}$ =944; metolachlor $t_{½}$ =32; 2,4-D $t_{½}$ =56 d) (Mercurio et al., 2015, 2016)) may help explain their widespread identification in the GBR.
- Grab samples have been taken during flood events as part of the MMP. Since 2016/17, 143 flood event grab samples have been collected at marine and estuarine sites near the Mulgrave-Russell River (including High Island), Tully River (including Bedarra Island and Dunk Island North) as well as the Burdekin or Barratta Creek (Gallen et al., 2019b; Grant et al., 2018; Thai et al., 2020). The results from these most recent MMP flood plume surveys are consistent with other studies and previous MMP surveys (**Table M7**). For example, the most frequently identified pesticides across all samples and sites include atrazine (94%) followed by diuron (89%) and hexazinone (84%). 95% of all grab samples that contained pesticides were found to be mixtures (**Table M8**). The highest concentration of pesticides during this period includes MCPA 0.61 µg L^{-1}, followed by atrazine 0.42 µg L^{-1}, 2,4-D 0.31 µg $L^{-1,}$ and diuron 0.30 µg L^{-1} all identified at the mouth of the Russell-Mulgrave River in the Wet Tropics region during the monitoring period of 2016/17. Higher concentrations were generally found near to the river mouth than offshore.

Main findings:

- Flood event sampling provides a snapshot of pesticide concentrations during flood plume events (relatively short spatial and temporal scales).
- Studies since mid-2000's have consistently demonstrated the pesticides identified in the GBR reflect those applied in adjacent catchments and that they undergo conservative mixing as they dilute in the marine environment.
- The most frequently identified pesticides across all samples and sites recorded in MMP surveys since 2016/17 include atrazine followed by diuron and hexazinone.
- The high mobility and very long persistence of herbicides such atrazine, diuron, hexazinone and metolachlor in seawater help explain their detection in marine waters of the GBR.
- The concentration of pesticides in marine grab samples indicate short-term exposure concentrations are often higher than those reported from passive samplers where concentrations are integrated over month-long deployments.

Spatial and temporal distribution of focus pesticides: marine ecosystems of the GBR

The fixed-location MMP passive sampler deployments provide an important source of data to assess trends in the spatial and temporal distribution of pesticides in marine ecosystems of the GBR. The concentrations reported from passive sampler data represents exposure periods equivalent to their deployment durations, typically one month in the wet season and three months in the dry season (Shaw et al., 2005; 2010; Thai et al., 2020). Passive sampler concentrations are usually lower than those reported for flood plume grab samples which might capture the peak concentration in a flood. The long deployment periods of passive samplers are advantageous for assessing long-term trends (Taucare et al., 2022), however the small number of samples limits statistical analysis. The main limitation of the MMP program is the limited spatial coverage of sites (11 sites across 4 NRM regions) which were not always optimally positioned to capture the main body of a flood plume (Skerratt et al., 2023). Two types of passive samplers were deployed and reported – polar (Empore Disks) and non-polar (semi-permeable membrane device), to detect pesticides with different properties.

The three most recent MMP surveys (2016/17 – 2018/19) of 11 fixed-location passive sampler sites (Table 14) monitored 44 pesticides and their transformation products; however, only 29 pesticides were quantitatively reported (Gallen et al., 2019b; Grant et al., 2018; Thai et al., 2020). During this period 22 pesticides and transformation products were identified in 98% of polar passive samplers (Table 15), with the PSII herbicides diuron, atrazine, hexazinone and tebuthiuron (most to least frequent), along with the growth inhibiting herbicide metolachlor and the insecticide imidacloprid being most frequently identified. Multiple pesticides (mixtures) were reported in 94% of polar passive samplers[11]. The reported types of pesticides and their identification frequency were consistent with previous MMP surveys and flood plume monitoring (Bartkow et al., 2008; Bentley et al., 2012; Gallen et al., 2013; 2014; 2016; Grant et al., 2017; Kennedy et al., 2010a; 2010b; 2011).

Table 14. The eleven fixed-location marine sites of the MMP across four Natural Resource Management regions and their characteristics. Most were monitored over three years.

NRM region	Basin	Major River/Creek	Fixed site name	Sampled since	Approx. distance from river mouth (km)
Wet Tropics	Mossman	Mossman River	Low Isles	Aug 2005	18
	Mulgrave - Russell	Mulgrave & Russell rivers	High Island	May 2015	8
			Normanby Island	Jul 2005	11
	Tully	Tully River	Dunk Island	Sep 2008	13
	Herbert	Herbert River	Lucinda	Jul 2014	12
Burdekin	Burdekin	Barratta Creek	Barratta Creek	Mar 2014	1.5
Mackay Whitsunday	O'Connell	O'Connell River	Repulse Bay	Sep 2014	3.3
	Pioneer	Pioneer River	Flat Top Island	Sep 2014	5
	Plane	Sandy Creek	Sandy Creek	Sep 2014	8.6
		Plane Creek	Sarina Inlet	May 2009	2.8
Fitzroy	Fitzroy	Fitzroy River	North Keppel Island	Aug 2005	50

[11] *As passive samplers are deployed typically for four weeks they report a single average concentration for each pesticide over the deployment period. Thus mixtures means that these pesticides did occur in the sampled waterbody over the period of deployment. It does not mean that at any given point in time the pesticides co-occurred.*

Table 15. Key findings on pesticide frequency of detection and mixtures for all pesticides and sites from the 2016/17, 2017/18 and 2018/19 MMP seasons: (Gallen et al., 2019b; Grant et al., 2018; Thai et al., 2020). Frequency of detection based on analytical concentrations above limit of reporting.

Pesticide data	Key findings: All sites, pesticides and years	Data location
Number of samples taken	325 passive samplers of two types were deployed and 243 samplers of two types (including 200 polar samplers) were retrieved from 11 locations representing 4 NRM regions over 3 monitoring years 2016/17, 2017/18 and 2018/19.	**Table M2** **Table M6**
Frequency of pesticides detection	Pesticides and transformation (breakdown) products were detected in 196 polar passive samples (98%) across all sites and years.	**Table M2**
Total number of pesticides	29 pesticides and transformation products were quantitatively reported in marine ecosystems, with 22 detected above the limit of reporting at least once.	**Table M1**
Most frequently detected pesticides	Photosystem II herbicides (% frequency) identified in polar passive samplers were: diuron 96%, atrazine 88%, hexazinone 86% and tebuthiuron 57%.	**Table M1**
Most frequently detected non-PSII pesticides	• Non-PSII herbicide metolachlor was in 67% of samples. • Insecticide imidacloprid was in 55% of samples. • No fungicide were identified above the limit of reporting.	**Table M1**
Mixtures	• Pesticides rarely occur in isolation: 94% of polar passive samples (187 of 200 samples) contained pesticide mixtures.	**Table M2**

Note: Appendices Tables available to download as a zip file from the 2022 SCS website.

The following section summarises spatial and temporal trends in pesticide distribution in marine passive sampler deployments from 2016/17 to 2018/19 (Table 16). It is not practical to summarise the spatial and temporal distribution of all 22 pesticides quantitatively reported across all sites in the current review, so the focus has been on 12 pesticides across these three most recent monitoring years. Nine of the 12 pesticides are ametryn, atrazine, diuron, hexazinone, imazapic, imidacloprid, metolachlor, MCPA, metsulfuron-methyl, as combined they typically account for at least 99% of the Total Pesticide Mixture toxicity in GBR waterways (Spilsbury et al., 2020; Warne et al., 2020a); see risk section below. Tebuthiuron, chlorpyrifos and 2,4-D were also included due to their high frequency of detection in the GBR. The main findings and data for the focus pesticides and sites are summarised in a series of figures and tables here (Table 15, Table 16) and in the attached Appendices.

Table 16. Spatial and temporal data summary findings per site and year from the 2016/17, 2017/2018, 2018/2019 MMP (Gallen et al., 2019b; Grant et al., 2018; Thai et al., 2020). Frequency of detection based on analytical concentrations above limit of reporting. Summary graphs here and tables in the Appendices cover the 12 focus pesticides and 11 sites, as well as summary data for all quantified pesticides over the same period. Wet season was 182 days from the start of summer rainfall, while the dry season represents the 182 days prior to the start of the wet season.

Pesticide data	Key findings: Spatial and temporal trends 11 sites and 12 focus pesticides	Data
Frequency of detection in polar passive samplers	• The five most frequently detected pesticides across all years and sites were diuron (96%), atrazine (88%), hexazinone (86%), metolachlor (67%) and tebuthiuron (57%). • Flat Top Island (70%) followed by Sandy Creek (66%), Repulse Bay (60%) and Sarina Inlet (56%), all in the Mackay Whitsunday region had the most frequent detections of all 12 pesticides across all years. • The 12 pesticides were detected more frequently in 2017/18 (54%) and 2018/19 (52%) compared to 2016/17 (38%).	**Table M1** **Table M3**
Median wet season concentrations	• The median wet season concentration of each pesticide varied between years for the different sites. • Flat Top Island had the highest median wet season concentrations across all years (diuron 229 ng L^{-1}, atrazine 69 ng L^{-1} and hexazinone 37 ng L^{-1} in 2017/18), followed by Repulse Bay.	Figure 6 **Table M4**
Median dry season concentrations	• Sandy Creek had the highest median dry season concentrations across all years: diuron 30 ng L^{-1}, atrazine 15 ng L^{-1} and hexazinone 10 ng L^{-1} (in 2016/17). • Flat Top Island has the next highest median dry season concentrations of atrazine, diuron, hexazinone and imidacloprid.	**Table M4**
Ratio of median wet/dry season concentrations	• Pesticide concentrations were higher in the wet season 4.6 times more often than they were higher in the dry season (all pesticides, sites, years). • There were wide ranges in median wet/dry pesticide concentration ratios. For example, at Flat Top Island ratios for atrazine ranged from 1.4 to 26.5, diuron from 0.9 to 60.3 and imidacloprid from 0.2 to 142. • The wet/dry season ratio (for the 12 focus pesticides) was >1 at all sites and sampling occasions apart from Low Isles in 2018/19. • Flat Top Island had the most wet/dry ratios >1. In 2017/18, ratios were >1 for all focus pesticides (average ratio was 30).	**Table M4**
Maximum annual concentrations	• Flat Top Island and Repulse Bay in the Mackay Whitsunday region and Barratta Creek in the Burdekin had the highest concentrations of all twelve focus pesticides across all years. • Among these sites Flat Top Island had the highest concentration of nine pesticides (2,4-D, atrazine, chlorpyrifos, diuron, hexazinone, imazapic, imidacloprid, MCPA, metsulfuron-methyl), while Barratta Creek had the highest concentrations of ametryn and metolachlor and the highest concentrations of tebuthiuron occurred at Sarina Inlet. • Diuron, atrazine, hexazinone, imidacloprid, and metolachlor recorded the maximum concentrations across all years (highest to lowest concentration). Flat Top Island had the highest concentrations of diuron (778 ng L^{-1}) and atrazine (405 ng L^{-1}) in 2017/18, and hexazinone (134 ng L^{-1}) and imidacloprid (53 ng L^{-1}) in 2016/17. The maximum concentration of metolachlor (28 ng L^{-1}) was recorded at Barratta Creek in 2017/18.	**Table M5**
Minimum annual concentrations	• The lowest frequency of pesticide detections consistently occurred at Low Isles (34%) and North Keppel Island (29%). • The minimum annual concentrations of all pesticides were below the limit of reporting at these sites apart from diuron at North Keppel Island (minimum 0.77 ng L^{-1} in 2018/19) and three pesticides at Low Isles (minimum atrazine 0.2 ng L^{-1}, diuron 0.53, hexazinone 0.013 ng L^{-1} across all years).	**Table M5**

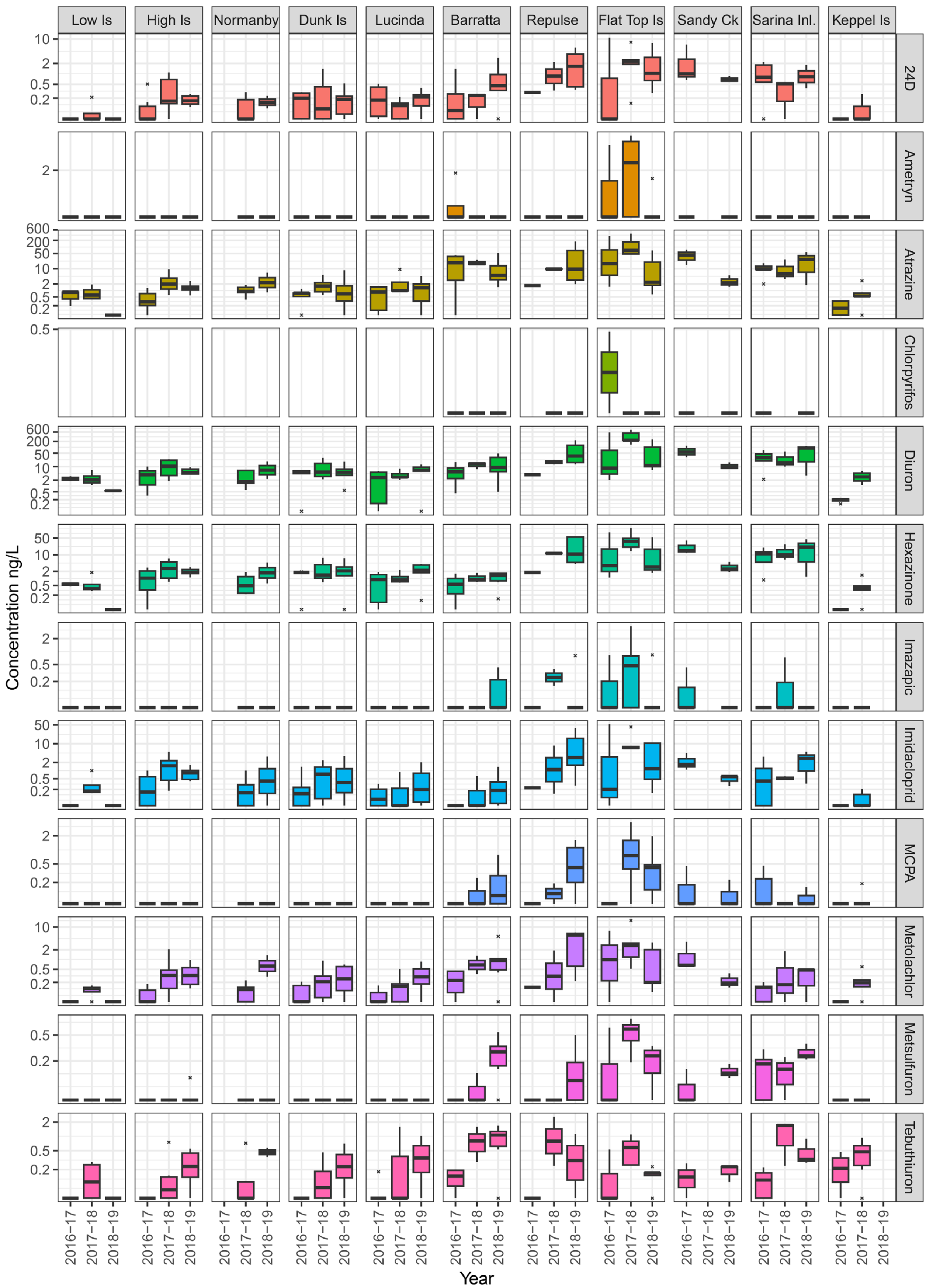


Figure 6. Median wet season pesticide concentrations for the 12 focus pesticides across 11 marine fixed passive sampler sites (Table 14). See ***Table M3*** *(Appendices) for the detection frequency of each pesticide at each focus site.*

Spatial distribution - marine

The frequency of detection of pesticides across the 11 marine sites was very high over the most recent three years, with diuron being detected at all sites year round (in 96% of all polar passive samplers), and high frequencies of detection of atrazine, hexazinone and metolachlor across all sites and years (Table 16). Sites in the Mackay Whitsunday region generally had the highest detection frequency and concentrations of pesticides year-round, followed by Barratta Creek in the Burdekin, while North Keppel and other Wet tropics sites (Low Isles) and Great Keppel Island in the Fitzroy region had consistently lower detection frequencies and concentrations than other sites (**Table M3, Table M5**). Summaries for each NRM region (excluding Cape York NRM) are provided below.

Wet Tropics region: The five sites in the Wet Tropics had intermediate pesticide concentrations over the last three MMP sampling years (Figure 6). The PSII herbicides diuron, atrazine, and hexazinone were identified more often and at higher concentrations than other pesticides in this region (**Table M3, Table M5**), and concentrations were seasonally higher during the wet months (**Table M4)**. There were few differences in concentrations of atrazine, diuron and hexazinone among the five sampling sites; however, Low Isles generally had lower concentrations of some other focus pesticides, including imidacloprid and metolachlor (Figure 6).

Burdekin region: This region was represented by a single fixed sampling site off the small but intensely cropped Barratta Creek. The Barratta Creek site had higher median wet season concentrations of atrazine and diuron than sites outside the Mackay Whitsunday region (Figure 6). It also recorded the highest concentrations of the non-PSII herbicide metolachlor and the herbicide 2,4-D of all 11 sites (Table 16). During the last three survey years, wet season concentrations were generally higher than dry season concentrations for most pesticides (**Table M4**). It should be noted that the pesticide concentrations at the Barratta Creek MMP site are not considered representative of the wider Burdekin region, with concentrations generally lower at previously monitored sites including Orpheus Island, Magnetic Island and Cape Cleveland that capture pesticide dispersal from the Haughton and Burdekin Rivers (Gallen et al., 2013; 2016).

Mackay Whitsunday region: The highest detection frequency of many of the 12 focus pesticides was at the Mackay Whitsunday sites, where Flat Top Island recorded all 12 pesticides on 70% of sampling occasions across the three years (Table 16). Pesticide detection frequency was also higher at Sandy Creek, Repulse Bay and Sarina Inlet, than at sites in other NRM regions. A similar pattern emerged for median wet season pesticide concentrations, which were highest for atrazine, diuron, and hexazinone at Flat Top Island, followed by Repulse Bay, while Sandy Creek and Flat Top Island also recorded the highest dry season concentrations of several pesticides, including diuron, atrazine, hexazinone, imidacloprid, and metolachlor. The maximum pesticide concentrations of diuron, atrazine, hexazinone, and imidacloprid were also recorded at Flat Top Island (Table 16).

Fitzroy region: The North Keppel sampling site of the Fitzroy region is the most distant (50 km) of all MMP sites from the end-of-catchment. As such, the frequency of detection and concentrations of pesticides are affected by the high opportunity for dilution as well as end-of-catchment loads and are generally lower at this site than other fixed sites in the MMP (Table 16). For example, atrazine and diuron were identified at lower concentrations at the North Keppel site than any other sites and only tebuthiuron was identified at concentrations similar to other fixed sites in the MMP.

The overall spatial distribution of pesticides among the 11 fixed marine sampling sites reflects the end-of-catchment concentrations during the same monitoring years (Figure 3, Figure 6). Furthermore, the frequency of detection and spatial distribution of pesticide concentrations at fixed monitoring sites are consistent with previous MMP surveys back to 2005 (Bartkow et al., 2008; Bentley et al., 2012; Gallen et al., 2013; 2014; 2016; Grant et al., 2017; 2018; Kennedy et al., 2010a; 2010b; 2011; Thai et al., 2020).

Studies which have modelled concentrations of pesticides in marine ecosystems of the GBR based on interpolation of flood plume concentrations (Lewis et al., 2012), coupling end-of-catchment concentrations with flood plume extent from satellite data (Devlin et al., 2012; Lewis et al., 2013; Waterhouse et al., 2012) or hydrodynamic models (Skerratt et al., 2023), indicate that while pesticide loads may be greater in the high rainfall Wet Tropics, concentrations are usually predicted to be higher in the marine waters of the Mackay Whitsunday region and smaller waterways with intense agriculture such as the Barratta Creek in the Burdekin. In a recent study, diuron loads were modelled at the end of each catchment using the GBR-Dynamic SedNet catchment model and dispersal (from the river mouths) was then simulated hourly using the 3D eReefs marine model (three wet seasons 2016 to 2018) (Skerratt et al., 2023). The model highlighted the consistent influence of coastal currents driving river plumes northward and how tides as well as currents affect flood plume dynamics and therefore the dispersal of diuron (including accumulation of diuron at some protected sites). Generally, diuron concentrations were greatest near river mouths and within “defined borders” of the coastal plumes and did not extend far into the GBR, with the exception of some sites (e.g., Dunk Island) where plume footprints can continue eastward due to protection from embayment and islands from the prevailing northerly current.

The concentrations of pesticides predicted from dispersal models are not often presented in a way that can be compared directly with the concentrations reported in the MMP. However, as part of a validation exercise (Skerratt et al., 2023) directly evaluated the simulated concentrations of diuron against those recorded by the MMP. In the Wet Tropics, diuron concentrations of up to 1 $\mu g\ L^{-1}$ were simulated at the Lucinda site off the Herbert River, while the fixed Dunk Island site off the Tully and Murray Rivers was expected to reach a maximum concentration of ~0.6 $\mu g\ L^{-1}$. In the Mackay Whitsunday region, the Repulse Island site was expected to experience concentrations of diuron >1 $\mu g\ L^{-1}$, with concentrations ~0.45 $\mu g\ L^{-1}$ predicted at the Sarina Inlet, Sandy Bay and Flat Top Island sites. Simulations (and field observations) demonstrated the highest concentrations of diuron to be within close proximity to the plumes and that over the three wet seasons 1,400 km^2 and 400 km^2 of GBR marine ecosystems “regularly” exceeded 0.075 and 0.43 $\mu g\ L^{-1}$ diuron, respectively (these figures are assessed relative to risk below). “Non-zero” concentrations were also predicted to extend along most of the inshore GBR coast.

Direct comparisons between the 2 hourly sampling of the diuron simulations and concentrations over passive sampler deployment periods (~1 month in the wet season) were made for all 11 fixed MMP sites (Skerratt et al., 2023). The diuron concentration simulations were generally well supported by the MMP passive sampler (and some grab sample) observations, with the best agreement at locations such as Low Isles, High Island and Dunk Island which were considered “well positioned to monitor diuron” based on their location with respect to plumes. Repulse Bay, Flat Top Island, Sandy Creek and Sarina Inlet sites on the other hand are near plume boundaries and may not always capture the highest diuron concentrations (plumes may bypass the fixed monitoring site) (Skerratt et al., 2023). Other limitations contributing to discrepancies between modelled and measured concentrations include uncertainties in total flow from some rivers (e.g., O’Connell) where gauging stations are poorly located, and limited year-round monitoring at some sites.

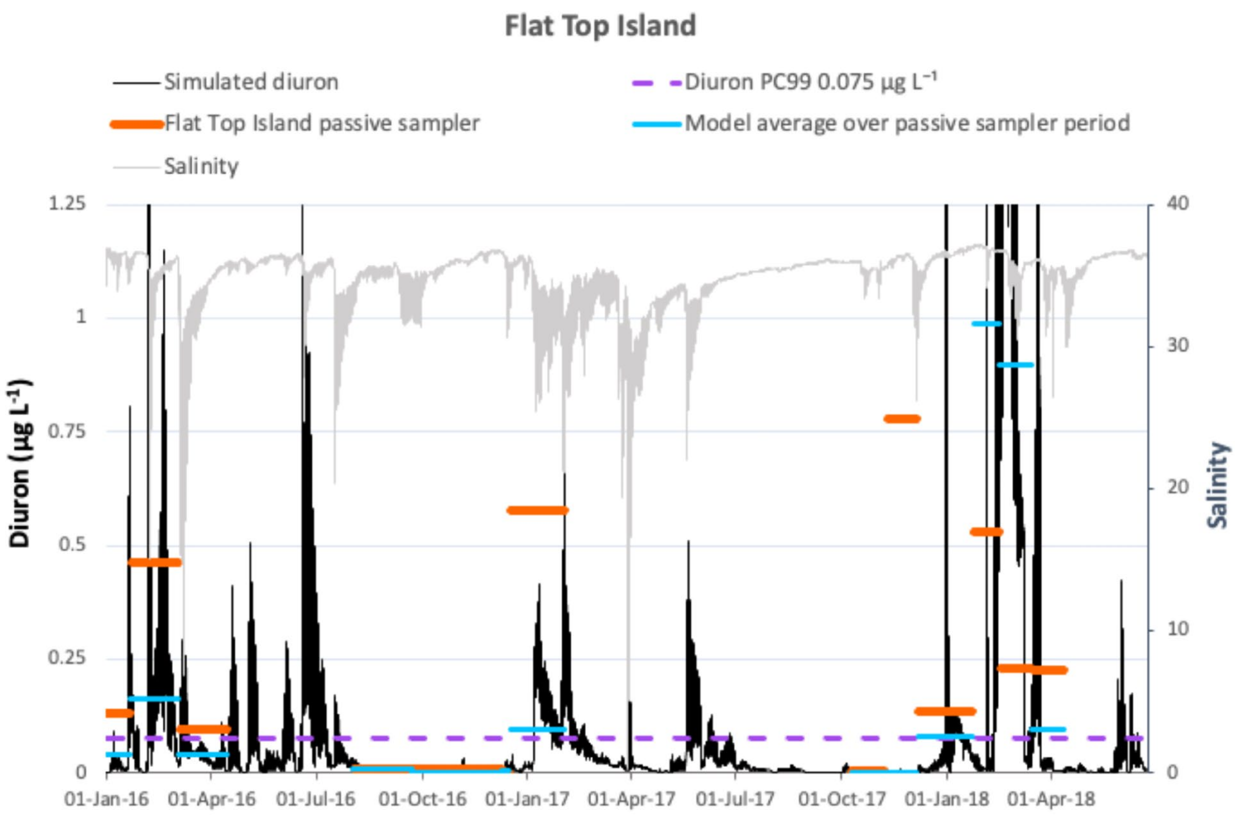


Figure 7. Simulated diuron concentration at Flat Top Island (black line), simulated diuron average equivalent to passive sampler deployment (light blue line), passive sampler observations (orange line) and salinity (grey line). PC99 for diuron (0.075 µg L^{-1} dotted purple line (Warne et al., 2020a)). Redrawn from (Skerratt et al., 2023).

Temporal distribution – marine

The distribution of pesticides varied greatly between days, years and sites. The MMP data from passive samplers at 11 sites provided the only long-term dataset to assess trends in temporal distribution. A recent study (Taucare et al., 2022) statistically analysed trends in concentration of five PSII herbicides (ametryn, atrazine, diuron, hexazinone, and tebuthiuron) over 14 years of the MMP program (Taucare et al., 2022). After accounting for season and flow, 16 of 43 combinations of pesticide and site showed statistically significant increases in PSII herbicide concentration (of between 10% and 216% annual change) over the monitoring period. Of these significant results, three sites (Low Isles, Sarina Inlet, and North Keppel) were notable as having statistically significant results with high enough statistical power to confidently conclude that there had been an increase in PSII herbicides over the previous 14 years. There were no statistically significant decreases in PSII herbicide concentrations at any of the sampling locations. Importantly, a power analysis in this study indicated that ~10 years of continuous passive sampler data were required to reliably detect long-term trends (Taucare et al., 2022). Only three years of MMP data were collected since the 2017 SCS report. During that time, the median wet season concentrations of the atrazine, diuron and hexazinone were relatively consistent, with annual differences more apparent in the other nine focus pesticides (Figure 6). As PSII herbicides are only a subset of the pesticides detected at the MMP sites, a further analysis of trends of all 12 focus pesticides at those sites with long monitoring histories (and therefore more likely to be characterised by greater statistical power) is warranted.

There were large differences in the ratios of median wet/dry season concentrations of the 12 focus pesticides over the three most recent monitoring years. For example, ranges at Flat Top Island included ratios: atrazine 1.4 to 26.5, diuron 0.9 to 60.3 and imidacloprid 0.2 to 142 (**Table M4**). However, pesticide concentrations were higher in the wet season 4.6 times more often than they were higher in the dry season (all pesticides, sites, years) (Table 16). When considering focus pesticides, the wet/dry season ratio was >1 at all sites and for all years, apart from Low Isles in 2018/19 when atrazine, diuron, imidacloprid, hexazinone and metolachlor were on average 2.7 times higher during dry season sampling.

Flat Top Island had the most frequent wet/dry ratios >1 in 2017/18, ratios were >1 for all focus pesticides (average ratio 30). Generally, higher pesticide concentrations in the 2016 to 2019 wet season passive samplers (Gallen et al., 2019b; Grant et al., 2018; Thai et al., 2020) is consistent with results from the previous MMP reports back to 2005/06 (e.g., Bartkow et al., 2008).

Grab samples during flood plume events have demonstrated conservative mixing of pesticides as they dissipate into the marine ecosystems of the GBR (Kennedy et al., 2012a; 2012b; Lewis et al., 2009). Earlier sections of this review also highlighted the complex relationship between the scale and timing of pesticide application, rainfall, waterway flows and pesticide concentrations at the end-of-catchment sites. All MMP reports compared end of system flow rates with pesticide concentrations in flood plume grab samples and passive samplers at the 11 fixed marine sites samplers (see Gallen et al., 2019b; Grant et al., 2018; Thai et al., 2020). Often, pesticide concentrations at the marine sampling sites matched expected pesticide concentration trends, with higher concentrations recorded at the start of or during high flow events. Higher pesticides and loads and concentrations have also been recorded during extreme flood events (Kennedy et al., 2012a). However, it is not possible for the frequency and spatial distribution of sampling during the MMP to fully describe spatial and temporal distribution of pesticides across the GBR. The diuron simulation exercise based on 3D hydrodynamic modelling (Skerratt et al., 2023) offers a unique insight into the temporal and spatial distribution of this herbicide over very short time periods (1-hourly steps) and longer periods (e.g., spanning three wet seasons). While higher concentrations of diuron often coincided with low salinity (freshwater plumes), simulated diuron concentrations did not always increase with flow due to the *first flush* effect where a high proportion of herbicide applied before the wet season would be discharged in early seasonal rainfall events. Sharp peaks in diuron were often observed (Skerratt et al., 2023), and varied from a baseline of less than 0.1 µg L^{-1} to greater than 1 µg L^{-1} within hours (Figure 7). This highlights, not only the dynamic exposure of nearshore marine organisms, but also the challenges in reliably capturing pesticide concentrations using traditional monitoring techniques.

Main findings:

- Fixed passive sampler data from the MMP provides the best spatial (11 to 15 sites) and temporal (14 years) pesticide data for the GBR.
- 22 different pesticides and their transformation products were identified in passive samplers over the last three monitoring periods 2016/17 to 2018/19. Pesticides were identified in 98% of all polar passive samplers and multiple pesticides were identified in 96% of samples.
- Diuron was the most frequently detected pesticide (in 96% of all polar passive samplers), while imidacloprid was the most frequently detected insecticide (55% of polar passive samplers).
- Similar to previous MMP monitoring reports, passive sampler sites at Flat Top Island and Repulse Bay in the Mackay Whitsunday region generally recorded the highest frequency and concentrations of pesticides year-round, followed by Barratta Creek in the Burdekin.
- A recent simulation exercise across the entire GBR indicated a similar distribution pattern for diuron to that reported for fixed sampling sites of the MMP. The diuron simulation, generated by coupling end of system concentrations with a 3D hydrodynamic model, indicated concentrations were greatest near river mouths and were transported northwards within defined boundaries of the coastal plumes, typically not extending far into the GBR.
- Passive sampler data showed a regular association between high pesticide concentrations and low salinity (flood plume events) and this was also supported by the diuron simulation exercise. Sharp peaks in diuron (<0.1 µg L^{-1} to > 1 µg L^{-1}) within hours highlighted the dynamic exposure of nearshore marine organisms, and the challenges in reliably capturing pesticide concentrations using traditional monitoring techniques.
- Consistent with previous surveys, greater concentrations of pesticides were recorded in passive samplers in the wet than the dry seasons (2016/17 to 2018/19).
- While there were insufficient observations to identify annual pesticide trends for all 12 focus pesticides over the last three monitoring periods, a recent analysis over the 14-year period of MMP passive sampler deployments identified significant increases in PSII herbicide concentrations at several locations, primarily in the Mackay Whitsunday and Burdekin regions.

Potential or observed ecological impacts of pesticides across GBR ecosystems

Studies that assess the potential or observed effects of pesticides on GBR ecosystems can be broadly categorised into two approaches. First, studies that have linked pesticides identified in the field to observed impacts on GBR species or sublethal effects in individual organisms sampled from the GBR. The second approach has been to experimentally identify pesticide concentrations that cause negative effects on GBR organisms (e.g., toxicity thresholds, which can be applied in risk assessments). Experimental studies have also contributed to guideline values, explored the toxicity of pesticide mixtures and other relevant interactions that can affect toxicity. This section summarises:

1) Reported effects of pesticides on GBR species in the field.
2) How GBR species respond to pesticides following experimental exposures.
3) Guideline values (GVs) for pesticides found in the GBR.
4) The sensitivity of GBR species in comparison to recent GVs.
5) The experimental assessment of toxicity of pesticide mixtures.
6) Experimental studies on the influence of other environmental factors on pesticide toxicity to GBR species.

1. Effects of pesticides on GBR taxa observed in the field

The effects of pesticide exposure events across GBR ecosystems are very difficult to observe and quantify *in situ* for a number of reasons: 1) precise exposure to pesticides are usually unknown; 2) the health status of the species/ecosystem are typically not known prior to exposure; 3) there are often no uncontaminated and environmentally equivalent sites for comparison; and 4) there are often other potential stressors (e.g., turbidity, nutrients, salinity and/or temperature) which occur simultaneously or sequentially that may contribute to observed impacts.

The large-scale (~30 km^2) mangrove dieback from the mid 1990's in the Mackay region is a good example of the complexity faced in assigning direct cause-effect relationships to pesticide contamination. Mangrove death, identified in aerial and field surveys was primarily restricted to a single species, *Avicennia marina,* and was reported to affect >80% of individuals in the Pioneer River basin which drains both agricultural and urban land (Duke, 2005). The study reported significant correlations between diuron in mangrove sediments and the health status of *A. marina,* plus the presence of diuron in the leaves of mangroves at affected sites. This evidence was supported by a study that experimentally exposed mangrove seedlings to diuron over 71 days which found *A. marina* to be more sensitive to PSII herbicides than other species tested (Bell & Duke, 2005). However, a later publication argued that a causal link between diuron exposure and mangrove dieback had not been established, with the earlier studies failing to demonstrate that diuron concentrations identified in the field were sufficient to explain the observed dieback (Abbot & Marohasy, 2011). Other reasons for the dieback were suggested, including smothering of pneumatophores; however, the cause(s) of the dieback remain to be definitively established and more research would be required to understand the potential harm to mangroves of low-level chronic exposure to PSII herbicides.

Ten other field studies have been identified that correlated changes in the health of GBR species (using biomarkers and physiological observations) with pesticide contamination in rivers and marine ecosystems of the GBR. The earliest (post-1990) study of this type surveyed fish embryos collected from 18 GBR sites and found embryonic malformation was higher at sites influenced by agriculture, urban and industrial activities; however, pesticide concentrations from these sites were not reported (Klumpp & von Westernhagen, 1995). Four linked studies examined molecular (and some physiological and histological) markers for stress in barramundi (*Lates calcarifer*) collected from GBR rivers and creeks where exposure to pesticides, especially PSII herbicides diuron and atrazine was highly likely (Hook et al., 2017a; 2017b; 2018b; Kroon et al., 2015a). These studies consistently reported increased expression of genes related to xenobiotic (potentially pesticide) exposure in fish that were collected from several GBR waterways (North Johnstone and Tully rivers and Barratta and Sandy creeks) contaminated with pesticides, in comparison to fish from uncontaminated reference sites. The molecular markers that were affected included those related to xenobiotic and lipid metabolism and to egg yolk production (e.g., vitellogenin, a marker for estrogenic effects), and all were reported as potential indicators of contaminant (potentially pesticide) exposure. Vitellogenin transcription levels in collected barramundi were significantly correlated to the amount of sugarcane in the catchment upstream of the fish collection and concentrations of pesticides applied to sugarcane (Kroon et al., 2015a). Coral trout (*Plectropomus leopardus* and *Plectropomus maculatus*) collected from reef islands were also assessed for vitellogenin responses (Kroon et al., 2015a). Vitellogenin transcription levels increased from north to south and the authors argued these were consistent with the distribution of pesticides in the GBR. These field studies were complemented by two highly controlled experiments that exposed barramundi (for 2 days) to atrazine (Kroon et al., 2014) or atrazine and diuron, both as pure compounds and in commercial formulations (Kroon et al., 2015a). Both studies reported no effects of pure atrazine or diuron on estrogenic (hormonal) or oxidative stress biomarkers at high concentrations. However, exposure to commercial formulations of atrazine and diuron, that would occur in GBR freshwaters and the GBR lagoon, both altered estrogenic biomarkers, indicating a sublethal response to the additives (several other biomarkers were not affected) (Kroon et al., 2015a). Together, these six studies demonstrate the utility of combining field biomarker studies with experimental studies for validation. They demonstrate that changes in water quality, potentially related to agriculture, can influence commercially and ecologically important GBR species at the sublethal level (which may in turn affect their fitness). However, as acknowledged in the field studies, a definite causal link between the pesticide exposure and fish health was difficult to establish as a range of other environmental and anthropogenic factors (including sediments, nutrients, pesticide additives, other pesticides, salinity and temperature) could contribute to sublethal responses.

An earlier study also examined multiple biomarkers from *L. calcarifer* collected from five GBR rivers during the dry season and found significant biomarker signals (cholinesterase activity, EROD activity and DNA damage) in fish from the two sites with the highest influence of agriculture (Herbert River, North Johnstone River) (Hook et al., 2017a). Reduced cholinesterase activity in fish was strongly linked with carbamate and organophosphorus insecticides; however, only the PSII herbicide diuron was identified in sediments at these sites. While most biomarker studies using organisms collected from the GBR have focused on fish, two further studies have assessed mud crabs (*Scylla serrata*) and microbial communities across contaminated and uncontaminated sites. Mud crabs from the Herbert, Burdekin and Fitzroy rivers exhibited higher glutathione S-transferase (GST) activity than crabs from the uncontaminated Normanby River (GST is involved in detoxification of xenobiotics, possibly pesticides) (van Oosterom et al., 2010). These results are similar to a previous study that found higher concentrations of legacy pesticides DDT and dieldrin in the same crabs from the same locations (Negri et al., 2009). Cholinesterase activity inhibition was greatest in mud crabs from the Fitzroy River (influence of grazing), indicating insecticide exposure but also the Normanby River which is largely undeveloped with respect to agriculture (van Oosterom et al., 2010). Wood et al. (2019) identified 298 benthic diatom taxa in 14 GBR waterways located in all the NRM regions except the Cape York region. The taxa were then classified using a new biological monitoring index they developed called SPEAR-herbicide as being either species at risk (SPEAR) or not at risk (notSPEAR) based on their sensitivity to herbicides and whether they were motile – with the sensitive and non-motile being classed as SPEAR. During the dry seasons and after the wet seasons of 2011/2012 and 2012/2013 they measured the prevalence of sensitive diatoms and a range of water quality parameters including a Toxic Equivalence Quotient (TEQ) based estimate of pesticide mixture toxicity. They observed that the number of sensitive diatom taxa decreased after each wet season but then recovered during the dry season. The decrease in sensitive diatom taxa was negatively correlated with TEQ, electrical conductivity, total suspended solids (TSS) and nutrients (filterable reactive phosphorus -FRP, ammonia and NO_x). Finally, Angly et al. (2016) assessed microbial (bacterial) community composition across seven inshore sites with different exposure indices in the Wet Tropics region. While there were clear differences in microbial communities, factors other than pesticides (salinity, sediments and nutrients) were again acknowledged as potentially contributing to the reported differences. A number of (as yet) unpublished studies have used environmental DNA to examine if there are differences in eDNA in waterways with different concentrations of pesticides. The two completed studies have shown that differences in eDNA in waterways were related to pesticide concentrations, salinity and nutrients and the third study is still underway.

Key finding:

- Links between organism response (mortality and biomarkers) and pesticide exposure have been postulated for freshwater and marine species of the GBR; however, more laboratory validated field studies (further pesticide-taxa combinations and greater specificity of measured responses to pesticides) are required before this type of evidence can be applied to quantitatively assess impacts of pesticides in the GBR for uptake in risk assessments. However, the results are consistent with the hypothesis that pesticides are exerting harmful effects.

2. The responses of GBR species to pesticides following experimental exposures

GBR-relevant herbicides, insecticides and fungicides have all been found to negatively affect the biota of the GBR in experimental studies. These effects on marine organisms are well documented for select PSII herbicides (36 studies in total) to seagrass (6 studies since 1990), coral (9) and microalgae (13), but there are far fewer studies on non-PSII herbicides (4), insecticides (6) and fungicides (3). Similar patterns were found for freshwater systems, where the studies were primarily focused on the effects of PSII herbicides (38 studies in total) including 9 studies on microalgae and 20 on aquatic plants, while fewer studies assessed the effects of non-PSII herbicides (14), insecticides (8) and fungicides (4). The total number of studies found for each combination of pesticide class and taxa for freshwater and marine ecosystems of the GBR are presented in Table 17.

Table 17. The number of quantitative experimental studies on the effects of pesticides to GBR species. Freshwater and marine toxicity thresholds can be found in ***Table T1*** *and* ***Table T2 (Appendices)****, respectively. Cited publications freshwater*[12]*. Cited publications marine*[13]*.*

Pesticide type (no. of studies)	Taxa					
Freshwater[11]	Microalgae	Macrophyte	Crustacean	Fish	Insect	Other
PSII herbs (8)	9	20	5	2	0	2
non-PSII herbs (3)	5	7	1	0	0	1
Insecticide (3)	0	0	3	2	3	0
Fungicide (2)	0	0	2	0	0	2
Marine[12]	Microalgae	Seagrass	Coral	Macroalgae	Fish	Other
PSII herbs. (15)	13	6	9	3	1	8
non-PSII herbs. (5)	4	0	0	0	0	0
Insecticide (8)	0	0	2	0	2	2
Fungicide (3)	1	0	1	0	0	1

This review found experimental studies on many pesticide-taxa combinations, and a wide range of negative effects were reported including those considered in the national guidelines as ecologically relevant (mortality, and various measures of growth and reproduction) and sublethal effects that are not necessarily ecologically relevant (photosynthesis endpoints and other biomarker responses) (Warne et al., 2018a).

[12] Freshwater publications cited (Ali et al., 1998; Baxter et al., 2011; Boxall et al., 2013; Brain et al., 2012; Camilleri et al., 1998; Cedergreen et al., 2004; 2005; Cedergreen & Streibig, 2005; Coquillé et al., 2015; Drost et al., 2003; Fairchild et al., 1994; 1998; Frontera et al., 2011; Humphrey & Klumpp, 2003; Humphrey et al., 2004; Kirby & Sheahan, 1994; Knauert et al., 2010; Knezevic et al., 2016; Knuteson et al., 2002; Kroon et al., 2014; Kumar et al., 2010; Larras et al., 2012; 2013; 2014; Lockert et al., 2006; Lytle & Lytle, 2005; Ma et al., 2008; 2011; McGregor et al., 2008; McMahon et al., 2013; Negri et al., 2020b; Peterson et al., 1997; Phyu et al., 2005; 2011; 2013; Rentz, 2009; Sanchez-Bayo & Goka, 2006; Song et al., 1997; Stevens et al., 2011; Stone et al., 2019; 2021; Tang et al., 1997; Teisseire et al., 1999; Teodorovic et al., 2012; Tunic et al., 2015; US EPA, 2004; van Dam et al., 2004; Wendt-Rasch et al., 2003; Wilson et al., 2000; 2008)

[13] Marine publications cited (Bengston Nash et al., 2005; Botté et al., 2012; Cantin et al., 2007; Chakravarti et al., 2019; Flores et al., 2013; 2020; 2021; Harrington et al., 2005; Haynes et al., 2000; Holzer et al., 2017; Hook et al., 2018a; Howe et al., 2017; Jones, 2005; Jones et al., 2003; Jones & Kerswell, 2003; King et al., 2022a; Klein et al., 2016; Kroon et al., 2014; Magnusson et al., 2008; 2010; 2012; Markey et al., 2007; Marques et al., 2020; Marzonie et al., 2021; McKenzie et al., 2020; Mercurio et al., 2018; Negri et al., 2005; 2011; 2015; 2020b; Olguin-Jacobson & Pitt, 2021; Rowen et al., 2017; Schreiber et al., 2002; Thomas et al., 2020a; 2020b; van Dam et al., 2012; 2015; Wilkinson et al., 2015a; 2015b; 2017)

Some key findings from the studies are summarised below:

- PSII herbicides, including diuron, atrazine and ametryn, consistently impact all marine photosynthetic organisms of the GBR that have been tested (31 species in 32 studies), including algae, plants (e.g., seagrass) and corals (e.g., **Table T2**).
- The primary effects of PSII herbicides diuron and hexazinone have been measured on photosynthetic efficiency, leading to reduced energy acquisition, growth and mortality (if assessed) in GBR phototrophs including: seagrass (Negri et al., 2015); coral (Cantin et al., 2007; 2009; Flores et al., 2021); coral symbionts (Marzonie et al., 2021); *Halimeda* sp. (Marques et al., 2020); and jellyfish (McKenzie et al., 2020; Rowen et al., 2017). Two studies, which found significant effects of atrazine on photosynthesis in jellyfish symbionts did not report reduced growth at the same low concentrations (Klein et al., 2016; Olguin-Jacobson & Pitt, 2021). A study on the aquatic macrophyte *Myriophyllum spicatum* found effects of diuron and atrazine on photosynthesis but not growth over the exposure period, showing that photosynthetic efficiency is a sensitive endpoint (Knauert et al., 2010).
- The effects of PSII herbicides (including diuron, atrazine, hexazinone, tebuthiuron, propazine, metribuzin, bromacil and simazine) on photosynthesis and growth were highly correlated in five microalgal species (Magnusson et al., 2008; Marzonie et al., 2021; Thomas et al., 2020a; 2020b), suggesting effects on photosynthesis in microalgae is an ecologically relevant metric for PSII herbicides. One publication demonstrated reductions in both photosynthetic efficiency and growth only at low light intensities in the presence of low diuron concentrations for the diatom *Phaeodactylum tricornutum* (King et al., 2022a).
- The composition of microalgal communities from estuarine and freshwater ecosystems of the GBR were affected by experimental exposures to atrazine and diuron (Magnusson et al., 2012; Wood et al., 2014). Further, the composition of a diatom community collected from an agricultural stream (Barratta Creek) was not affected by atrazine exposure, while sensitive taxa in a diatom community from an unpolluted site (Alligator Creek) declined after chronic exposure to atrazine (Wood et al., 2017).
- Recent studies indicated five species of marine microalgae were insensitive to non-PSII herbicides including 2,4-D, haloxyfop, imazapic and fluroxypyr, MCPA (Marzonie et al., 2021; Negri et al., 2020b; Thomas et al., 2020a; 2020b). Similarly, the non-PSII herbicide imazapic was not toxic to three species of tropical freshwater algae to concentrations reported in GBR waterways (Stone et al., 2019). However, growth rates in three freshwater microalgae and four freshwater macrophytes were affected by non-PSII herbicides including: haloxyfop, imazapic, isoxaflutole, triclopyr, fluroxypyr, glyphosate and pendimethalin (Cedergreen & Streibig, 2005; Negri et al., 2020b).
- PSII herbicides have only been reported to affect early life stages of corals at very high concentrations (Mercurio et al., 2018; Negri et al., 2005), while no effects on biomarkers were found in fish exposed to pure atrazine (Kroon et al., 2015b). Little is known of the toxic mechanisms or long-term, low exposure concentration effects on non-photosynthetic taxa.
- Insecticides, including imidacloprid, fipronil, diazinon, bifenthrin, endosulfan, chlorpyrifos, carbaryl and permethrin have been shown to affect marine invertebrates relevant to the GBR including corals, barnacles, crabs, shrimp and prawns (Flores et al., 2020; Hook et al., 2018a; Markey et al., 2007; Negri et al., 2020b), and fish (Botté et al., 2012; Holzer et al., 2017) and at very high concentrations can reduce growth in microalgae (Negri et al., 2020b).
- There are far fewer studies on the effects of fungicides on GBR species; however, reduced settlement in coral larvae has been reported following exposures to chlorothalonil, propiconazole and methoxyethyl mercury chloride (MEMC) (Flores et al., 2020; Markey et al., 2007).

The sensitivity of GBR taxa to pesticides is addressed in the following sections.

3. Guidelines values (GVs) for pesticides found in the GBR

In Australia, water quality guideline values (GVs) are usually presented as protective concentrations (PCx), which, if not exceeded should protect x% of species in an aquatic ecosystem (Warne, 2001; Warne et al., 2014; 2018a). PCx values are typically derived from a cumulative distribution of toxicity values for diverse species called a species sensitivity distribution (SSD). The preferred measures of toxicity to be used in constructing SSDs and calculating GVs are *No Effect Concentrations* (NEC), *No Observed Effect Concentrations* (NOEC) and *10% effect or lethal concentrations* (EC10 or LC10) (Warne et al., 2018a). Other measures of toxicity can be used or converted before use in SSDs (e.g., a LC50 can be converted to a LC10) (Warne et al., 2018a). An advantage of SSDs is that they can be used to determine either the percentage of species that will be affected or protected at a given pesticide concentration or the concentration that must not be exceeded in order to protect a given percentage of species (Warne et al., 2020a).

There is an asymptotic relationship between toxic concentrations and the length of exposure (with toxic concentrations initially decreasing rapidly as exposure time increases but then the rate of toxic concentration decrease decreases) (e.g., Baas et al., 2007). The Australian and New Zealand guideline values aim to protect aquatic organisms from lifelong exposure (ANZG, 2018). For these reasons toxicity data from long-term exposures are the preferred type of toxicity data to calculate guideline values. Most chronic toxicity data are derived following exposures of less than 30 days while in most of the monitored GBR freshwaters, organisms are exposed to pesticides throughout the wet season (182 days). Also, the chronic toxicity data do not account for multi-generational exposure. Therefore, the guideline values may underestimate the toxicity experienced by aquatic organisms in the fresh and marine waters of the GBR.

The review found various water quality GVs that have been applied in pesticide risk assessments for the GBR over the last two decades (summarised in Table 18). These date back to the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC & ARMCANZ, 2000) which included limited, often low reliability, GVs for some pesticides identified in the GBR. These were complemented by GVs developed by the Great Barrier Reef Marine Park Authority (GBRMPA), which also considered pesticide toxicity thresholds for several PSII herbicides to important GBR taxa, including seagrass and corals (GBRMPA, 2010). Subsequently, the relative toxicity of each herbicide was determined to estimate the combined toxicity (Gallen et al., 2014; Smith et al., 2012). Smith et al. (2017a; 2017b) then developed a toxic equivalency (TEQ) approach to calculate toxic loads (expressed as diuron equivalent loads). More recently, freshwater and marine GVs have been proposed for 27 pesticides based on updated toxicity datasets (King et al., 2017a; 2017b; King & Warne, 2017; Warne et al., 2018b). Finally, GVs for 22 pesticides incorporating toxicity data for both freshwater and marine ecosystems have been developed as part of the PRM (Warne et al., 2020a) to improve SSD and GV quality, and allow risks posed by pesticide mixtures to be consistently assessed across all aquatic ecosystems.

Key findings: The PRM GVs (Warne et al., 2020a) were derived using nationally recognised criteria (Warne et al., 2018a) from the largest and most reliable threshold datasets available and are applicable across all aquatic ecosystems of the GBR.

Table 18. Pesticide guideline values used in risk assessments for Great Barrier Reef ecosystems.

Guidelines relevant to or used in GBR risk assessments	Characteristics
Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC & ARMCANZ, 2000)	Of the 15 pesticides that contribute 99% of risk to GBR ecosystems (Table 19), eight (chlorpyrifos, MCPA, 2,4-D, atrazine, hexazinone, diuron, tebuthiuron, metolachlor) have GVs for the protection of aquatic systems in this set of guidelines. Four of these pesticides (MCPA, hexazinone, diuron, metolachlor) have interim guidelines of low reliability (now categorised as being of unknown reliability that require revision). Guideline values for seven of the chemicals have either recently been revised (metolachlor), or are in the process of being revised (atrazine, hexazinone, diuron, 2,4-D, MCPA, tebuthiuron) at the time of writing.
Water Quality Guidelines for the Great Barrier Reef	Included updated GVs for seven of the focus pesticides (ametryn, atrazine, diuron, hexazinone, tebuthiuron, 2,4-D and chlorpyrifos) as well as simazine, endosulfan, 2-methylethyl mercuric chloride and diazinon. GVs were derived according to

Guidelines relevant to or used in GBR risk assessments	Characteristics
Marine Park (GBRMPA, 2010)	national water quality guidelines (Warne et al., 2018a), but have since been superseded with GVs derived from larger, more recent and extensive datasets.
PSII-HEQ index (Gallen et al., 2014; Kennedy et al., 2010b)	Included thresholds based on photosynthesis inhibition and data from tropical marine species. These thresholds were used to assess the relative potency and predict additive effects of 11+ PSII herbicides and their transformation products expressed as diuron equivalent concentrations (PSII herbicide equivalent index). These toxicity metrics were updated during the MMP program but are not consistent with the national water quality guidelines (Warne et al., 2018a).
Australian Pesticides and Veterinary Medicines Authority diuron guidelines (APVMA, 2011a)	A set of GVs for diuron derived using the species sensitivity distribution (SSD) method. The derived guideline values formed the basis of an APVMA risk assessment for herbicides containing diuron. However, the SSD and GVs were not consistent with nationally endorsed methods for deriving GVs (Warne et al., 2018a) because the SSD was heavily reliant on converted acute EC50 data and data from toxicity tests that used formulated products.
Toxic equivalent factor (TEF) (Smith et al., 2012)	Toxic equivalent factor is similar to the PSII-HEQ method but used atrazine as the reference herbicide. Toxic equivalent quotients (TEQ) were generated to predict additive effects of five PSII herbicides (ametryn, atrazine, diuron, simazine and prometryn) in mixtures.
Tropical species threshold (Pathiratne & Kroon, 2016)	This journal publication described the derivation of tropical toxicity thresholds for seven (ametryn, atrazine, hexazinone, diuron, tebuthiuron, metolachlor, imidacloprid) of the 15 pesticides that contribute 99% of risk to GBR ecosystems (Table 7). Although largely consistent with the nationally endorsed methods for calculating GVs (Warne et al., 2018a), in constructing the SSDs, the authors did not consider the modes of action of the various pesticides and did not differentiate between taxa that may be significantly less or more sensitive than others. Consequently, the authors derived several SSDs that were clearly bimodal using a combination of phototrophs (plants and algae) and heterotrophs (e.g., insects, crustaceans, chordates). This has resulted in poor-fitting regression functions in some of the SSDs (i.e., hexazinone, diuron, tebuthiuron, metolachlor and imidacloprid).
Proposed freshwater and marine GVs (PGV) (King et al., 2017a; 2017b; Warne et al., 2018b)	Of the 15 pesticides that contribute 99% of risk to GBR ecosystems (Table 19), these three publications provide the most recent iterations of freshwater- and/or marine water-specific SSDs and associated GVs values for 11 of the focus pesticides (ametryn, diuron, hexazinone, imazapic, MCPA, imidacloprid, isoxaflutole, triclopyr, fipronil, tebuthiuron, 2,4-D). The GVs were calculated using the nationally endorsed method (Warne et al., 2018a). The SSDs in these publications: • Formed the basis of the recently endorsed Australian and New Zealand guidelines for metolachlor and metsulfuron-methyl. • Formed the basis for guideline values for diuron, imazapic, MCPA, imidacloprid, fipronil and 2,4-D that are currently under review for endorsement as Australian and New Zealand guidelines. • Largely formed the basis for the combined fresh/marine SSDs calculated by Warne et al. (2020) and used in the PRM that estimates the risk posed by mixtures of pesticides in GBR ecosystems.
Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZG, 2018)	Of the 15 pesticides that contribute 99% of risk to GBR ecosystems (Table 7), nine (chlorpyrifos, MCPA, 2,4-D, atrazine, hexazinone, diuron, tebuthiuron, metolachlor, metsulfuron-methyl) have GVs for the protection of aquatic systems in this set of guidelines. Three of these pesticides (MCPA, hexazinone, diuron) have interim guidelines of unknown reliability that require revision. Guideline values for six of the chemicals are in the process of being revised (atrazine, hexazinone, diuron, 2,4-D, MCPA, tebuthiuron) at the time of writing.
Pesticide Risk Metric GVs	The risk associated with pesticides to aquatic ecosystems of the Great Barrier Reef World Heritage Area (GBRWHA) and its associated catchments is best estimated

Guidelines relevant to or used in GBR risk assessments	Characteristics
(Warne et al., 2020a)	using combined fresh/marine SSDs. This publication provides the most up-to-date combined fresh/marine SSDs and associated guideline values for 22 pesticides, including the 15 pesticides that contribute to 99% of the risk to GBR ecosystems and freshwater catchments that flow into the Great Barrier Reef. The GVs were calculated using the nationally endorsed method (Warne et al., 2018a).
Pesticide Decision Support Tool (Warne et al., 2022a)	This report aims to provide information to enable farmers, resellers, agronomists and extension officers to choose pesticides that pose a lower threat to freshwater ecosystems. They used the nationally endorsed method for deriving GVs (Warne et al., 2018a) but they only sourced toxicity data from the US EPA ECOTOX database and the US EPA Office of the Pesticide Program database and did not conduct a search of the literature. The limits they derived were termed Ecotoxicity Threshold Values (ETVs) as they had not gone through the approval process necessary to become GVs. Nonetheless, ETVs were derived for 47 pesticides – all the pesticides that can be applied to sugarcane. Currently another 53 ETVs are being derived for pesticides that can be applied to the major crops grown in rotation with sugarcane.

Table 19. Guideline values derived from toxicity data for both freshwater and marine species and applied in the PRM for all aquatic ecosystems of the GBR (Warne et al., 2020a) with the 12 focus pesticides of the current study indicated by shaded cells for both freshwater and marine ecosystems.

Pesticide class	Pesticide	Guideline values (µg L^{-1})				Focus pesticides	
		99%	95%	90%	80%	Freshwater	Marine
PSII herbicides	Atrazine	0.27	1.2	2.6	6.2		
	Diuron	0.075	0.22	0.4	0.88		
	Ametryn	0.079	0.36	0.73	1.6		
	Hexazinone	1.8	2.5	3.1	4		
	Tebuthiuron	4.7	11	17	27		
	Metribuzin	2	2.6	3	3.7		
	Terbuthylazine	0.5	1.4	2.3	4.1		
	Simazine	71	87	99	138		
	Prometryn	0.089	0.43	0.88	1.9		
Non-PSII herbicides	MCPA	0.0075	1.5	15	142		
	Metolachlor	0.0079	0.4	2.2	13		
	Imazapic	0.049	0.44	1.2	3.6		
	Metsulfuron-methyl	0.0063	0.033	0.091	0.36		
	Triclopyr	21	47	81	162		
	Isoxaflutole	0.37	0.69	1.0	1.7		
	2,4-D	7.3	17	28	56		
	Fluroxypyr	114	275	409	631		
	Haloxyfop	589	1969	3399	6147		
	Pendimethalin	0.054	0.27	0.58	1.4		
Insecticides	Imidacloprid	0.057	0.13	0.23	0.46		
	Chlorpyrifos	0.00054	0.016	0.077	0.46		
	Fipronil	0.0034	0.01	0.019	0.041		

4. Sensitivity of GBR species to pesticides compared to guideline values

A large amount of pesticide toxicity data for GBR species (species that are known to occur in the GBR or in the waterways that discharge to the GBR) was found during this review (Table 17). This provides an opportunity to assess whether the GVs in Table 19 are protective of GBR species. For freshwater species, atrazine had the most toxicity data having 66 toxicity values for 22 species across 7 phyla, which included effects on mortality (2 datapoints), growth (61), reproduction (2) and other sublethal effects (1) (**Table T1**). The measures of toxicity (i.e., chronic NOEC, EC10, NEC) for each toxicity endpoint (mortality, growth, reproductive, photosynthetic, other) were selected from **Table T1**. For marine species, diuron was the best represented, with 82 toxicity values for 34 species across 10 phyla, which included effects on mortality (7 datapoints), growth (12), reproduction (5), photosynthesis (52) and coral bleaching (6) (**Table T2**). This comparison was conducted by plotting the toxicity values for atrazine, diuron and hexazinone for freshwater and marine GBR taxa against the current GVs (Figure 8) and all the other pesticides with appropriate data (**Appendix 2, Figures A1 and A2**). These three pesticides are illustrated as there is far more toxicity data for GBR species to these pesticides than others and they have more toxicity values lower than the PC99 values.

There were very few freshwater GBR species that showed sensitivity to the focus pesticides at concentrations below the PC95 and PC99 values (Figure 8 and **Figures A1 and A2**). Exceptions included reduced growth of a single fungal species to atrazine, a single microalgal species to diuron (Figure 8) and a single aquatic plant species to isoxaflutole (**Figure A1**). Otherwise, the PC95 and PC99 GVs were protective of all freshwater GBR species for which toxicity data are available. Marine species were also generally not affected by the 12 focus pesticides at concentrations lower than their PC99 values. Exceptions were one species of jellyfish, the growth of which was affected by diuron at concentrations below the PC99 (Figure 8). Inhibition of photosynthesis was reported as occurring below the PC99 for hexazinone (Figure 8), ametryn and tebuthiuron (**Figure A2**). Currently, photosynthetic inhibition is not considered an ecologically relevant endpoint and are not considered in deriving GVs (Warne et al., 2018a).

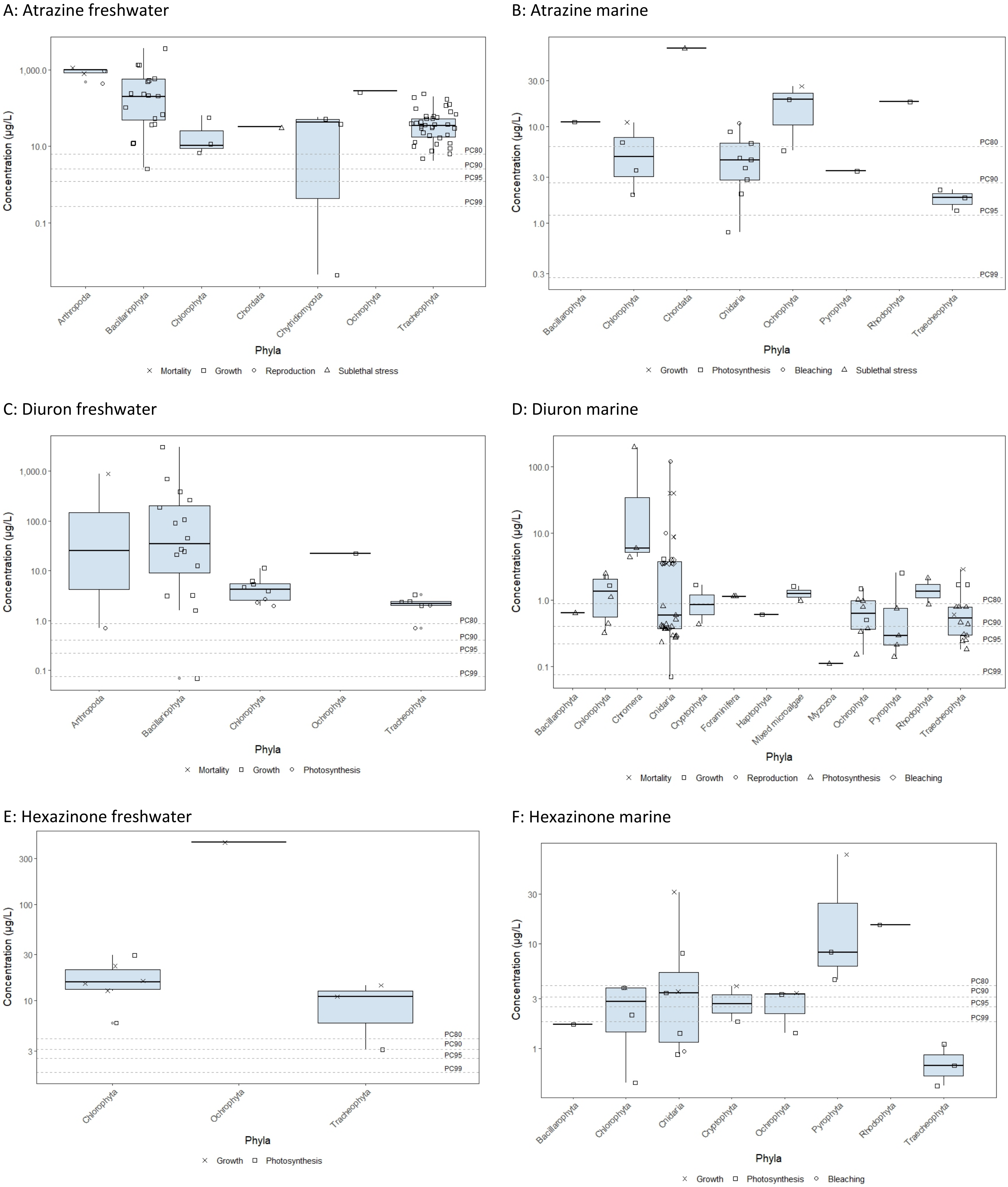
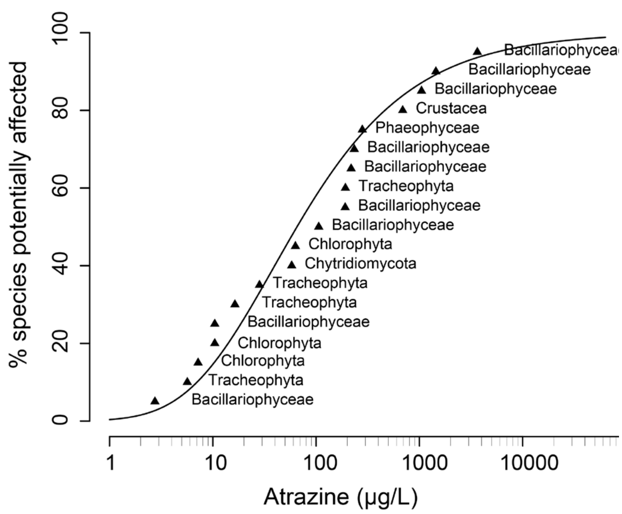


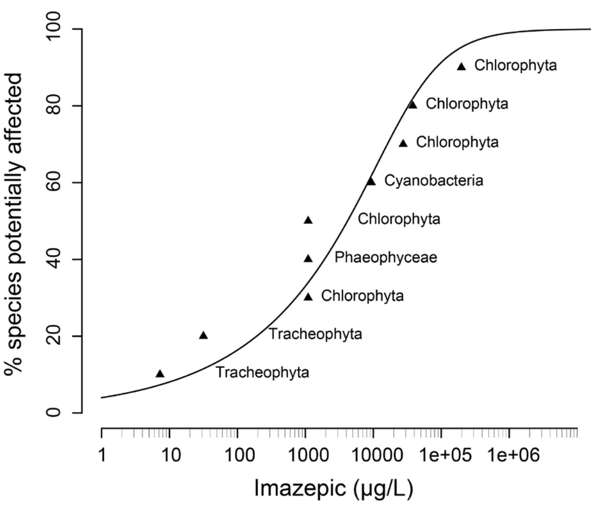
Figure 8. Plots of toxicity data for freshwater (A, C, E) and marine (B, D, F) GBR species exposed to atrazine (A, B), diuron (C, D) and hexazinone (E, F) against GVs (PC99, PC95, PC90, PC80) obtained from Warne et al. (2020). Cnidaria include corals and Tracheophyta includes seagrass. The effect types include mortality, growth, reproduction, photosynthesis and bleaching for corals.

Further comparison was possible as there were sufficient toxicity data to derive GVs using the SSD approach (i.e., they met the minimum data requirements of having toxicity data for at least five species that belong to at least four taxonomic groups (Warne et al., 2018a)) for atrazine, diuron and imazapic to freshwater species and for diuron to marine species. The fit of the SSDs to the GBR species toxicity data are presented in Figure 9. The generated PCx values for atrazine and diuron for freshwater were of very high reliability (as they have chronic toxicity data for more than 15 species and the fit of the SSD to the data was good), those for imazapic were high reliability (having 9 chronic data and the fit of the SSD to the data was good), and diuron in marine waters were moderate reliability (as there were chronic data for 9 species with a poor fit of the SSD to the data) (Warne et al., 2018a). The resulting PCx values were compared to the corresponding PCx values for the same pesticides used in the PRM (Table 20) (Warne et al., 2020a) and for fresh and marine water guidelines (King et al., 2017a; 2017b). The PCx values for atrazine and for diuron in both fresh and marine waters that were derived in this study using only GBR freshwater species were larger than the GVs calculated using all available toxicity data (Warne et al., 2020a). The PC99 value for imazapic derived in the current study was markedly smaller than the corresponding GV (Warne et al., 2020a) but the PC95, 90 and 80 were all markedly larger than the corresponding GVs (Warne et al., 2020a).

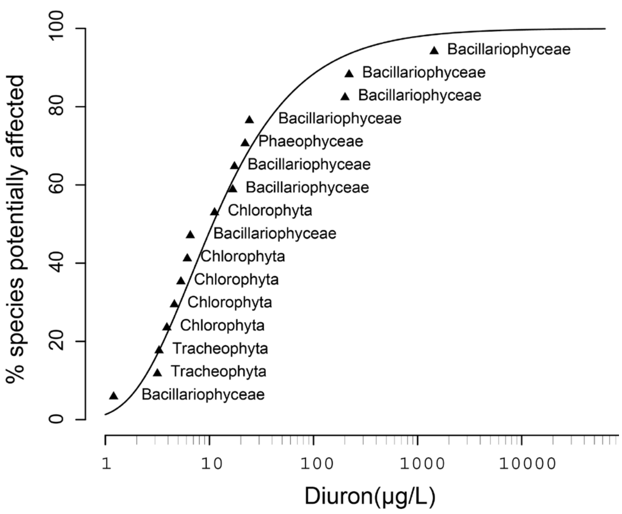
Atrazine freshwater



Imazapic freshwater



Diuron freshwater



Diuron marine

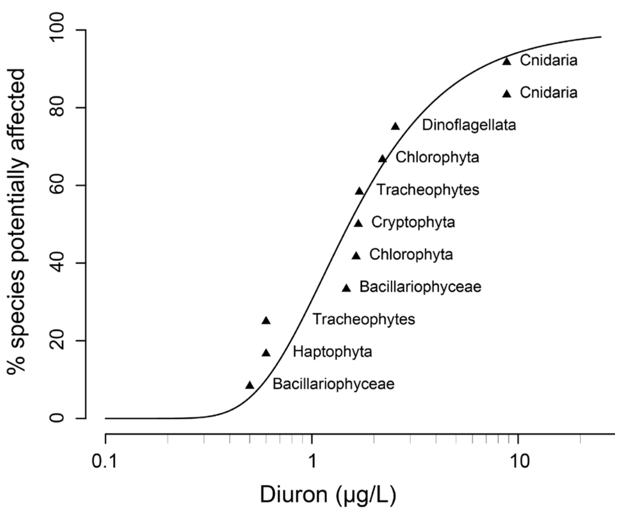


Figure 9. Species sensitivity distribution plots for atrazine, diuron and imazapic to freshwater GBR organisms and for diuron to marine GBR species.

Table 20. Comparison of protective concentration (PCx) values derived using toxicity data for only GBR species (fresh and marine) (Figure 9). Units µg L^{-1}.

Pesticide (ecosystem)	Freshwater or marine	Source of PCx values	PC99	PC95	PC90	PC80
Atrazine (F)	Fresh	This study	1.6	4.1	7	14
	Both	(Warne et al., 2020a)	0.27	1.2	2.6	6.2
Diuron	Fresh	This study	0.93	1.6	2.3	3.6
	Fresh	(King et al., 2017a)	0.08	0.23	0.42	0.9
	Marine	This study	0.28	0.5	0.68	0.99
	Marine	(King et al., 2017a)	0.43	0.67	0.86	1.2
	Both	(Warne et al., 2020a)	0.075	0.22	0.4	0.88
Imazapic (F)	Fresh	This study	0.011	2.1	20	192
	Both	(Warne et al., 2020a)	0.049	0.44	1.2	3.6
	Fresh	(King et al., 2017a)	0.036	0.41	1.2	4.0

Key findings:

- Current PC99 GVs were protective of the vast majority of GBR species: there were very few freshwater GBR species that showed sensitivity to the focus pesticides at concentrations below the PC95 and PC99 values.
- The most sensitive toxic effects (lowest thresholds) were generally photosynthetic. In particular, PSII herbicides affected photosynthetic efficiency of freshwater and marine phototrophs at low concentrations. Some of the effects, particularly for hexazinone, ametryn and tebuthiuron to marine phototrophs, occurred below the PC99 – meaning that the PC99 values may allow some adverse effects to occur.
- The PC99 values derived using GBR species toxicity data for atrazine (freshwater only) and diuron (freshwater and marine) are greater than the PC99 GVs, indicating: 1) GBR species are not more sensitive than the species used to derive the GVs; and 2) the GVs summarised in Table 19 are protective of the GBR species tested (both freshwater and marine). The PC99 value derived for freshwater GBR species for imazapic are lower than the PC99 GV – the latter probably does not provide sufficient protection.

5. Total toxicity of pesticide mixtures

When pesticides are identified in water samples from the GBR, they predominantly occur as mixtures (Table 10, (Lewis et al., 2012; Warne et al., 2020b)). The toxicity to GBR species of pesticide mixtures, including the influence of formulation additives has been experimentally assessed in two ways: 1) studies assessed the responses of GBR species to known mixtures of pesticides; and 2) studies assessed both the toxicity and pesticide composition of water sampled from the GBR or its catchments.

The potential effects of simultaneous exposure of GBR species to multiple pesticides has been addressed by assuming their effects conform to Concentration Addition (CA) in freshwater (Spilsbury et al., 2020) and marine risk assessments (Thai et al., 2020). This assumption has been experimentally validated for the effects of known mixtures of PSII herbicides to seven GBR species. For example, CA was shown to occur for photosynthetic impacts on two estuarine microalgae with binary mixtures of diuron, atrazine, simazine and tebuthiuron (Magnusson et al., 2010) and the seagrass species *Halophila ovalis* with mixtures of up to ten PSII herbicides (Wilkinson et al., 2015b). Another study tested the effects of diuron and atrazine mixtures on an aquatic macrophyte *Myriophyllum spicatum* and again reported CA for effects on photosynthetic endpoints (Knauert et al., 2010). Mixtures of up to four PSII herbicides were found to have CA effects on growth (frond number) in the macrophyte *Lemna minor* (Drost et al., 2003; Knezevic et al., 2016) and in two freshwater microalgae in a multispecies growth assay (Stone et al., 2021).

Less validation is available for the application of additivity for pesticides with different modes of action to GBR species. For example, an aquatic macrophyte found in the GBR was exposed to atrazine in the presence of three other pesticides (chlorpyrifos, monosodium methanearsonate and methylmercury) but tests were not performed in a way that could confirm or reject the mode of joint toxicity (Lytle & Lytle, 2005). The toxicity of mixtures of the insecticide permethrin, the herbicide atrazine and the fungicide chlorothalonil to the cladoceran *Ceriodaphnia* cf. *dubia* were reported (Phyu et al., 2011). They found that applying the Independent Action (IA) model of joint action (usually applied when modes of action are different) resulted in lower estimates of mixture toxicity than estimates when the CA method was used. It was also demonstrated that very low concentrations of chemicals with different modes of action, including the GBR-relevant pesticides, atrazine, chlorpyrifos, diuron, fipronil, hexazinone, metolachlor, simazine, triclopyr contribute in a CA manner to total mixture toxicity in the bacterium *Vibrio fischeri* (Tang et al., 2013). Importantly, a comparison of IA and CA demonstrated very similar predictions for total toxicity (on average IA predictions were 10% smaller than CA predictions) in 3,063 pesticide mixtures from the GBR waterways (Spilsbury et al., 2020).

While low concentrations of pesticides are usually additive, much less is known of the potential contribution of commercial formulation additives (e.g., surfactants to increase solubility, uptake and efficacy) to the toxicity of pesticides to GBR species. In one study, the toxicity of two pesticide formulations containing diuron and hexazinone or diuron alone to two microalgal species could be explained by the measured concentration of diuron (Stone et al., 2021). However, another study demonstrated that atrazine and diuron only affected estrogenic biomarkers in barramundi when exposed as commercial formulations, indicating a response to the additives (Kroon et al., 2015a). Schmuck et al. (1994) conducted a large international review and found that between 65 and 75% of the available toxicity data for commercial formulations were not more toxic than the corresponding active ingredient for green algae, cladocerans and fish, respectively. They also found that at least 98% of all formulations were no more than 10-times more toxic than the technical material to those organisms.

Three studies experimentally assessed the toxicity of water from GBR ecosystems with bioassays using GBR species to grab or passive samples in combination with chemical analysis of the same samples (Magnusson et al., 2013; Shaw et al., 2009; 2012). This approach accounts for the contribution of all pesticides, even those that could not be identified by chemical analysis. In the first study, passive samplers deployed at GBR river mouths and marine sites were analysed for herbicides and were tested for toxicity using bacterial, microalgal, urchin, and coral bioassays (Shaw et al., 2009). There was a close correlation between the analytical and diatom bioassay results for PSII herbicides in these samples, while the coral and urchin assays detected sublethal toxicity from unknown chemicals. Another study assessed the phototoxicity of 16 flood plume samples from the Mackay Whitsunday region with a coral symbiont bioassay and again found a positive relationship between the analytical and bioanalytical results, indicating toxic additivity of the PSII herbicides atrazine, diuron, hexazinone and tebuthiuron in these samples (Shaw et al., 2012). Analysis of pore water from estuarine sediments of the Herbert, Tully, Johnstone and Daintree rivers contained up to seven pesticides that contributed to total toxicity in bioassays using two GBR microalgal species (Magnusson et al., 2013). The bioassay results indicated either, the presence of some phototoxic compounds (potentially herbicides) that were not detected analytically, or that the combined effects of pesticides in the mixtures was greater than additive.

Key findings:

- Most experimental studies using GBR species indicate the effects of multiple pesticides in mixtures conform with concentration addition.
- Multiple small effects caused by low concentrations of pesticides can combine to impact GBR species.
- Independent Action and concentration addition models of joint action predict similar total toxicity values for GBR-relevant pesticide mixtures.
- Little is known of the potential influence that additives in commercial pesticide formulations may have on pesticide toxicity to GBR species and this applies internationally.
- Bioassays of water collected from the GBR further validate that the toxicity of PSII herbicide mixtures conforms with concentration addition.

6. Experimental studies on the influence of other environmental factors on pesticide toxicity to GBR species

Sixteen experimental studies have demonstrated that co-exposure to additional factors such as elevated temperatures, future climate conditions (elevated temperature and CO_2), shading (relevant to high turbidity), reduced salinity and sediments can all affect the sensitivity of GBR species to pesticides (Table 21). Light intensity plays a very complex role in the sensitivity of GBR phototrophs to PSII herbicides. For several species of microalgae and aquatic macrophytes, shading (a proxy for high turbidity) results in increased photosynthetic efficiency in an effort to harvest more photons for energy, but growth is ultimately reduced the most by PSII herbicides in low light conditions (Cedergreen et al., 2004; King et al., 2022a; 2022b). For other aquatic macrophytes and seagrass, the effects of PSII herbicides can be exacerbated under high light intensity, potentially due to increased oxidative damage to photosystems (Brain et al., 2012; Cedergreen et al., 2004; Wilkinson et al., 2015a). While the reduced salinity and co-exposure to sediments can also increase the sensitivity of GBR species to PSII herbicides (Harrington et al., 2005; Klein et al., 2016), more work needs to be done to confirm whether this is consistent among other GBR taxa.

Evidence on the influence of temperature on the toxicity of PSII herbicides to GBR species is more consistent (Table 21). Most (7 of 8) studies demonstrated that temperatures above acclimation levels increase the harmful effects of PSII herbicides and an insecticide (chlorpyrifos) on corals, *Halimeda* and fish. Furthermore, two studies have shown that the effects of diuron on corals and seagrass can also increase at lower than optimal temperatures (Jones & Kerswell, 2003; Wilkinson et al., 2017). The development of a tropical species SSD for thermal stress has allowed the combined effects of diuron and thermal stress for GBR species to be predicted using the Independent Action (IA) model of joint action (Negri et al., 2020a). This showed that increased temperature increased the toxicity of diuron to marine organisms and that GVs should be decreased when accounting for heat stress. This approach can be applied to other PSII pesticides and is consistent with international experimental data (see references in Negri et al., 2020a).

Key findings:

- Thermal stress (e.g., heatwave conditions) is likely to increase the vulnerability of GBR species to PSII herbicides, and the scale of this influence can be predicted using Independent Action.
- However, the influence of light intensity on species sensitivity is more complex, and (like the co-exposures to sediments and low salinity) requires more research.
- The studies to date suggest that experimentally derived thresholds for GBR species such as those shown in (**Tables T1 and T2**) likely underestimate sensitivity in the field, since experimental thresholds are typically derived under optimal conditions, in the absence of other potential stressors.

*Table 21. Effects of additional stressors on Great Barrier Reef species sensitivity to pesticides. FW = freshwater, L = lethal, PS = photosynthetic, G = growth, R= reproductive or early life stages, *species had been chronically exposed to diuron for several years.*

Pesticide	Additional stressor	Taxa (effect type)	Species sensitivity	Reference
Atrazine	Light intensity	FW macrophyte (G)	Increased in high light	Brain et al., 2012
Terbuthyla-zine	Light intensity	7 FW macrophytes (G)	Increased in low light (2 sp.) Reduced in low light (4 sp.) No difference (1 sp.)	Cedergreen et al., 2004
Diuron	Light intensity	Marine microalgae (PS, G)	Increased for growth in low light Decreased for PS in low light	King et al., 2022b
Diuron	Light intensity	Marine microalgae (PS, G)	Increased for growth in low light Decreased for PS in low light	King et al., 2022a
Diuron	Nitrogen	Marine microalgae (PS, G)	No effect on PS	King et al., 2022a

Pesticide	Additional stressor	Taxa (effect type)	Species sensitivity	Reference
Diuron	Light intensity	Seagrass (PS)	Increased damage to PSII under highest intensity light	Wilkinson et al., 2015a
Diuron Atrazine	Reduced salinity Reduced salinity	Coral (PS) Jellyfish (PS)	No effect over the salinity range Increased with decreasing temperature	Jones et al., 2003 Klein et al., 2016
Diuron	Sediments	Crustose coralline algae (PS, L)	Increased with sediment exposure	Harrington et al., 2005
Diuron Chlorpyrifos Diuron Atrazine, diuron, hexazinone Diuron Diuron	Temperature Temperature Temperature Temperature Temperature Temperature	5 species of coral symbiont (PS) Freshwater fish ® Coral (PS) Coral (PS) 2 species of coral symbionts Seagrass	Increased with temperature (4 sp.) Decreased with temperature (1 sp.)* Increased with temperature Increased with reduced temperature Increased with temperature Increased with temperature (2 sp.) Most sensitive above and below optimal thermal conditions	Chakravarti et al., 2019 Humphrey & Klumpp, 2003 Jones & Kerswell, 2003 Negri et al., 2011 van Dam et al., 2015 Wilkinson et al., 2017
Diuron Diuron	Future climate Future climate	Adult coral (PS, G) *Halimeda* macroalgae (PS, G)	Increased with higher temperature and pCO_2 Increased with higher temp. and pCO_2	Flores et al., 2021 Marques et al., 2020

Risks of pesticides to GBR ecosystems

There are two main types of ecological risk assessment: prospective or pre-release and retrospective or post-release. These are not contrary to each other but rather complimentary and work in an adaptive management approach (Warne & van Dam, 2020). The Australian Pesticides and Veterinary Medicines Authority (APVMA) conducts prospective (pre-release) risk assessments using models that contain numerous assumptions and minimal ecotoxicity and no monitoring data. The results *predict* the estimated environmental concentrations and risk that pesticides pose to aquatic environments. The results of these risk assessments are subsequently used to determine whether a pesticide can be imported into or manufactured in Australia as well as setting the label conditions (where, when and how much of a pesticide can be applied and to what crops/organisms) (Warne & van Dam, 2020). In contrast, retrospective (post-release) risk assessments use *measured* concentrations of pesticides from monitoring programs such as the GBRCLMP and MMP to estimate the actual risk that is occurring in the environment. There are far fewer assumptions made in retrospective than prospective risk assessments and the current review concentrates on retrospective assessments for that reason. The intention of the conditions stated in pesticide labels is, if they are adhered to, that no or minimal environmental harm should occur. If pesticide monitoring data and retrospective risk assessments estimate that significant environmental harm is happening this leads to a re-assessment of the prospective risk assessment of the pesticide (i.e., adaptive management). An example of this was diuron, where the monitoring data and retrospective risk assessments led the APVMA to re-assess this herbicide (APVMA, 2011a). The APVMA stated "The APVMA has decided that the continued use of, or other dealings with products containing diuron may have an unintended harmful effect on the environment. In addition, the APVMA has decided that the instructions on approved labels associated with products affected by this finding may no longer be adequate” (APVMA, 2011b). The labels for diuron pesticides were subsequently modified to include reductions in spray windows and application rates (APVMA, 2012). This example shows that prospective risk assessments are not always accurate and the system of having prospective and retrospective risk assessments that feed into each other works, and that neither one on its own would provide the desired environmental protection.

There have been several retrospective pesticide risk assessments that have reported concentrations of pesticides or pesticide mixtures in freshwater, wetland and marine ecosystems of the GBR that exceed GVs and/or concentrations that affect aquatic species (e.g., Brodie et al., 2013; Lewis et al., 2013; Smith et al., 2012; 2015; Vandergragt et al., 2020; Waterhouse et al., 2017) . This section primarily assesses risks posed by pesticides detected in GBR ecosystems between 2016/17 and 2021/22. Information on the spatial and temporal distribution and risk of pesticides in the freshwater ecosystems of the GBR since 2016 was drawn from GBRCLMP data published in the Pesticide Reporting Portal (Water Quality & Investigations, 2020b). GBRCLMP data are also summarised in five reports (Ten Napel et al., 2019a; 2019b; Water Quality & Investigations, 2020a; 2021; 2023a), while MMP data are summarised in three reports (Gallen et al., 2019b; Grant et al., 2018; Thai et al., 2020). The risk assessment reports estimated the percentage of species affected for the focus 12 freshwater and all 11 marine sites by year. The PRM for all other monitored sites can be accessed in the GBRCLMP story maps (Ten Napel et al., 2019a, 2019b; Water Quality & Investigations, 2020a; 2021; 2023a) and the risks posed by all individual pesticides through the Pesticide Reporting Portal for 24 individual pesticides (Water Quality & Investigations, 2020b). The pesticides contributing the most to risk at each site are identified. The outcomes of previous pesticide risk assessments that have estimated the spatial scale of potential risk to freshwaters, wetlands and marine ecosystems are also summarised and synthesised. It is important to note that because pesticides have differing toxicities (e.g., diuron is ~80 times more toxic than 2,4-D; (Warne et al., 2020a)), those pesticides that are prevalent in waterways in a concentration sense are not necessarily prevalent in a toxicity or risk sense.

Pesticide Mixtures and the Pesticide Risk Metric

As stated earlier, most water samples that have been collected in GBR freshwater ecosystems (e.g., Lewis et al., 2012; Spilsbury et al., 2020; Thai et al., 2020; Vandergragt et al., 2020; Warne et al., 2020b, Table 10) and essentially all samples collected in GBR marine systems (Table 15) contain mixtures of pesticides. When water samples contain mixtures of chemicals, the Australian and New Zealand Guidelines for Fresh and Marine Water Quality state that their combined toxicity must be assessed (ANZG, 2018). Therefore, (Warne et al., 2020a) developed a method referred to as the Pesticide Risk Metric (PRM) to estimate the total toxicity of up to 22 different pesticides simultaneously present in water samples. The PRM uses a number of methods (the multi-substance potentially affected fraction (msPAF), the independent action model of joint action (IA) and multiple imputation) all of which have been extensively peer reviewed, published and used internationally. A detailed justification for important aspects of the PRM is provided in Warne et al. (2020a). These methods were selected for use in the PRM as they use SSDs and the results are expressed as the percentage of aquatic species affected or protected due to the presence of pesticides – thus the results are consistent with the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZG, 2018). The 22 pesticides included in the PRM (**Table P1**) were selected as they: 1) are detected in GBR waterways; 2) are registered for use in Australia; and 3) have SSDs and/or ecosystem protection guideline values available.

A number of studies (Munz et al., 2017; Posthuma & de Zwart, 2006; 2012; Smetanová et al., 2014), though none conducted in the GBR region, have compared msPAF values to observed *in situ* biological effects in natural waterways. Posthuma and De Zwart (2006) found that a change in msPAF values for fish from 10 to 50% species affected corresponded to a 10,000-fold change in the ratio of observed to expected fish species in rivers in Ohio, USA. Further, Posthuma and de Zwart (2012) found that changes in acute msPAF values resulted in an almost 1:1 change in the fraction of taxa exhibiting at least a 50% reduction in abundance. The studies by Smetanová et al. (2014) and Munz et al. (2017) both found that msPAF values lower than 5% corresponded to adverse biological effects. Smetanová et al. (2014) found that chronic toxicity msPAF values of 0.00023% and 0.0013% corresponded to 5 and 10% changes, respectively in SPEAR index values. The SPEAR index is a widely used measure of aquatic macroinvertebrate composition. Similarly, Munz et al. (2017) found that acute toxicity msPAF values of 0 to 2.1% in Swiss rivers corresponded to SPEAR index values of 50 to 15, respectively. These studies indicate that GBR waterways with msPAF greater than 10% of aquatic species are highly likely to experience large biological change. More importantly, waterways with msPAF values of less than 5% and even less than 1% (i.e., the low and very low risk classes, respectively (see below) may experience adverse effects to species that are sensitive to pesticides based on their mode of action.

The PRM is used by both the GBRCLMP and MMP to estimate the risk associated with pesticide exposure, but the way the PRM is reported is different for the two programs because of the way pesticides are sampled. The GBRCLMP analyses the pesticide concentrations in grab samples of water collected over the entire year and report the PRM as the average of multiple daily PRM scores over the wet season (182 days) (Warne et al., 2020a). The MMP analyses the pesticide content of passive samplers that are deployed for multiple weeks at a time over the entire year, calculating the PRM for each deployment and reporting the highest PRM score over the year as the annual risk (Gallen et al., 2019b; Thai et al., 2020). These estimates of risk are compared to the pesticide target – to protect at least 99% of aquatic species at the mouth of GBR waterways. This target was proposed by Brodie et al. (2017) and subsequently adopted in the Reef 2050 WQIP (Australian Government & Queensland Government, 2018). The PRM risk estimates are distributed into five risk classes – very low risk (≥99% species protected), low risk (95 to <99% species protected), moderate risk (90 to <95% species protected), high risk (80 to <90% species protected) and very high risk (<80% species protected).

The results of the PRM are not absolute values, rather, they are estimates of the risk posed and they only estimate the risk posed by the 22 pesticides included in the PRM (Warne et al., 2020a). As over 74 pesticides have been detected in GBR fresh waterways, the PRM is likely to underestimate the actual toxicity of all pesticides in water samples. In addition, Warne et al. (2020a) states that "a PRM risk estimate of 95% species protection should not be interpreted literally to mean that exactly 95% of species will be protected. Rather, the estimates were developed to determine if the pesticide target has been met or whether further land management change is required to reduce pesticide runoff and meet the target. Importantly these estimates of pesticide mixture toxicity can be used for relative assessments: 1) spatially to prioritise catchments, basins, or regions for on-ground improvements; and 2) temporally, to assess changes in the pesticide mixture toxicity at locations over time and improvements towards the target". Studies that have examined the relationship between PRM risk values (msPAF values) and adverse ecological effects are summarised in the next section.

Spatial variation in freshwater pesticide mixture risk

The risks posed by pesticides were spatially quite varied. For the 12 sites over the six years, the risk ranged from very low (>99% of aquatic species being protected) over four wet seasons in the Daintree and Burdekin rivers and once in the Burnett River, to very high (<80% of aquatic species being protected) over four wet seasons in Barratta Creek and six wet seasons in the Sandy Creek (Table 22). The lowest estimated level of protection was 57.9% of aquatic species for Sandy Creek in 2020/21, although at this site the estimated level of protection was never greater than ~67% of aquatic species. The average difference between the maximum and minimum risk values across all sites and years was 38% of aquatic species. Only 13% of the 68 estimates of wet season risk for the focus sites (Table 22) met the pesticide target at the river mouth (Australian Government & Queensland Government, 2018). The remaining 87% of the wet season risk values were low risk (47% of samples), moderate risk (~18%), high risk (~7%) and very high risk (15%). Warne et al. (2020b) calculated the risk posed by pesticides for considerably more waterways (i.e., for 31 GBR waterways) but only for samples collected between 2015/16 and 2017/2018 found very similar percentages of the various risk classes - the percentage of very low, low, moderate, high and very high risk datasets were 15%, ~42%, ~22%, ~9% and ~12%, respectively.

Over the six years studied in this Evidence Review, the average risk posed by pesticides was greatest in the Mackay Whitsunday region, where on average approximately 19% of aquatic species were estimated to be adversely affected. The average risk posed by pesticides in the other regions was

Burdekin (~10% affected), Wet Tropics, Burnett Mary and the Fitzroy (all ~3% affected). Although determined by using a different method, the ranking of the risk posed to regions determined by Warne et al. (2020b) was identical – decreasing in the order Mackay Whitsunday, Burdekin, Wet Tropics, Burnett Mary and the Fitzroy regions. The current spatial distribution of risk among regions and waterways is consistent with a risk assessment conducted as part of the 2017 SCS report based on msPAF analysis of five PSII herbicides[14] over the previous six years of GBRCLMP data 2010/11 to 2015/16 (Waterhouse et al., 2017).

Table 22. Pesticide risk expressed as percent species protected at the 12 focus catchments between 2016 and 2022 as calculated using the PRM (Warne et al., 2020a). Risk classes: very low (VL) risk (≥99% species protected, dark green), low (L) risk (95 to <99% species protected, light green), moderate (M) risk (90 to <95% species protected, yellow), high (H) risk (80 to <90% species protected, orange) and very high (VH) risk (<80% species protected, red). Data sourced from Water Quality and Investigations (2023b).

Region	Catchment	2016/17	2017/18	2018/19	2019/20	2020/21	2021/22
Wet Tropics	Daintree River at Lower Daintree	ND	ND	99.2 (VL)	99.9 (VL)	99.7 (VL)	99.6 (VL)
	Russell River at East Russell	95.5 (L)	93.4 (M)	97.9 (L)	97.1 (L)	97.9 (L)	96.7 (L)
	Tully River at Euramo	92.6 (M)	93.3 (M)	95.5 (L)	96.9 (L)	95.1 (L)	95.3 (L)
Burdekin	Barratta Creek at Northcote	73 (VH)	77.6 (VH)	84.2 (H)	82 (H)	79 (VH)	70.7 (VH)
	Haughton River at Powerline / Giru Weir Tailwater	93.9 (M)	97.5 (L)	96.2 (L)	94.7 (M)	97.2 (L)	91.0 (M)
	Burdekin River at Home Hill Inkerman Bridge	98.5 (L)	99.4 (VL)	99.5 (VL)	99.0 (VL)	99.6 (VL)	95.8 (L)
Mackay Whitsunday	O'Connell River at Caravan Park	87.6 (H)	92.1 (M)	91.9 (M)	92.3 (M)	87.1 (H)	89.8 (H)
	Sandy Creek at Homebush	61.1 (VH)	58.3 (VH)	63.5 (VH)	66.6 (VH)	57.9 (VH)	63.9 (VH)
	Plane Creek at Sucrogen Weir	ND	ND	95.9 (L)	94.2 (M)	95.3 (L)	92.8 (M)
Fitzroy	Fitzroy River at Rockhampton / Fitzroy River Water	98.0 (L)	97.6 (L)	97.9 (L)	96.9 (L)	98.0 (L)	96.2 (L)
Burnett Mary	Burnett River at Ben Anderson Barrage Headwater / Quay Street Bridge	98.2 (L)	96.9 (L)	98.7 (L)	98.1 (L)	99.0 (VL)	95.6 (L)
	Mary River at Home Park / Churchill Street	97.2 (L)	96.7 (L)	94.1 (M)	97.5 (L)	97.6 (L)	96.5 (L)

Temporal variation in freshwater pesticide mixture risk

There was also temporal variation in the risk posed by pesticide mixtures. The largest variation in wet season risk values over the six years for an individual waterway occurred at Barratta Creek with an absolute difference of ~13% of aquatic species (Table 22). The average variation for all sites and years was considerably smaller at 4%. Temporal variation was greatest in the Burdekin region with an average difference across sites and years of ~8%. The temporal variation in the Mackay Whitsunday region was ~6%, followed by the Burnett Mary (3.7%), the Wet Tropics (3.5%) and finally the Fitzroy (1.3%). A similar study but examining 28 sites in GBR waterways between 2015/16 and 2017/2018 (Warne et al., 2020b) found very similar temporal variation to the current study. They stated that the largest

[14] ametryn, atrazine, diuron, hexazinone and tebuthiuron

difference was an absolute difference of 8.5% for the Pioneer River and that the average difference at all GBR waterways that had at least two years data was 3.1% by (Warne et al., 2020b).

Contribution of individual pesticides to pesticide mixture risk

Across the 12 focus sites there were considerable differences in the major contributors to the PRM values, but despite annual variation in the PRM values, there was clear within-site consistency in the major contributors across the six monitoring years (Figure 10). There were four pesticides that were the major contributors to all focus waterways – atrazine, diuron, imidacloprid and metolachlor (Figure 10) but their contribution varied by waterway and region. Diuron was a major contributor to PRM values in waterways in the Wet Tropics (averages of 30 – 60% across sites and years), the Burdekin (averages of 5 – 40%) and in the Mackay Whitsunday region (averages of 23 – 40%) (Figure 10, **Table A1**), but only a minor contributor in the Burnett Mary region (averages of 10 – 18%). Imidacloprid was another major contributor to PRM values in all regions except the Fitzroy region, contributing on average 12 – 35% of the PRM values. Metolachlor was the largest contributor to PRM values in Burnett Mary waterways (averages of 50 – 62%), the Fitzroy (86%), Burdekin (50%) and the Haughton rivers (33%). Atrazine was a major contributor to PRM values in most Burdekin (averages of 21 – 28%) and Mackay Whitsunday waterways (average of 10% at Sandy Creek).

Apart from these four pesticides listed above, three other pesticides are worthy of mention. Metsulfuron-methyl (a herbicide) was the major contributor to PRM values in Plane Creek (average 34% across four years) (Figure 10, **Table A1**), likely because of the high percentage of urban land use (14%) in the catchment (Water Quality & Investigations, 2023a). This herbicide is also prevalent in recent PRM scores at new sites in the Burnett Mary region (Water Quality & Investigations, 2023a; 2023b). Isoxaflutole has recently become a more prevalent contributor to PRM values in Barratta Creek (13% and 7% in 2020/21 and 2021/22, respectively) in the Burdekin (Figure 9, **Table A1**). Lastly, imazapic is always an important contributor to PRM values in the Mackay Whitsunday region (e.g., average 8% across six years in Sandy Creek) (Figure 10, **Table A1**).

Only two other pesticide risk assessments of GBR waterways have been conducted using the msPAF method across multiple years (Star et al., 2018; Waterhouse et al., 2017). Neither study reported on the contribution of individual pesticides to the PRM values, but Warne et al. (2020a) reported the contribution of three pesticide groups – PSII herbicides, other herbicides and insecticides. Between 2015/16 and 2017/18 the contribution of the three pesticide groups varied extensively reflecting changes in land use at waterways and in regions. The estimated percent contributions of PSII herbicides ranged from 0 to 65%, other herbicides ranged from 0 to 97% and insecticides ranged from 0 to 98% for the 35 GBR basins. At the region level there were three different scenarios. In Cape York the dominant contributor was PSII herbicides. In the Wet Tropics and Mackay Whitsunday regions PSII herbicides and other herbicides were the major contributors. In the Burdekin, Fitzroy and Burnett Mary regions other herbicides were the main contributor supported by PSII herbicides (Warne et al., 2020b).

Spilsbury et al. (2020) determined the contribution of fifty pesticides to the pesticide mixture risk using the CA model of joint action. Averaged across 3,741 samples from 18 GBR rivers between 2011 and 2016 they found 16 pesticides contributed to >99% of the pesticide mixture toxicity. The four main contributors were the same as those found in this Evidence Review, but their ranking was different: diuron (45.7%), imidacloprid (26.1%), atrazine (14.5%) and metolachlor (3.5%). Further analysis revealed that while these four pesticides on average accounted for approximately 90% of the pesticide mixture toxicity, 24 different pesticides were ranked in the top five contributors in at least one sample (Spilsbury et al., 2020). No other pesticide risk assessments of GBR waterways have determined the contribution of individual or groups of pesticides to the risk posed by mixtures.

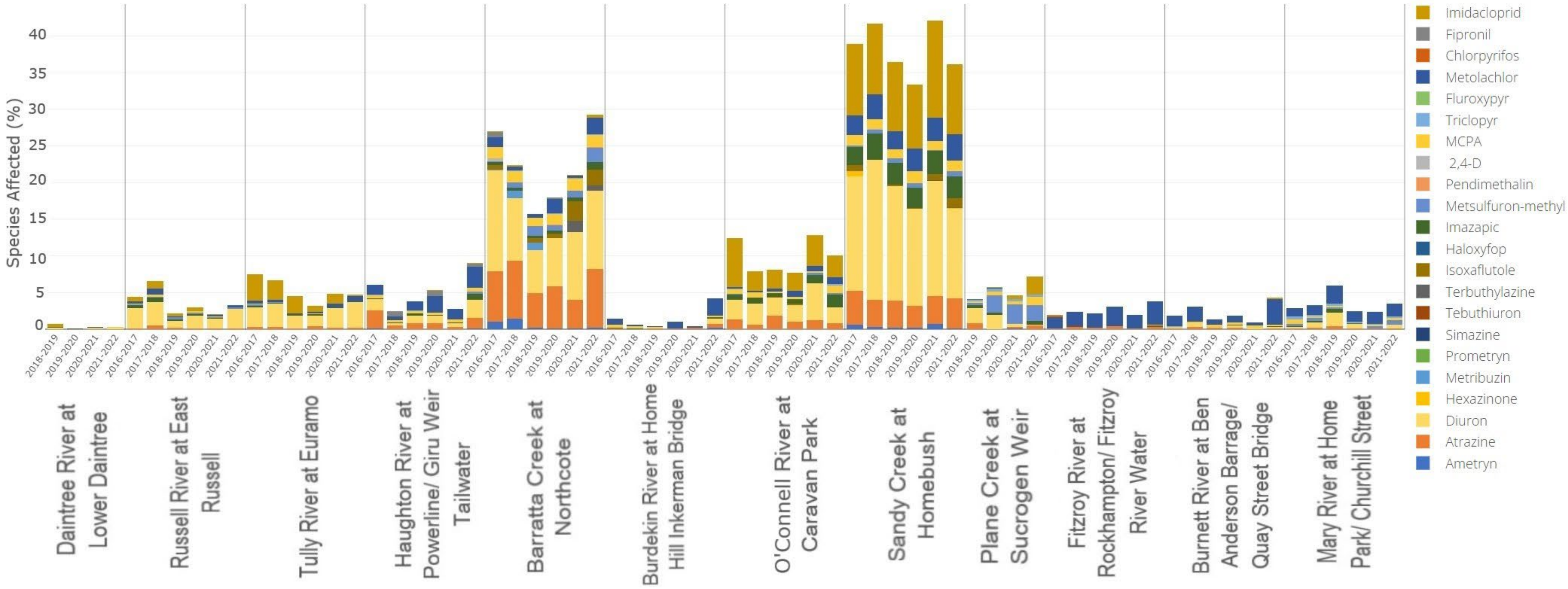


*Figure 10. Individual pesticide contributions to annual wet season PRM values (expressed as percent species affected) for the 12 focus waterways between 2016/17 and 2021/22. Data sourced from Water Quality and Investigations (2023b). See Appendix 2 for **Table A1** for more detail.*

Pesticide risk in Palustrine Wetlands

Vandergragt et al. (2020) compared the average aqueous concentrations estimated by passive samplers to either the PC99 or PC95 values obtained from GVs (either proposed by King et al., 2017a; 2017b or the current Australian and New Zealand GVs (ANZG, 2018)). There were 18 instances where the average aqueous pesticide concentrations were greater than the relevant GVs. In the two largest exceedances the average concentrations were 48 and 58-times larger than the relevant GVs (PC95 for diuron). The estimated level of protection provided in the palustrine wetlands was up to 44% of species lower than the prescribed level of protection (i.e., 51% compared to 95% species protection). On average the wetlands protected 13% less species than prescribed and the median wetland protected 8% fewer species. For seven of the 18 exceedances the wetlands protected up to 5% less species than was prescribed. The exceedances occurred for atrazine in one wetland, diuron in four wetlands, hexazinone in four wetlands, metolachlor in three wetlands, and DDE (a metabolite of DDT) in 1 wetland. The risk posed by pesticides to wetlands was greatest in the Mackay Whitsunday and Burnett Mary regions. Vandergragt et al. (2020) concluded that individual pesticides pose a substantial threat to the aquatic ecosystems in some of the monitored wetlands. The risks posed by mixtures of pesticides in the 22 palustrine wetlands are currently being assessed (Warne & Vandergragt, *in prep.*) using the PRM (see earlier sections for details). The resulting risk estimates can only be the same or larger than those for individual pesticides.

Spatial variation in marine pesticide mixture risk

Only three years of the MMP data have been assessed for risk using the PRM (Gallen et al., 2019b; Thai et al., 2020) (Table 23) as the MMP was not reporting pesticide data from 2018/19 till 2022/23. Each site was subject to between one and nine deployments of passive samplers. Variation in the number of deployments was usually caused by loss of samplers during deployment. At some sites, the MMP reported very few data; notably at the Repulse Bay site where there were data for a single deployment in 2016/17 and at the Sandy Creek Site where there were two deployments in 2017/18 – both outside the wet season. Table 23 and Figure 11 represent data for the deployments with the highest percent species affected at each of the 11 monitoring sites in each of the three years. During the three years assessed, all the Wet Tropics monitoring sites (Low Isles, High Island, Normanby Island, Dunk Island and Lucinda Jetty) and the Fitzroy (North Keppel Island) monitoring site experienced a very low risk (i.e., ≥99% species protection) throughout the year. Only the monitoring sites in the Mackay Whitsunday and Burdekin regions experienced lower levels of species protection (see Table A2 for % contribution data).

Table 23. Pesticide risk at the 11 fixed marine sites between 2016 and 2019 calculated using the PRM (Warne et al., 2020a). Risk classes: very low (VL) risk (≥99% species protected), low (L) risk (95 to <99% species protected), moderate (M) risk (90 to <95% species protected), high (H) risk (80 to <90% species protected) and very high (VH) risk (<80% species protected). Data sourced from (Gallen et al., 2019b; Thai et al., 2020).

Region	Passive Sampling Site	2016/17	2017/18	2018/19
Wet Tropics	Low Isles	99.8 (VL)	99.6 (VL)	99.8 (VL)
	High Island	99.5 (VL)	99.2 (VL)	99.5 (VL)
	Normanby Island	ND	99.6 (VL)	99.5 (VL)
	Dunk Island	99.8 (VL)	99.4 (VL)	99.6 (VL)
	Lucinda	99.6 (VL)	99.3 (VL)	99.6 (VL)
Burdekin	Barratta Creek	99.2 (VL)	96.4 (L)	98.1 (L)
Mackay Whitsunday	Repulse Bay	99.8 (VL)	98.9 (L)	92.1 (M)
	Flat Top Island	82.3 (H)	78.1 (VH)	92.2 (M)
	Sandy Creek	96.8 (L)	99.5 (VL)	99.1 (VL)
	Sarina Inlet	98.5 (L)	98.5 (L)	97.2 (L)
Fitzroy	North Keppel Island	99.8 (VL)	99.4 (VL)	99.8 (VL)

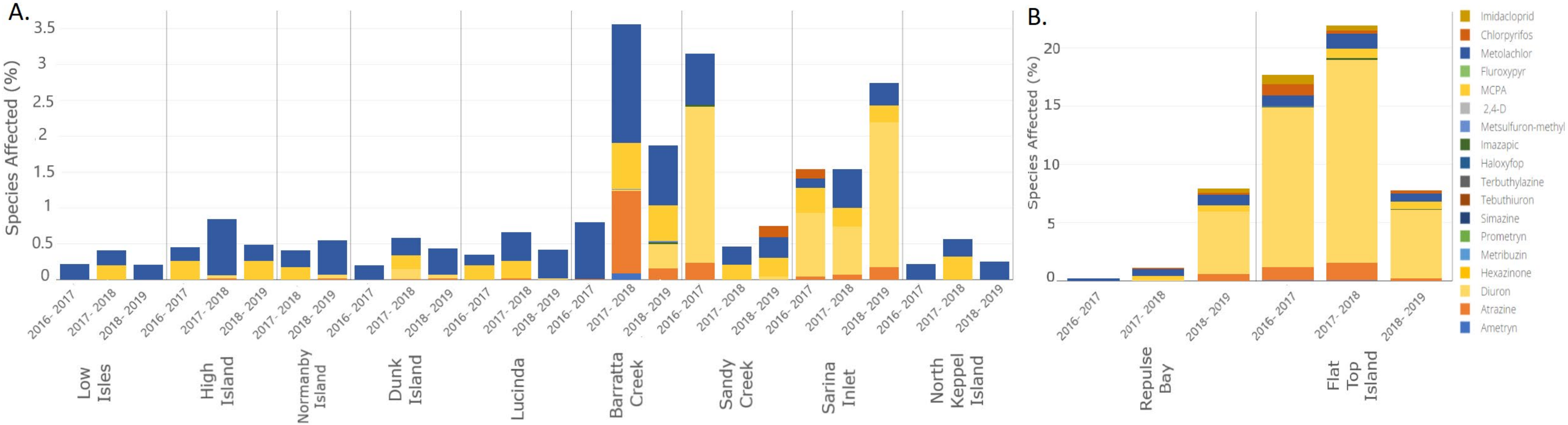


*Figure 11. Individual pesticide contributions to annual wet season PRM values (expressed as per cent species affected) for the 11 fixed marine monitoring sites between 2016/17 and 2018/19. A) majority of sites with PRM values <4% affected, and B) Flat Top Island and Repulse Bay where the risk was markedly higher. Data sourced from (Gallen et al., 2019b; Thai et al., 2020). See **Table A2** (Appendix 2) for more detail.*

Temporal variation in marine pesticide mixture risk

Almost without exception, the highest risk occurred during the wet season (November to April); the exception being the site at Barratta Creek which, in 2017/18, experienced the highest risk (94.6% species protection) during July 2017. The lowest estimated level of species protection of 78.1% was at Flat Top Island (referred to in Gallen et al. (2019b) as Round Top Island) in December 2017, placing this site in the very high risk class (<80% protected) at that time. This same site experienced high risk (80% - <90% species protection) in February 2017 and February 2018 and moderate risk (90% - <95% species protection) in March, April and December 2018. Moderate risk was estimated for Repulse Bay sites in January 2019. The other two Mackay Whitsunday sites (Sarina Inlet, Sandy Creek) were estimated to be at low risk (95% - <99% species protection) between the months of January and March in most years except when wet season deployments were unavailable (lost). Similarly, the Barratta Creek site in the Burdekin region was estimated to be at very low risk throughout 2016/17 (passive samplers were lost in February and March 2017), and low risk in July 2017, January 2018, and February, March and May 2019. Although previous MMP reports used different risk metrics, all indicated similar spatial risk profiles, with the Mackay Whitsunday sites showing the highest risk, usually followed by Barratta Creek, then individual Wet Tropics sites, and finally the North Keppel Island site in the Fitzroy Region (e.g., Gallen et al., 2014; 2016; Grant et al., 2017). The spatial risk at the fixed marine sites across NRM regions is also consistent with spatial risk reported for freshwater sites (Table 22) at a regional scale.

With so few years of data available, it is difficult to assess whether there is an underlying trend in the risk posed by pesticides to marine ecosystems. However, a recent trends analysis in the concentrations of five PSII herbicides over the entire 14 years of MMP reporting (Taucare et al., 2022) did indicate that there were some increasing trends in marine waters. Significant increasing trends were most pronounced at those sites less influenced by wet season pulses (Skerratt et al., 2023), such as atrazine at Low Isles, North Keppel Island and Sarina Inlet, hexazinone at Low Isles and Sarina Inlet and diuron at Sarina Inlet (Taucare et al., 2022). The temporal variation in the risk posed by pesticide mixtures can only be assessed by applying the current PRM method to pesticide concentrations from earlier MMP reports. This is possible and should be undertaken, but is beyond the scope of this review.

Contribution of individual pesticides to pesticide mixture risk in marine ecosystems

The chemicals that contribute to PRM for each of the deployments representing the highest annual risk values are presented in Figure 10. It is important to note that the pesticides analysed in the MMP passive sampling program differed from that in the GBRCLMP program; specifically, triclopyr, pendimethalin, isoxaflutole and fipronil were not included in the MMP analyses. Despite the wide geographical range of the passive sampler deployments, the pesticides that contributed to mixture toxicity were remarkably similar. As with the freshwater catchments, only a few pesticides dominated the contribution to PRM values – metolachlor, MCPA, diuron and atrazine. Metolachlor was the only pesticide that made significant contributions to PRM values at all 11 focus sites, which is testament to the long half-life of this chemical in water (King et al., 2017a; Mercurio et al., 2016). Across all three years in the Wet Tropics sites and the Fitzroy site, metolachlor accounted for 42 to 100% (Figure 11, **Table A2**) of the PRM values with MCPA accounting for the remainder (0% to 57%) most of the time (Figure 11, **Table A2**). At sites closer inshore, where residence time in the water column is likely to be shorter, the contributing pesticides were more varied. At Barratta Creek in the Burdekin region in particular, a wider variety of pesticides, including metolachlor (45% to 99%), MCPA (0% to 27%), atrazine (1% to 32%) and diuron (0% to 18%) contributed to the PRM values with little consistency between years (Figure 11, **Table A2**). In the Mackay Whitsunday region, diuron dominated the PRM score in those years when the PRM value indicated more than a very low risk. At Flat Top Island, diuron accounted for 76% to 79% of the PRM value (Figure 11) over the three years. At the other Mackay Whitsunday sites (Repulse Bay, Sandy Creek and Sarina Inlet) diuron accounted for 44% to 73% of the PRM value, but only in those years when the PRM values were <99% species protection. In other years, metolachlor (38% to 54%) and MCPA (35% to 45%) dominated (Figure 11, **Table A2**).

The two insecticides, chlorpyrifos and imidacloprid, were only evident as contributors to PRM values at Mackay Whitsunday sites (Figure 11, **Table A2**). Chlorpyrifos, in particular, accounted for 20% of the PRM value in the 2018/19 year at Sandy Creek (Figure 10, **Table A2**). The prevalence of chlorpyrifos at the MMP sites compared with the absence of chlorpyrifos in the GBRCLMP analyses is likely explained by the relatively low water solubility of this chemical. The PDMS passive samplers used by the MMP, combined with the use of gas chromatography analysis (Thai et al., 2020), means that the MMP program is much more likely to detect this pesticide compared to the GBRCLMP program in the catchments, which relies on grab samples and a liquid chromatography method that is less likely to detect the low quantities that may be dissolved in water samples (Water Quality & Investigations, 2023c).

Modelling studies assessing the scale of pesticide risk

The estimates of spatial risk posed by pesticides to GBR ecosystems presented above are limited to freshwater, wetland and marine monitoring sites. Monitored waterways are well represented along the entire GBR; however, the 11 MMP sites provide few datapoints for the estimation of risk relative to the enormous spatial scale of the GBR. However, there have been a few numerical estimates, based on modelling, of the spatial scale of risk posed by pesticides to marine and estuarine ecosystems of the GBR ecosystems, including habitats of high ecological value including seagrass meadows and coral habitats (Table 24). Three risk assessments mapped marine habitats where the additive effects of six PSII herbicides exceeded toxicity thresholds for phototrophs (e.g., seagrass) or earlier GVs (Devlin et al., 2012; Lewis et al., 2012; 2013). One study interpolated measured herbicide concentrations from the marine environment (Lewis et al., 2012), while the other two simulated PSII concentrations in flood plumes of freshwater by coupling catchment load data with plume extent (based on salinity values estimated from satellite data) (Devlin et al., 2012; Lewis et al., 2013). The most recent assessment of the scale of risk coupled recent catchment loads for diuron alone with a 3D hydrodynamic model to simulate diuron between 2016–2018, including three wet seasons, in hourly increments (Skerratt et al., 2023). Exceedances of the most recent PC99 GV (0.075 µg L^{-1}) applied in the PRM (Warne et al., 2020a) were mapped for the entire GBR over this period (Skerratt et al., 2023).

All four of the above studies predicted the greatest risk to marine species by PSII herbicides (or diuron alone) is in estuarine and coastal waters close to the end-of-catchment All agreed that the marine habitats in the Mackay Whitsunday region would be among the most at-risk with respect to PSII herbicides, generally followed by those near the Wet Tropics and Burdekin (adjacent to Barratta Creek) regions. Risk to marine habitats of the Burnett Mary and Fitzroy regions were considered to be lower, with one exception in the Fitzroy region (reported in Lewis et al., 2012), where a very low GV for tebuthiuron was applied, increasing the apparent risk. Three studies assessed exceedances of toxicity thresholds or GVs over seagrass meadows and coral habitats (Table 24). Predicted area of exceedances ranged from 175 – 881 km^2 in seagrass habitats and 20 – 450 km^2 over coral habitats (Devlin et al., 2012; Lewis et al., 2013; Skerratt et al., 2023). The larger predicted areas of impact to seagrass and coral habitats (made using satellite-derived plume extent data): 1) applied toxicity thresholds or GVs that were often lower than the most recent values used in the PRM; and 2) accounted for additive toxicity of only six PSII herbicides (Devlin et al., 2012; Lewis et al., 2013), rather than the 22 pesticides included in the PRM (Warne et al., 2020a). The lower areas of risk to coral and seagrass predicted from the hydrodynamic modelling of diuron dispersal (Skerratt et al., 2023): 1) applied the most recent GV for diuron (Warne et al., 2020a); and (2) did not account for additional risk posed by the presence of other pesticides in the freshwater plume events. Regardless of the limitations of these methods, all demonstrate the likelihood that substantial areas of coastal seagrass and coral habitat are regularly exposed to harmful concentrations of PSII herbicides. Importantly, the plume dynamics revealed in Skerratt et al. (2023) demonstrate that it is likely pesticide risk has been underestimated in the GBR marine environment due to the inability of individual monitoring locations to adequately describe the vast spatial extent of the plumes in a dynamic coastal ocean environment.

Although focusing on a single herbicide, the Skerratt et al. (2023) diuron simulation offers the most promising approach to predict exposure of and risk to estuarine and marine habitats of the GBR to pesticides. Advantages over other methods include: uninterrupted plume modelling based on current and tidal data; hourly temporal resolution allowing exposure periods of exceedances to be assessed and validated against passive sampler concentrations over identical periods; exposure and risk simulations at the water surface and at depth; and the future capacity to account for all pesticides in PRM using msPAF. Other risk assessments that attempted to incorporate the potential effects of PSII herbicides with other water quality parameters such as chlorophyll *a* and TSS did not present contributions of PSII herbicides separately and cannot be directly compared with those discussed above (Petus et al., 2016; Waterhouse et al., 2012). The risks posed by pesticides to floodplain wetlands in the GBR catchment area were also assessed as part of the 2017 SCS (Waterhouse et al., 2017). Land use data informed risk categories which were then mapped across floodplain wetlands to generate estimates of total area at *high* to *very high* risk. The modelled risk to wetlands would appear to have been corroborated by Vandergragt et al. (2020) who recently estimated relatively high risk at 22 palustrine wetlands in the GBR catchments. No further advances have been made in validating this large scale of high risk to wetlands (2,870 km^2) with monitoring and the PRM.

Modelling of PRM values in freshwater waterways was also undertaken by Warne et al. (2020a). The model used a forward and backward stepwise regression to develop relationships using % land use values, hydrological variables and site-specific variables that could accurately predict PRM values. These models were derived using pesticide monitoring data. As the relationships use percent land use values for the land above the monitoring sites they can be used to predict PRM values at any point on a waterway provided values for the relationship parameters are available. The relationships were then used to predict the PRM values for the period 2015/16 to 2017/18 at all 35 basins in the GBR catchment area, the 6 NRM regions and the entire GBR catchment. The PRM values (expressed as % of aquatic species affected) for the 35 basins ranged from <1 (very low risk) to 29% (very high risk, with regional risk profiles matching other studies (Table 24). The predictions for basins, regions and the GBR catchment area assume that each basin is drained by a single waterway and they estimate the PRM at the mouth of that theoretical waterway. As such, care should be applied when interpreting estimates of the risk posed by pesticides as they are aggregate or summary values and may not reflect the risk faced at finer spatial scales which could face higher or lower risks. For example, the end-of-catchment estimate is a combination of the risk of all its tributaries which, as they are closer to the source of pesticides, may face considerably greater risk. Similarly, a region with a low risk could contain one or more basins and/or catchments that face a markedly higher or lower risk. This occurs in the Burdekin NRM region, which faces a low risk from pesticide mixtures, while the Haughton basin faces a high risk.

Table 24. Studies reporting the spatial scale of pesticide risk.

Risk assessment type	Method	Main findings
Modelled risk of PSII herbicides to phototrophic species. (Lewis et al., 2012)	Assessed the additive risks posed by six PSII herbicides in four NRM regions: Wet Tropics, Burdekin, Mackay Whitsunday and Fitzroy. Risk was based on measured concentrations (additive, 2005-2008) exceeding phototoxicity thresholds or GBRMPA GVs (2010). Spatial risk was assigned based on interpolation of concentrations between monitoring sites.	Risk was additive, effects of PSII herbicides expected to affect phototrophs was greatest in the Mackay Whitsunday and Fitzroy regions followed by the Wet Tropics and Burdekin. Study did not account for non-PSII herbicides. Total area of risk was not quantified.
Modelled exposure of PSII herbicides. (Devlin et al., 2012)	PSII herbicide load coupled with flood plume distribution from satellite imagery to generate quantitative surface exposure (E) values (accounting for frequency 2000-2010) for PSII herbicides (whole of GBR). Expressed as four exposure levels. The modelled surface exposures were overlaid with maps of distribution of coral reefs and seagrass meadows to assess scale of exposure to each category.	Estimated exposure to PSII herbicides in the medium to very high E categories were in the Wet Tropics and Mackay Whitsunday regions, totals: coral: 450 km^2, seagrass: 881 km^2. Categories were relative rather than absolute against a GV or toxicity threshold. The *risk* expressed in this study was therefore of exposure rather than harm.
Modelled risk of PSII herbicides	Catchment load data from 2009-2011 coupled with salinity values (estimated from satellite data) to predict	Risk (minor to major) where PSII herbicides expected to affect photosynthesis in phototrophs was

Risk assessment type	Method	Main findings
to phototrophic species. (Lewis et al., 2013)	concentrations of 6 PSII herbicides during flood plumes. Three methods used to assess mixture risk: 1) additive effects of PSII herbicides; 2) msPAF PSII herbicides; and 3) exceedances of individual pesticide GVs. Consequences values were based on expert opinion (*no risk* to *catastrophic*).	greatest in the Mackay Whitsunday >Wet Tropics, Burdekin (due to Barratta Creek and Haughton Rivers) >, Fitzroy and Burnett Mary NRM regions. Total areas of potentially affected coral: 174 km^2, seagrass: 639 km^2. Risk expressed in this study did not account for non-PSII herbicides.
Risk from PSII herbicides to floodplains. (Waterhouse et al., 2017)	The area of floodplain wetlands at high to very high risk from pesticide exposure were estimated based on a 2015 Department of Science, Information Technology and Innovation (DSITI) land use report which attributed hazard scores to land use (e.g., sugarcane, horticulture. Hazard scores were then mapped across floodplain wetland habitats.	A total area of 2,870 km^2, of floodplain wetlands were described as at high to very high risk from pesticide exposure. Highest risk was to coastal floodplains near sugarcane cropping. The greatest areas of floodplain wetlands at risk were in the Comet, Herbert, Plane, Pioneer and Dawson Rivers. More emphasis should be placed on assessing risk to GBR wetlands by applying methods consistent with the PRM.
Risk from simulated diuron entire GBR lagoon (Skerratt et al., 2023).	SedNet catchment model (estimated diuron loads) coupled with a 3D eReefs marine model (2 hour steps) to assess diuron dispersal across the GBR from 2016-2018. Validated with MMP measurements during the same period. Simulated diuron concentrations were compared with PC99 values and spatially across seagrass and coral habitats.	The simulation revealed dynamic diuron concentrations, strongly linked to river discharge and tides. Diuron was highly localised to the plume footprints and was dispersed northwards along the coastline by the prevailing currents. Diuron concentrations of 0.075 $\mu g\ L^{-1}$ (PC99) often exceeded 1,000 km^2 (peaking at 1,400 km^2), including 175 km^2 seagrass and 20 km^2 coral habitat. This scale of risk identified for coral and seagrass is likely underestimated since diuron comprises a high proportion of total pesticide risk at marine sites.
Risk from 22 pesticides, entire GBR freshwater systems. (Warne et al., 2020a)	Relationships using % land use values, hydrological variables and site-specific variables that could accurately predict pesticide mixture risk values for 22 pesticides (calculated using pesticide monitoring data) were developed using forward and backward stepwise regression. As the relationships use percent land use values for the land above the monitoring sites, they can be used to predict PRM values at any point on a waterway provided values for the relationship parameters are available. The relationships were used to predict the PRM values for the period 2015/16 to 2017/18 at all 35 basins in the GBR catchment area, the 6 NRM regions and the entire GBR catchment area.	The PRM values (expressed as % of aquatic species affected) for the 35 basins ranged from <1 (very low risk) to 29% (very high risk). The percentage of basins in each risk class was: very low risk (~46%), low risk (20%), moderate (~23%), high risk (~6%) and very high risk (~6%). The very high risk basins were the Pioneer and Plane in the Mackay Whitsunday region. The estimated PRM values for the NRM regions were: Cape York (<1% aquatic species affected), Burdekin (2%), Burnett Mary (3%), Fitzroy (4%), Wet Tropics (5%) and Mackay Whitsunday (19%).

Key findings:

- Based on previous sections, the most appropriate method to evaluate risks posed by pesticides to GBR ecosystems was to assess the percentage of species potentially affected by the mixtures (Warne et al., 2020a) reported in the GBRCLMP and MMP (data available from 2016/17). Applying the GVs developed for the PRM enabled direct comparison for both freshwater and marine ecosystems and comparison to the Reef 2050 WQIP pesticide target of protecting at least 99% of species at the boundary of the GBRWHA.
- Focus sites in the Mackay Whitsunday region (Freshwater: Sandy Creek and O'Connell River; Marine: Flat Top Island, Sarina Inlet, Repulse Bay) were generally at higher risk than most other locations. Barratta Creek was also at high to very high risk across the six monitoring years. Other sites in the Burdekin (i.e., Haughton River) and Wet Tropics regions were at lower risk followed by sites in the Fitzroy and Burnett Mary regions and the Daintree River and Burdekin River freshwater sites.
- The end-of-catchment sites showed relatively consistent risk across the six years. Similarly, those marine sites located far from riverine sources of pesticides were also stable with respect to risk, while those marine sites more likely to be influenced by riverine pulses showed greater variability. Care needs to be exerted in interpreting estimates of the risk posed by pesticides as they are aggregate or summary values and may not reflect the risk faced at finer spatial scales which could face higher or lower risks.
- Long-term trends analyses suggest an increase in the concentrations of PSII herbicides in marine waters; however, the increased importance of non-PSII herbicides such as metolachlor and MCPA as contributors to risk (i.e., in PRM values) at MMP sites further from the riverine sources of pesticides, suggests that an assessment of trends of PSII herbicides alone may underestimate the overall trends in pesticide risk. The trends in risk due to all pesticides will only be apparent when longer data series are assessed with a consistent metric (i.e., PRM, Warne et al., 2020a).
- Risk to aquatic ecosystems typically reduces with distance from the source of pesticides. This is evident by the PRM values (expressed as percent species protected) at freshwater monitoring sites and palustrine wetlands having larger exceedances of the PC99 than marine sites.
- A diuron dispersal simulation (3D hydrodynamic model (Skerratt et al., 2023)) also showed marine exceedances of PC99 GVs were highest closest to the source and dispersed in plumes in a northerly direction due to prevailing currents. The simulation showed broad spatial risk patterns similar to those generated from GBRCLMP and MMP data.
- The diuron guideline value of 0.075 µg L^{-1} (PC99) (from Warne et al., 2020a) was often exceeded across 1,000 km^2 (peaking at 1,400 km^2) in the dispersal simulations from 2016 to 2018 and included 175 km^2 of seagrass and 20 km^2 of coral habitat.
- Estimated area of seagrass and coral habitats at risk from pesticide exposure were lower than some previous estimates but this could be accounted for by different methodologies. Coupled with passive sampling, the diuron simulation methodology offers the most promising approach to predict exposure of, and risk to, estuarine and marine habitats of the GBR and should be developed and validated for all pesticides in PRM.
- Finally, toxicity thresholds and GVs used in the typical risk assessments do not account for sublethal responses that can accumulate over long-term exposure to pollutants affecting the fitness, function and structure of ecosystems over years and decades (Hook, 2020). Although the assessments presented here report some risk when >1% of species are affected, they do not account for the potential effects on GBR ecosystems to the prolonged exposures to pesticides reported.

4.1.2 Recent findings 2016–2022 (since the 2017 SCS)

The review had a strong focus on recent studies and the Key Conclusions section describes all important findings from 2016–2022. This Recent Findings section instead highlights the key studies since 2016. Approximately 44 studies were found for the period 2016–2023, including studies on pesticide concentration in the GBR (n=15), pesticide effects/toxicity (n=27) and pesticide risk (n=16). Most studies that assessed pesticide distribution also assessed risk as exceedances of GVs.

Information on the spatial and temporal distribution of pesticides in the freshwater and marine ecosystems of the GBR since 2016 was primarily drawn from GBRCLMP data published in the Pesticide Reporting Portal (Water Quality & Investigations, 2020b) and MMP data. GBRCLMP data are also summarised in five reports (Ten Napel et al., 2019a, 2019b; Water Quality & Investigations, 2020a; 2021; 2023a), while MMP data are summarised in three reports (Gallen et al., 2019b; Grant et al., 2018; Thai et al., 2020). Information from these sources were contrasted with other publications that assessed pesticide distribution and the risk of exceeding pesticide GVs from 2011/12 to 2014/15 (Spilsbury et al., 2020; Warne et al., 2020b) and imidacloprid trends (2009/10 to 2015/16) (Warne et al., 2022b). Of great relevance was a recent analysis of spatial and temporal trends of PSII herbicides based on 14 years of MMP data (Taucare et al., 2022). One prominent modelling exercise simulated the spatial and temporal distribution of the PSII herbicide diuron in the GBR, as well as the spatial risk of exceeding the published guidelines for the protection of aquatic species in event flood plumes (Skerratt et al., 2023). Information on the spatial and temporal distribution of pesticides in the wetland ecosystems of the GBR since 2016 was available in only two studies: Allan et al. (2017) and Vandergragt et al. (2020). Only palustrine wetlands were considered in this report and estuaries were not assessed separately due to a paucity of data.

Approximately 27 studies published information on the observed or potential effects of pesticides on GBR species since 2016 (**Tables T1 and T2**). Five assessed indications of toxicity in the field, while 22 quantified toxicity thresholds for pesticides to GBR species in laboratory studies (4 freshwater and 18 marine). There were seven studies that reported evolving guideline values for pesticides that could be applied in GBR waters (Table 18). The combined effects of pesticide mixtures on GBR species were assessed in one publication (Stone et al., 2021), while the influence of other simultaneous pressures (e.g., heatwave conditions) were assessed in seven publications since 2016 (Table 21).

Studies that assessed the risk of pesticides to the freshwater, estuarine, wetlands, and marine ecosystems of the GBR since 2016 included 16 that compared monitored or modelled pesticides concentrations (often as mixtures) against pesticide GVs. The 2020 publication of the PRM provided the basis to assess the risk posed by multiple pesticides (up to 22) alone or in mixtures across freshwater, wetland and marine ecosystems (Warne et al., 2020a). A diuron dispersal simulation (3D hydrodynamic model) revealed spatial risk patterns across the entire GBR consistent with those generated from GBRCLMP and MMP data (Skerratt et al., 2023). It also showed regular periods when less than 99% of species were protected from diuron across >1,400 km^2 of the GBR. Long-term trend analyses suggest an increase in the concentrations of imidacloprid in freshwaters and PSII herbicides in marine waters that may indicate increasing risk (Taucare et al., 2022; Warne et al., 2022b), but this needs to be assessed further by applying the PRM.

4.1.3 Key conclusions

What is the spatial and temporal distribution of pesticides across GBR ecosystems?

- Pesticides are ubiquitous across monitored GBR ecosystems including end-of-catchment waterways, palustrine wetlands and in estuarine and nearshore marine habitats. Detection of pesticides in seagrass, mangroves and marine sediments demonstrates exposure; however, most contemporary pesticides partition strongly into water (i.e., they have high aqueous solubility). Therefore, the spatial and temporal distribution of pesticides have been assessed based on the data from extensive water quality monitoring programs from 2016/17 onwards.
- Over 70 pesticides and their transformation products were identified in GBR waters: 74 at the end-of-catchment, 59 in palustrine wetlands and 22 in marine waters (fewer pesticides were monitored in marine samples).
- The most frequently quantified pesticides across the GBR from 2016/17 to 2021/22 were the herbicides atrazine, diuron, hexazinone, metolachlor and imazapic and the insecticide imidacloprid.
- The vast majority of pesticides across all GBR habitats were found in mixtures. For example, in 72% and 96% of all end-of-catchment and marine samples, respectively and in all palustrine wetland samples (with an average of 15 pesticides per sample).

- It was not practical to assess the distribution of 20+ pesticides across 37 freshwater sites, so this review focused on 12 pesticides at 12 end-of-catchment freshwater and estuarine sites and 11 marine sites. The 12 focus pesticides, when combined, typically accounted for at least 99% of the total toxicity of pesticide mixtures in GBR waterways. Estuarine habitats were not assessed separately due to a lack of consistent monitoring data.
- Sites in the Mackay Whitsunday region, along with Barratta Creek in the Burdekin region which featured intense cropping and lower discharge (related to rainfall), recorded consistently higher concentrations of pesticides than other locations. Sites in the Fitzroy and Burnett Mary region as well as the Daintree River (northern Wet Tropics) had the lowest maximum annual concentrations across all years.
- A diuron dispersal simulation exercise for 2016/2018 indicated concentrations were greatest near river mouths and were transported northwards within plumes, with high concentrations typically not extending far into the GBR. Rapid changes in diuron concentrations (e.g., <0.1 μg L^{-1} to > 1 μg L^{-1}) within hours highlighted the dynamic exposure of nearshore marine organisms. Not all 11 sites in the MMP, for the period studied, reliably captured flood plumes, and therefore, the results may have underestimated marine pesticide concentrations nearby.
- Pesticide concentrations were typically higher in fresh and marine waters during wet seasons compared to dry seasons, with rapid increases at the start of the wet season followed by a gradual decrease.
- There are generally insufficient observations to identify annual pesticide trends for all 12 focus pesticides since 2016/17; however, recent studies report significant increases in imidacloprid in some freshwater sites (2009/10 to 2015/16) in the Burdekin, Mackay Whitsunday and Wet Tropics regions and in PSII herbicide concentrations over 14 years of MMP monitoring, primarily in the Mackay Whitsunday and Burdekin regions.

What are the (potential or observed) ecological impacts in these ecosystems?

- Pesticides are designed to control agricultural pest species and virtually all tested pesticides were reported as harmful to non-target aquatic species of the GBR. For example, PSII herbicides, consistently impact all photosynthetic marine organisms of the GBR that have been tested, including corals and seagrass. Pesticides, or their mixtures, pose a risk if they occur at concentrations greater than a relevant toxicity threshold or guideline value.
- A review of the GVs applied to pesticides detected in the GBR, indicated that the most up to date and reliable are those developed for application in the PRM. The PRM GVs were developed in accordance with the Australian and New Zealand guidelines, are applicable to both fresh and marine ecosystems, and can be applied to assess the combined effects of 22 pesticides in mixtures - an essential criteria for application to assess risk in the GBR.
- An extensive review demonstrated that PRM protective concentration (PCx) values, including the PC99 (recommended by the Reef 2050 WQIP for application in GBR in waters at the end-of-catchment and marine ecosystems), are protective of the vast majority of GBR species (i.e., there are few GBR species that are affected at concentrations below the PRM PC values). The PRM PCx values are therefore applicable to assess the risk of pesticides (and pesticide mixtures) in the GBR.
- Experimental studies with GBR species demonstrated that the effects of mixtures of herbicides are generally additive and that low concentrations of individual pesticides (below a toxicity threshold) add to the overall effect of the mixture. These results, along with international evidence, validate the application of the PRM to assess risk to GBR ecosystems posed by simultaneous exposure to multiple pesticides. To date, there is little evidence that additives in pesticide formulations contribute to toxicity to GBR species.
- Other simultaneous pressures, including heatwave conditions and variation in light were shown to increase the sensitivity of GBR species to pesticides. Standard experimental studies used to derive GVs do not account for additional pressures and GVs, are therefore, likely to underestimate sensitivity under some conditions in the field and therefore the risk to aquatic ecosystems.

What evidence is there for pesticide risk?

- The Reef 2050 WQIP pesticide target of protecting 99% of species has consistently not been met at numerous end-of-catchment sites (e.g., ~87% of end-of-catchment (or freshwater) focus sites between 2016/17 and 2021/22). There have also been substantial shortfalls in protection recorded in palustrine wetland ecosystems (based solely on individual pesticides, not mixtures) and sometimes coastal marine ecosystems of the GBR.
- The risk metric applied (based on the most comprehensive analysis of pesticide distribution and effect available) is intended to track improvements towards the Reef 2050 WQIP targets; however, the summary risk values reported may not reflect the risk encountered at finer spatial scales which could face higher or lower risks.
- While the risk assessments were able to account for the presence of more than one pesticide (found in the vast majority of water samples), the reported risks are likely to be underestimated by not accounting for: all pesticides present (only 22); other pressures such as heat and light stress; the conservative nature of the IA model used to predict mixture toxicity; adverse biological effects occurring below the PC99 and likely cumulative sublethal effects of very prolonged exposures to pesticides in some habitats.
- The greatest risk posed by pesticides were closest to the source in palustrine wetlands, followed by freshwater and coastal marine ecosystems, with sites in the Mackay Whitsunday region and Barratta Creek in the Burdekin region estimated as being the most affected by exposure to pesticide mixtures between 2016/17 and 2021/22.
- A diuron dispersal simulation (3D hydrodynamic model) showed broad spatial risk patterns across the entire GBR similar to those generated from GBRCLMP and MMP data. It also showed regular periods when less than 99% of species were protected from diuron across >1,400 km^2 of the GBR.
- Long-term trend analyses suggest an increase in the concentrations of PSII herbicides in marine waters; however, the increased importance of non-PSII herbicides such as metolachlor and MCPA as contributors to risk (i.e., in PRM values) at some sites, suggests that an assessment of trends of PSII herbicides alone may underestimate the overall trends in pesticide risk. The trends in risk due to all pesticides across GBR ecosystems will only be apparent when longer data series are assessed with a consistent metric.

4.1.4 Significance of findings for policy, management and practice

Spatial and temporal distribution

This Evidence Review quantitatively assessed the spatial and temporal distribution of pesticides in the GBR based on datasets assembled from the most comprehensive monitoring programs available (GBRCLMP and MMP). Pesticide concentrations were driven by pesticide use, land use and rainfall patterns, with the highest concentrations found in waterways with intense sugarcane activities and lower rainfall. Pesticides were virtually ubiquitous in catchment and nearshore GBR waters and were usually present in mixtures. These findings are consistent with previous studies, with three important advances. Firstly, there have been significant increases in imidacloprid concentrations in freshwater sites (2009/10 to 2015/16) and in PSII herbicide concentrations over 14 years of MMP monitoring at several locations, indicating pesticide exposure may not be decreasing in GBR waters in accordance with targets of the Reef 2050 WQIP (Australian Government & Queensland Government, 2018), although it should be pointed out that temporal trend analysis of pesticides has been very limited to date. Secondly, the first comprehensive (but short-term) survey of palustrine wetlands found very high concentrations of pesticides across most locations, always in complex pesticide mixtures. This study represents an important first step in addressing a large data gap in long-term monitoring to assess spatial and temporal trends of pesticide distribution in an important GBR habitat. Finally, a sophisticated modelling exercise revealed a larger spatial extent of diuron dispersal in the GBR than previously reported. Diuron is transported northwards within defined boundaries of the coastal plumes, and sharp peaks in concentration occur within hours highlighting the dynamic exposure of nearshore marine organisms. The study also showed that diuron exposure is likely underestimated by current MMP monitoring since several fixed sampling sites do not reliably capture flood plumes. As most contemporary pesticides are relatively water soluble (like diuron), this study provides an estimate of the potential spatial distribution of other pesticides in the GBR.

Potential effects

The review assessed GVs that have been applied to estimate the risk of pesticides in GBR waters. It found the GVs developed for application in the PRM were generated from the most comprehensive toxicity datasets available and are applicable to both freshwater and marine species, meaning the relative risk to both ecosystems from pesticide exposure can be directly compared. The PRM also addresses the effects of multiple (22) pesticides using the msPAF method that the review found had been validated for several GBR species. The review also found that the simultaneous pressures such as heatwave and reduced light conditions can increase species sensitivity to pesticides (with additivity being the most common outcome) and that future developments of the PRM approach might account for the effects of additional stressors. Importantly, the review conducted a comprehensive assessment of the sensitivity of GBR taxa to pesticides and concluded that the PRM GVs are generally protective of GBR species and can be applied with confidence in risk assessments.

Risks posed by pesticides to GBR ecosystems

The review assessed the risk of pesticide exposure since June 2016 at 12 focus freshwater sites and 11 marine sampling sites based on the PRM approach (accounting for the 22 pesticides in the PRM). Although this method has been followed by individual reports over several GBRCLMP and MMP monitoring years, publishing of the Pesticide Reporting Portal (Water Quality & Investigations, 2020b) has made all monitoring data publicly accessible for scrutiny. Importantly the potential risk of exposure to all pesticides identified (22 individual pesticides or as mixtures) can be readily accessed across the GBRCLMP and MMP sites. This is the first time a consistent metric for risk has been applied to freshwater and marine ecosystems of the GBR to assess progress towards meeting the GBR pesticide target of 99% species protection (Australian Government & Queensland Government, 2018). **By revealing locations at highest relative risk from pesticides, the assessment provides information to focus investment and guide improvements in land management practices required to meet the pesticide target in the future.** The risk assessment also identified the individual pesticides contributing most to risk in freshwater and marine ecosystems, providing further opportunities to manage risk through substitution to pesticides with lower toxicity to non-target species. Recent studies revealed increasing trends in subsets of some pesticides over long periods. The application of the PRM to assess the total risk of a wider range of pesticides (22 so far) provides an excellent opportunity for future studies to improve our understanding of long-term trends and whether pesticide risk is changing. Although an effective program to assess long-term trends of pesticide concentrations and risk to marine ecosystems of the GBR, the MMP relies on data from a limited number of sites (11 between 2010 and 2018 and 12 from 2022) that are not spatially representative of the entire GBR. The recent diuron simulation model (using the eReefs marine model) offers the most promising approach to predict pesticide exposure of seagrass and coral habitats of the GBR, and further development and validation, incorporating all pesticides in PRM and supported by *in situ* monitoring, would present a step-change in our appreciation of pesticide risk across the entire GBR.

4.1.5 Uncertainties and/or limitations of the evidence

Spatial and temporal distribution of pesticides

- The catchment monitoring of pesticides in waterways of the GBR catchments as part of the GBRCLMP is extensive (72 unique sites monitored over the 6 years with between 34 and 51 sites monitored each year). The program used grab samples which provide concentrations at an instant in time and may underestimate or overestimate concentrations over ecologically relevant exposure periods. However, grab samples are taken frequently during the wet season and particularly during high flow events which illustrates the temporal variation in pesticide concentrations. There has been limited sampling of small coastal waterways that drain catchments with very high percentages of land used for agriculture. Such waterways may experience very high risk from pesticides.

- The most comprehensive study of pesticides in wetlands within GBR catchments is limited to 22 palustrine wetlands over two years. The survey: 1) may not have been representative of the range of wetland types; and 2) used passive sampler devices that provide average concentrations over a longer (ecologically relevant) deployment period but are likely to miss high concentration events that may cause acute harm to GBR taxa.
- There has been little recent focus on the distribution of pesticides in estuarine ecosystems of the GBR. While there are some estuarine monitoring sites in the GBRCLMP, future studies should classify and report on these as a distinct habitat. Furthermore, there is an opportunity to model pesticide concentrations in estuaries by combining the GBR-Dynamic SedNet catchment model and dispersal using the 3D eReefs marine model.
- The monitoring of pesticides in the GBR (MMP) was limited to 11 fixed sites (and some flood plume sites) and has not been reported since 2018/19. The survey used passive sampler devices that provide average concentrations over a longer (ecologically relevant) deployment period, but are likely to miss high concentration events that may cause acute harm to GBR taxa. Eleven fixed sites are not sufficient to adequately inform risk to marine habitats of the GBR, given the scale of the GBR and the strong likelihood that several of the fixed sites are not well located to reliably sample pesticide dispersal in plumes (resulting in underestimates). The absence of the last three years of MMP monitoring is a major data gap but pesticide monitoring recommenced in the 2022/23 year with sites refined to capture the full (known) range of pesticide concentrations. This data gap will hinder future temporal trend analysis to determine if pesticide concentrations are changing in response to land management practice change.
- The large amount of data collected by the GBRCLMP (74 pesticides detected at least once over all sites – and up to 51 sites in a single year) meant that a full quantitative assessment was not possible within the scope of the current review. While the more limited assessment of 12 focus pesticides across 12 sites provided a good overview of their spatial and temporal distribution, the synthesis is likely to have missed some important findings.
- While a single study assessed the inter-annual trends in a subset of pesticides (PSII herbicides) over the 14-year period of the MMP, and another on imidacloprid over 8 years of the GBRCLMP, insufficient research has been conducted on the temporal trends in pesticide concentrations accounting for all pesticides detected in GBRCLMP and MMP surveys. No research has been conducted on the temporal variation in risk posed by pesticide mixtures.
- There are too few surveys of biota and sediments to meaningfully contribute to an understanding of the GBR-wide spatial and temporal distribution of pesticides in these compartments.

Effects of pesticides

- Links between organism response (mortality and biomarkers of sublethal responses) and pesticide exposure in the field are uncertain due to the possibility that other environmental factors confound responses. More validation is required.
- While there have been many experimental studies that identify toxicity thresholds for pesticides for freshwater and marine taxa of the GBR, most of these have tested only a small subset of pesticides; therefore, the sensitivity of GBR taxa to many pesticides remain largely unknown.
- Guideline values (GVs) applied in the PRM are generally protective of GBR species; however, this has not been validated for all 22 pesticides.
- While additivity is the most common response of GBR organisms exposed to multiple pesticides or pesticides and other stressors, not all combinations have been tested. The effects of pesticide formulation additives such as surfactants are also largely unknown.

Risks posed by pesticides

- The PRM risk values are estimates posed by exposure to the mixtures of pesticides detected and are not absolute values. In other words, an estimate of 99% species protection is not intended to be interpreted literally as meaning precisely 99% of species will be protected (Warne et al., 2020a). Rather, the PRM estimates are intended for relative evaluation of risk (spatially and temporally) to track improvements towards the Reef 2050 WQIP targets (Australian Government & Queensland Government, 2018).

- The risks posed by pesticides to GBR species were primarily calculated by assessing measured pesticide concentrations (as mixtures when relevant) against GVs of the PRM. Therefore, uncertainties in assigning risk primarily result from uncertainties contributed by monitoring programs and the PRM (i.e., limited spatial and temporal monitoring etc., see above).
- In addition, the PRM does not include GVs for all pesticides detected in the GBR (22 of 74), and therefore, pesticide risk is likely to be underestimated.
- The PRM does not account for non-pesticide stressors (e.g., heatwave conditions) which can increase pesticide toxicity; therefore, total risk is likely to be underestimated in many circumstances.
- The PRM does not account for very long-term exposures to low concentrations of pesticides often observed in GBR waters due to the long persistence of many pesticides. Therefore, total risk is likely to be underestimated in many circumstances.
- Although a recent risk assessment which applied a 3D-hydrodyamic model represents a major advance over previous modelling exercises, the simulated diuron concentration relied on multiple assumptions (end-of-catchment loads, half-lives, conservative mixing etc.) and these require further assessment to improve certainty in absolute diuron concentrations. The estimated areas of seagrass and coral habitats at risk of harm are likely to be underestimated as the simulation only accounted for a single pesticide.
- There are limited field measurements of the effects of pesticides on GBR species, but the available studies are consistent with the comparison of pesticide concentrations to GVs.

4.2 Contextual variables influencing outcomes

Table 25. Summary of contextual variables for Question 5.1.

Contextual variables	Influence on question outcome or relationships
Climate change (or climate variability)	Rainfall frequency and intensity influences runoff and pesticide concentrations (e.g., Davis et al., 2008; 2012; Gallen et al., 2019; Grant et al., 2018; Lewis et al., 2009; Rohde et al., 2013; Skerratt et al., 2023; Smith et al., 2011; Ten Napel et al., 2019a; 2019b; Thai et al., 2020; Water Quality & Investigations, 2020a; 2021; 2023). Rainfall frequency and intensity influences salinity in runoff and low salinity increases the effects of PSII herbicides on jellyfish (Klein et al., 2016) but effects of salinity on toxicity to corals is uncertain (Jones et al., 2003). Increased temperature increases the sensitivity of GBR species to pesticides (Chakravarti et al., 2019; Humphrey & Klumpp, 2003; Negri et al., 2011; van Dam et al., 2015; Wilkinson et al., 2017). Future climatic conditions (simultaneous increases in pCO_2 and temperature) increase the sensitivity of GBR species to herbicides (Flores et al., 2021; Marques et al., 2020). Temperature and light exposure effects pesticide persistence (half-lives) (Mercurio et al., 2014; 2015; 2016).
Co-exposure to sediments	Light reduction as a proxy for increased turbidity (from elevated sediments) increases the sensitivity of phototrophic species to PSII herbicides, especially under low light conditions (Cedergreen et al., 2004; King et al., 2022a; 2022b), although the influence of the sensitivity of phototrophic species to pesticides is complex (Cedergreen & Streibig, 2005; King et al., 2022a; 2022b). Sediment deposition increased the effects of diuron on crustose coralline algae (Harrington et al., 2005).

4.3 Evidence appraisal

Relevance

The overall relevance of the body of evidence to the question was High (7.7/9.0). The relevance of each individual indicator was: High for the relevance of the study approach and reporting of results to the question, High for spatial relevance, and High for temporal relevance. Of the 231 articles included in the review, 68% (158 of 231) were given a High score for overall relevance to the question, while 60% (130 of 218) had a High spatial relevance score, and 67% (143 of 214) had a High temporal relevance score. This was due to a number of factors described below.

- The relevance of the study approach and study results was High (sources averaged scores of 2.6/3 or 87% relevance). Most of the 93 studies that reported pesticides in the GBR applied sensitive, reliable techniques to detect and report the concentrations of GBR-relevant pesticides and were assigned a High score. Those that reported pesticides less quantitatively were not scored as highly. Most of the 118 studies that assessed the effects of pesticides on GBR species were also rated highly. These typically exposed GBR-relevant species to GBR-relevant pesticides and reported threshold concentrations that had an ecologically relevant effect. Scores were reduced for studies that tested species with limited distribution in the GBR or that tested legacy pesticides or those less frequently found in the GBR. Risks posed by pesticides were usually reported as exceedances by pesticide concentrations of a guideline or toxicity threshold and/or % of affected species. Of the 75 studies that reported risk in this way, the highest scores were given to studies that applied the most reliable methodologies (e.g., concentration estimates and recent guideline values). Good examples of High scoring sources for relevance include recent GBRCLMP or MMP reports such as Thai et al. (2020), which reported multiple contemporary pesticides from 11 sites in GBR waters and assessed their risk of affecting % of species, based on the most recent PRM GVs.
- The relevance or generalisability of the spatial scale of studies was High (sources averaged scores of 2.5/3 or 85% for spatial relevance). Of the 93 studies reporting pesticide concentrations, those that scored highly sampled water, sediment or biota from multiple sites, e.g., across 4 NRM regions. Studies reporting effect concentrations of pesticides on GBR species (117 in total) were generally given High scores, since the response of a species is relevant on a spatial scale beyond the site of collection. Of the 75 studies reporting risk, the highest scores were given to studies that applied the most reliable methodologies (as above) across multiple locations (e.g., sites that were representative of catchments across multiple NRM regions). Good examples of High scoring sources for spatial relevance again included recent GBRCLMP or MMP reports, which recorded multiple contemporary pesticides from 38 freshwater (Water Quality & Investigations, 2023a) and 11 marine sites (Thai et al., 2020) in GBR waters. Modelling exercises such as Skerratt et al. (2023) that simulated pesticide concentrations and risk across the entire GBR also scored highly with respect to spatial relevance.
- Relevance or generalisability of the temporal scale of studies was High (sources averaged scores of 2.6/3 or 86% for temporal relevance). Of the 93 studies reporting pesticide concentrations, those that scored highly sampled water, sediment or biota at multiple timepoints which could be over the course of a flood plume, through a year (multiple wet and dry season samplings) or from the same locations across years. For example, a typical MMP report deployed approximately nine passive samplers for 1 – 3 months within a year (Thai et al., 2020). This report scored a “2” based on high temporal sampling within a year but presented only a single year of monitoring data. Nevertheless, the consistent methods of collection and analysis ensured the data made critical contributions to identifying 14-year trends in Taucare et al. (2022) which scored a “3”. Studies reporting effect concentrations of pesticides on GBR species (117 in total) were generally given High scores as the response of a species is relevant to risk assessments across temporal scales. Of the 65 studies reporting risk, the highest scores were given to studies that applied the most reliable methodologies (as above) across multiple seasons or years. A good example of a High scoring source for temporal relevance included a publication that assessed the risk posed by the insecticide imidacloprid across eight years (2009/2010 to 2016/2017) (Warne et al., 2022b).

All the studies shortlisted related to one or more aspects of the conceptual model: 1) spatial and temporal distribution of pesticides in the GBR; 2) observed or potential impacts of pesticides on GBR ecosystems; and/or 3) risk of pesticides to the GBR. The large body of evidence available ensured that virtually all evidence in the studies was directly related to pesticides, biota and ecosystems of the GBR.

Consistency, Quantity and Diversity

Consistency for the overall body of evidence was considered High across the sub-group analysis.

Spatial and temporal distribution

Virtually all 93 studies that analysed for pesticides in the GBR were able to identify pesticides in waters, sediments and/or biota. There was very High consistency in the types and concentrations of pesticides detected at individual sites in the GBRCLMP or MMP reports. Since consistent methodologies were used in these monitoring programs year on year, differences in pesticides reported are likely due to real differences in pesticides in fresh and marine waters. There were some factors that differed between studies that make direct comparisons difficult:

- Different pesticides may be dominant in different compartments (water, sediment, biota) at the same location. This is mainly due to the physico-chemical characteristics of each pesticide (e.g., diuron is far more water soluble than DDT and is more likely to be detected in water rather than sediments and biota).
- Pesticide concentrations measured from grab and passive samplers represent different temporal measures, with the former sampling instantaneous concentration and the latter the average concentration over month(s) long deployment periods.

Earlier studies often assessed a restricted number of pesticides. Therefore, the review focused on quantitative comparisons with data reported since 2016 when a more extensive suite of pesticides has been reported.

Effects of pesticides

Experimental studies (72 in total) generally applied standard techniques to assess the effects of pesticides on GBR species. Although each species and each measure of toxicity (e.g., growth versus mortality) will have a unique toxicity threshold, very few of these thresholds were lower than guideline values, indicating that the sensitivity of GBR species reported in these studies were consistent with each other and with previous datasets used to generate the guidelines. There were inconsistencies in guideline values that have been applied in pesticide risk assessments over the years. These GVs have become more reliable (and consistent with the sensitivity of GBR species) when generated using nationally-recognised criteria (Warne et al., 2018a) and have incorporated more reliable toxicity data.

Risk of pesticides

The risks posed by pesticides (i.e., the % species affected by a measured pesticide mixture) can be predicted using a consistent metric such as the PRM with data reported since 2016. However, limitations in the number of pesticides monitored and differences in pesticide GVs in previous studies makes direct comparison difficult. Therefore, pesticide risk reported in this synthesis focused heavily on assessments since 2016. Nevertheless, the sites and regions reported as being at highest risk from pesticides were consistent over a decade of studies, even when applying different approaches. For example, habitats from the same regions were assessed as being at greatest risk based on different methods: 1) grab samples from the end-of-catchment applying the PRM for 22 pesticides (this review); 2) dispersal of 6 PSII herbicides (modelled from catchment load data coupled with salinity values, estimated from satellite data and applying msPAF to account for additivity of effect) (Lewis et al., 2013); 3) diuron loads (estimated from a catchment model) coupled with a 3D hydrodynamic model (to assess diuron dispersal) and applying a diuron GV from the PRM (Skerratt et al., 2023).

Alternative theories

To the author's (APN, RMM, MStJW) knowledge, all published reports: 1) have detected contemporary pesticides in GBR waters (when using sensitive methods) and; 2) report effects of pesticides on non-target organisms (that have physiologies compatible with the target pests i.e., PSII herbicides are expected to affect all phototrophs but not necessarily heterotrophs). The risk to GBR species estimated by the PRM that is expressed as % affected species or exceedance of a PC99 guideline differs with location and timing. Risk calculated this way is not intended to be taken literally, rather it is an estimate and a comparative metric towards achieving Reef 2050 WQIP pesticide targets (Australian Government & Queensland Government, 2018; Warne et al., 2020a).

There have been *unpublished* claims by some stakeholders that the risks posed by pesticides to GBR ecosystems are insignificant. These claims have been carefully and objectively considered and are comprehensively addressed in the body of the SCS. For example:

- The pesticide concentration data has been thoroughly examined with respect to methodology, consistency, spatial distribution (based on monitoring and modelling) and temporal trends for three key GBR ecosystems using the most recent and comprehensive datasets.
- The methods used to develop guideline values (GVs) for pesticides applied in risk assessments were outlined, including: toxicity studies to derive thresholds, species sensitivity distributions, protective concentrations (PCx).
- The evolution of guideline values applied in pesticide risk assessments in the GBR has been explained, including reasons for applying the PRM GVs in the current risk assessments.
- The scientific rigour of the PRM method and the difference between prospective and retrospective risk assessment were discussed.
- The suitability of PRM GVs were comprehensively assessed against GBR species sensitivity.
- The necessity of- and methods applied to estimate total toxicity due to pesticide mixtures has been described.
- Limitations regarding pesticide distribution, effects and risk have been clearly stated.

Using **pre-defined exclusion criteria and quality appraisal the reasons why studies were excluded** from the synthesis were due to:

- Not being geographically relevant to the GBR.
- Relevant to artificial wetlands, channels, dams, farms, groundwater.
- More relevant to question 5.2 (Templeman & McDonald, this SCS) on sources transport - outside scope.
- More relevant to Question 5.3 (Davis et al., this SCS) on management - outside scope.
- Did not refer to aquatic organisms.
- Reviews or position pieces – which contain little primary evidence.
- Non-peer reviewed literature.
- Non-English language.
- A lack of information on pesticides.
- A lack of information on pesticides since 1990.
- Using pesticide loads which have been superseded.
- Reports were superseded in later peer-reviewed articles.
- Methods not being designed to identify effect thresholds or very insensitive monitoring method.

A total of **231** studies were used for the synthesis. This is considered to be a large number of due to:

1) The experience the authors hold in the fields of pesticide monitoring, ecotoxicology and risk assessment.
2) Consideration of the inclusion/exclusion criteria used for the question.
3) The number of studies used by similar reviews or other syntheses.
4) The frequency of duplicate returns during the search process across multiple academic databases.

There were three different evidence types used in the review: 1) primary studies (experimental, observational or modelled); 2) secondary studies (reviews, Systematic Reviews or meta-analysis); or 3) mixed (involve a mixture of experimental, modelled and/or observational studies).

Findings across the primary, secondary and mixed studies were generally consistent in relative patterns of pesticide distribution and risk.

Additional Quality Assurance (Reliability)

The initial searches found 1,045 individual papers and reports. After an assessment of title and abstract **368** were deemed eligible and retained for full text screening. From the full text assessment **137** publications that did not directly address the question (see Data Extraction Table) were excluded. The **232** studies that remained (including additional publications found by the Authors) were assessed for internal validity to note any obvious potential bias and to identify high quality studies most influential in drawing conclusions from the body of evidence. **One** study was removed from the synthesis as a result of the internal validity assessment (leaving a total of **231**).

All the 93 observational studies on spatial and temporal distribution of pesticides in the GBR had a low risk of bias with respect to the pesticide concentrations reported. These publications acknowledged limitations that sometimes included a narrow breadth of pesticides analysed and often a limited number of sampling sites able to be assessed. A strong focus was placed on quantitatively describing the spatial and temporal distribution of pesticides from publications that: 1) monitored a large number of sampling sites; 2) assessed a large number of pesticides; and 3) applied standard techniques with good quality control/quality assurance processes since 2016 (GBRCLMP and MMP programs). Other observational publications were valuable for context including, descriptions of the pesticides identified in the GBR prior to 2016 as well as the descriptions of pesticides in GBR sediments and biota.

Similarly, initial screening ensured the review only included experimental studies that were able to reliably quantify and/or attribute observed effects to pesticide exposure (**118** in total). Some showed effects only at concentrations much higher than those observed in the GBR; however, those were still valuable as they help to identify which pesticides presented an ecologically relevant hazard. Of the **11** observational studies that indicated effects of pesticides in the field, two were identified as presenting bias in their interpretation of the likelihood that pesticides were responsible for the observed effects. Nevertheless, the studies both presented relevant information, and limitations in their interpretation were noted in the review.

All guideline values that have been applied in risk assessments for pesticides to the GBR have limitations, usually related to insufficient toxicity data. Of the ~**12** publications that proposed or presented GVs used for assessing the risk of pesticides in freshwater and marine ecosystems, the **four** most reliable publications were among the most recent which all applied nationally-recognised methodologies to the most comprehensive toxicity datasets available (King et al., 2017a; 2017b; Warne et al., 2020a; 2018b).

A total of **66** studies, including **13** reviews compared pesticide concentrations measured in GBR waterways against toxicity thresholds or GVs to estimate risk. Prior to 2016, the majority of these studies assessed the risk of only a subset of pesticides identified and applied GVs that have now been superseded. Although limited in this way, all of those studies provide valuable historic information on pesticide concentrations over the last 30 years and their conclusions are largely consistent with post 2016 studies. Assessment of risk in the current synthesis relied most heavily on comparison of pesticide concentrations from recent GBRCLMP and MMP programs ecosystems (Gallen et al., 2019b; Ten Napel et al., 2019a; 2019b; Thai et al., 2020; Water Quality & Investigations, 2020a; 2020b; 2021; 2023a) with the most recent and reliable GVs for pesticides relevant to the GBR (Warne et al., 2020a).

Six studies modelled spatial risk to GBR ecosystems and all were limited or biased due to a range of issues including: limited (or no) validation against measured pesticide concentrations; the reliance of obsolete GVs; assessing the risk of a limited number of pesticides (rather than all which might contribute to risk); uncertainty in end-of-catchment loads and in the prediction of plume dispersal. Although assessing the spatial risk of only one pesticide, the recent diuron simulation (Skerratt et al., 2023) was found to present the most reliable approach. This study applied recent and reliable end-of-catchment loads, an advanced 3D hydrodynamic plume dispersal model, the most recent GVs that are compatible with the PRM and, presented a comprehensive validation exercise against concentrations reported by the MMP. However, all spatial modelling exercises at least provided qualitative estimates of risk and were included in the review, along with their approaches and limitations. The inclusion of the modelled risk assessments with limitations did not influence the findings of the review.

Overall, it was determined that most studies (**95%**) had a low risk of bias. The findings of those studies that were rated as having some potential risk of bias were generally consistent with the findings from the larger body of evidence or included other information that was not considered biased, hence the studies were retained in the synthesis.

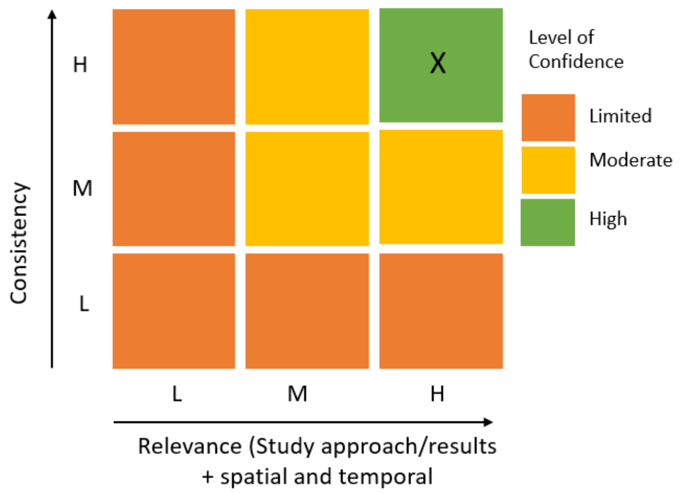
Confidence

The Confidence rating for the primary, based on the overall relevance rating and consistency was High as shown in Table 26 below.

As discussed above Consistency for the overall body of evidence was High. The Relevance rating for the body of evidence was also determined to be High.

A High confidence rating is influenced by the authors' views that a large number of eligible studies were used in the synthesis and that, with few exceptions, generally resulted in consistent findings from observational, experimental, modelled and secondary studies.

Table 26. Summary of results for the evidence appraisal of the whole body of evidence in addressing Question 5.1. The overall measure of Confidence (i.e., Limited, Moderate and High) is represented by a matrix encompassing overall relevance and consistency. The final row summarises the additional quality assurance step needed for questions using the SCS Evidence Review method.

<table>
<tr><th>Indicator</th><th>Rating</th><th>Overall measure of Confidence</th></tr>
<tr><td>Relevance (overall)</td><td>High</td><td rowspan="7">
</td></tr>
<tr><td>-To the Question</td><td>High</td></tr>
<tr><td>-Spatial (if relevant)</td><td>High</td></tr>
<tr><td>-Temporal (if relevant)</td><td>High</td></tr>
<tr><td>Consistency</td><td>High</td></tr>
<tr><td>Quantity</td><td>High

(231 items)</td></tr>
<tr><td>Diversity</td><td>High
(45% experimental, 29% observational, 18% mixed, 8% secondary studies)</td></tr>
<tr><td>Additional Quality Assurance (Reliability)</td><td colspan="2">Narrative of reliability
Of the 231 studies reviewed, there were concerns regarding the reliability of 13 studies (5.6%) to address the question.
The most common reliability concerns were due to low reliability of pesticide concentration/load or toxicity data that might lead to biases in predicted or modelled risk.
Most of these lower reliability studies provided qualitative estimates of risk and were included in the review, along with their approaches and limitations. However, less emphasis was placed on their findings.</td></tr>
</table>

4.4 Indigenous engagement/participation within the body of evidence

A number of Indigenous groups collect samples for the GBRCLMP and some are involved in ongoing research projects including:

- Laura Rangers who have sampled the East and West Normanby rivers and Laura River at Caroll's Crossing and Coalseam Creek since 2016/17.
- Jangga Operations Pty Ltd who sample the Burdekin River at Selheim and at Burdekin Falls Dam but only for 2022/23.

4.5 Knowledge gaps

The key research gaps and what the potential outcomes could be for policy/management if these research gaps were addressed are presented in Table 27.

Table 27. Summary of knowledge gaps for Question 5.1. Each knowledge gap is ranked High, Medium or Low priority.

Gap in knowledge (based on what is presented in Section 4.1)	Possible research or Monitoring & Evaluation (M&E) question to be addressed	Potential outcome or Impact for management if addressed
The single large-scale study on pesticides in wetlands was conducted across only two years but identified widespread and often very high concentrations of pesticides in these ecosystems. Further routine monitoring of pesticides in wetlands is required. The risk posed by mixtures of pesticides should also be determined. **High**	This would reveal the risk posed to wetlands spatially and temporally, including likely sources and the pesticides contributing most to risk.	Guiding improved land management practices towards limiting pesticide risk to assist with meeting the Reef 2050 WQIP targets.
Reinstatement of pesticides in the MMP, including new sites identified by eReefs models as more reliably intersecting with flood plumes. This pesticide monitoring was recommenced for the 2022/23 wet season. **High**	Extend the temporal datasets at appropriate sites and help to validate eReefs models on pesticide dispersal into the GBR.	Improved position of new fixed monitoring sites to increase certainty of risk estimates. Guiding improved land management practices towards limiting pesticide risk to assist with meeting the Reef 2050 WQIP targets.
Increase in the number of pesticides quantified in monitoring programs. **High**	Improve analytical techniques and expand reporting (for example glyphosate which is not presently included in analytical suites due to limitations in analytical methods.	Improved certainty that the risks posed by all pesticides identified in the GBR waters are accounted for. Guiding improved land management practices towards limiting pesticide risk to assist with meeting Reef 2050 WQIP targets.
Increase in the number of pesticides identified in the GBR that are included in the Pesticide Risk Metric. **High**	Develop species sensitivity distributions for additional pesticides for the PRM. This may require further toxicity threshold data for some	Improved certainty that the risks posed by all pesticides identified in the GBR waters are accounted for. Guiding improved land management practices towards

Gap in knowledge (based on what is presented in Section 4.1)	Possible research or Monitoring & Evaluation (M&E) question to be addressed	Potential outcome or Impact for management if addressed
	pesticides (experimental testing).	limiting pesticide risk to assist with meeting Reef 2050 WQIP targets.
Insufficient research has been conducted on the inter-annual temporal trends in pesticide concentrations and risk in GBR waterways. This should be an area of high research priority. **High**	Statistically analyse pesticide concentrations and risk according to PRM methodologies for select GBR monitoring sites over at least the last decade.	Reliably identifying long-term trends in monitored pesticide concentrations and risk will help validate and improve Source Catchment models and therefore more reliably guide land management practices towards limiting pesticide risk to assist with meeting Reef 2050 WQIP targets.
Further investigation into chronic and sublethal effects of pesticides on GBR species in wetlands, rivers and marine ecosystems. **Medium**	Further experimental evidence is required (experimental and field studies) to assess whether long-term exposure to low concentrations of pesticides contributes to additional risk, not identified by the PRM.	Improved certainty that the risks posed by long-term low concentration pesticides exposure is accounted for. Guiding improved land management practices towards limiting pesticide risk to assist with meeting Reef 2050 WQIP targets.
While most evidence points to additive effects of pesticides in mixtures, the evidence is relatively limited among pesticide classes and GBR species and has not been thoroughly reviewed. **Medium**	A thorough review of the type of joint action that occurs when pesticides with different modes of action co-occur to further confirm that the use of response addition in the PRM is appropriate and if not what type of joint action should be used for certain combinations of pesticides. This may need to be augmented by further experimental evidence where little exists.	Improved certainty that the PRM adequately captures the risks posed by co-exposure of GBR species to pesticide mixtures. Guiding improved land management practices towards limiting pesticide risk to assist with meeting Reef 2050 WQIP targets.
Limited evidence of *in situ* impacts of pesticides. **High**	Further studies to assess the impacts of pesticide exposure to GBR species, including biomarker studies to indicate significant exposure.	Improved certainty that the links between exposure and response identified in experiments and used as a basis for reporting also occur on the GBR. Guiding improved land management practices towards limiting pesticide risk to assist with meeting Reef 2050 WQIP targets.
Incorporation of other pressures including thermal	The further development of species sensitivity distributions	Improved certainty that the risks posed by heatwave

Gap in knowledge (based on what is presented in Section 4.1)	Possible research or Monitoring & Evaluation (M&E) question to be addressed	Potential outcome or Impact for management if addressed
stress (e.g., heatwave conditions) into the PRM. **Medium**	for thermal stress (desktop and/or experimental), coupled with incorporation of temperature anomaly data in monitoring programs would allow the additional risks posed by heatwave conditions to be included in PRM assessments.	conditions are accounted for in pesticide risk assessments. Guiding improved land management practices towards limiting pesticide risk in a changing climate to assist with meeting Reef 2050 WQIP targets.
Improve 3D pesticide dispersal models to help assess risk to marine ecosystems across the entire GBR. **High**	Further development of the eReefs model to simulate dispersal of additional pesticides (beyond diuron) into the GBR, including integration with the PRM to predict total risk (% species affected) by pesticide mixtures and refinement of estimates of seagrass and coral habitat exposed.	Improved confidence in estimates of the risks posed by all pesticides to key GBR habitats. Guiding improved land management practices towards limiting pesticide risk to assist with meeting Reef 2050 WQIP targets.
The concentrations of, and risk posed by, pesticides and pesticide mixtures in the vast majority of rivers and creeks that discharge to the GBR are not known. **High**	The land use versus pesticide mixture toxicity relationships (Warne et al., 2020a) should be used to estimate the risk posed by pesticide mixtures.	Improved spatial understanding of the risks posed by individual pesticides and pesticide mixtures to GBR freshwater ecosystems. Guiding improved land management practices to assist with meeting the Reef 2050 WQIP pesticide target.
Risk from individual pesticides and pesticide mixtures are only known for sampling sites. But no estimates of the risk at other points along rivers and creek are available. **Medium**	The land use versus pesticide mixture toxicity relationships (Warne et al., 2020a) should be used to estimate the risk posed by pesticide mixtures for every 1 km stretch of waterways that discharge to the GBR.	Improved spatial understanding of the risks posed by individual pesticides and pesticide mixtures to GBR freshwater ecosystems. Guiding improved land management practices to assist with meeting the Reef 2050 WQIP pesticide target.
There has been minimal Indigenous participation in research and monitoring of pesticides on the GBR and little application of Indigenous knowledge on the effects of pesticides on the GBR ecosystem. **Medium**	Assessing the presence and effects of pesticides on culturally important waterways of the GBR.	Draws on Indigenous knowledge and facilitates a more inclusive and culturally sensitive approach to pesticide management.

5. Evidence Statement

The synthesis of the evidence for **Question 5.1** was based on 231 studies, undertaken primarily in the Great Barrier Reef and published between 1990 and 2022. The synthesis includes a *High* diversity of study types (45% experimental, 29% observational, 18% mixed studies, and 8% secondary) and has a *High* confidence rating (based on *High* consistency and *High* overall relevance of studies).

Summary of findings relevant to policy or management action

Pesticides are ubiquitous across monitored Great Barrier Reef ecosystems including end-of-catchment waterways, palustrine wetlands (e.g., vegetated swamps) and in estuarine and nearshore marine habitats. Concentrations of pesticides are greatest in wetlands, followed by end-of-catchment then marine locations, with concentrations decreasing with greater distance from river mouths. The majority of pesticides in all Great Barrier Reef habitats occur as mixtures. Exposure of marine ecosystems to pesticides is closely linked to flood plume dispersal and is highly dynamic, changing by orders of magnitude within hours. Based on the available, but limited, published data, there is more evidence that pesticide concentrations are increasing rather than decreasing in Great Barrier Reef marine ecosystems. Pesticides are designed to control agricultural pest species and virtually all tested pesticides are reported as harmful to non-target aquatic species of the Great Barrier Reef. For example, photosystem II (PSII) herbicides consistently impact all photosynthetic marine organisms of the Great Barrier Reef that have been tested, including corals and seagrass. Other simultaneous pressures, including heatwave conditions and variation in light were shown to increase the sensitivity of Great Barrier Reef species to pesticides, indicating that guideline values applied under some conditions in the field are likely to underestimate the risk to aquatic ecosystems. The guideline values in the Pesticide Risk Metric were used to assess the simultaneous exposure risks of 22 pesticides on aquatic species in the Great Barrier Reef. Sites in the Mackay Whitsunday region, along with Barratta Creek in the Burdekin region which featured intense cropping and lower discharge (related to rainfall), recorded consistently higher concentrations of pesticides and higher risk than other locations. Pesticides that contribute most to risk in all Great Barrier Reef ecosystems monitored include atrazine, diuron, imidacloprid and metolachlor, but their contribution varies with site. Risk to aquatic ecosystems reduces with distance from the source of pesticides.

Supporting points

- Extensive monitoring programs in the Paddock to Reef program (primarily the Great Barrier Reef Catchment Loads Monitoring Program and the Marine Monitoring Program) have consistently identified pesticides in >99% of water samples. Since 2016/17: 1) over 70 pesticides and their transformation products have been identified in Great Barrier Reef waters; 2) most pesticides were detected as mixtures (>70% of samples); 3) the most frequently quantified pesticides across all Great Barrier Reef habitats were atrazine, diuron, hexazinone, imazapic, imidacloprid and metolachlor.

- Pesticide concentrations were typically higher in fresh and marine waters during wet seasons compared to dry seasons, with rapid increases at the start of the wet season followed by a gradual decrease.

- The concentration of imidacloprid at some freshwater sites and PSII herbicides at some marine sites has increased.

- The effects of PSII herbicides on photosynthetic efficiency have been measured in Great Barrier Reef species including seagrass, coral, coral symbionts, algae and jellyfish and include reduced growth and mortality (if assessed). Laboratory tests indicate that contemporary insecticides negatively affect marine invertebrates including corals, barnacles, crabs, shrimp and prawns and fish. Non-PSII herbicides and fungicides have also been shown to negatively affect Great Barrier Reef species, but more research is needed to improve water quality guideline values for these pesticides.

- An extensive review of toxicity studies with species relevant to the Great Barrier Reef found that the Pesticide Risk Metric Guideline Values are suitable to assess the risk of pesticides and pesticide mixtures.
- In line with international evidence, several experimental studies on species found in the Great Barrier Reef have shown that mixtures of herbicides generally conform with the concentration addition model of joint action. Additional studies focused on Great Barrier Reef species would strengthen current evidence that low concentrations of individual pesticides with different modes of action contribute to the overall effect of the mixture.
- All *in situ* biological studies to date have found strong correlations between adverse biological effects and concentrations of individual pesticides, sometimes with pesticide mixtures. However, the adverse effects might also be correlated with other co-stressors in the field, so it has not yet been possible to determine causation.
- A simulation exercise using the eReefs marine model indicated that diuron is typically transported by coastal plumes in a northward direction from river mouths. Rapid changes in diuron concentrations (within hours) highlighted the dynamic exposure of marine waters and that the Pesticide Risk Metric PC99 Guideline Value for this herbicide was often exceeded across 1,000 km^2 (peaking at 1,400 km^2) of inshore areas in simulations from 2016 to 2018 (including 175 km^2 of seagrass and 20 km^2 of coral habitat). Further model developments are required to improve the ability to estimate patterns of pesticide risk, such as expanding the model to include all pesticides identified in the Great Barrier Reef, and additional *in situ* field validation using observations of pesticide concentrations from the Marine Monitoring Program.

6. References

The 'Body of Evidence' reference list contains all the references that met the eligibility criteria and were counted in the total number of evidence items included in the review, although in some cases, not all of them were explicitly cited in the synthesis. In some instances, additional references were included by the authors, either as background or to provide context, and those are included in the 'Supporting References' list.

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Appendix 1: 2022 Scientific Consensus Statement author contributions to Question 5.1

Theme 5: Pesticides – catchment to reef

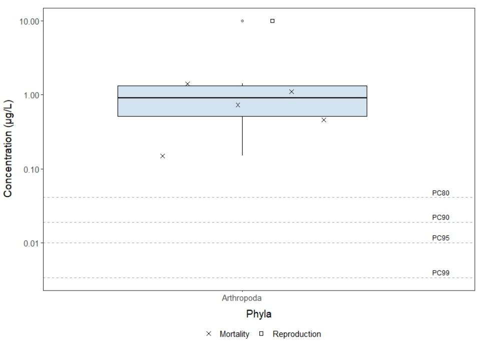
Question 5.1 What is the spatial and temporal distribution of pesticides across Great Barrier Reef ecosystems? What are the (potential or observed) ecological impacts in these ecosystems? What evidence is there for pesticide risk?

Author team

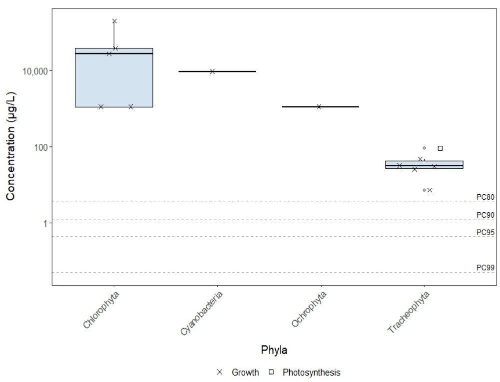
Name	Organisation	Expertise	Role in addressing the Question	Sections/Topics involved
1. Andrew Negri	Australian Institute of Marine Science	Tropical aquatic ecotoxicology: 20 years' experience in pesticide research	Lead Author	All Sections
2. Grechel Taucare	University of Queensland	Trend analysis	Contributor	Searches, data extraction, data analysis for marine data section
3. Peta Neale	University of Queensland	Water quality assessment	Contributor	Data extraction and data analysis for freshwater pesticide monitoring and toxicity threshold sections
4. Catherine Neelamraju	University of Queensland and Queensland Department of Environment and Science	Large scale catchment water quality sampling program management, GBRCLMP Program Leader (prev.), ecotoxicology, pesticide mixture risk assessment, Pesticide Risk Metric co-developer, coding and applied statistics.	Contributor	Data extraction and data analysis for freshwater pesticide monitoring and toxicity threshold sections, Pesticide Risk Metric calculations, toxicity data plotting.
5. Hayley Kaminski	Queensland Department of Environment and Science	Pesticide Risk Metric (PRM) within GBRCLMP. Expertise in developing PRM contribution plots within R Shiny and general interpretation of PRM.	Contributor	Risk of pesticides to GBR ecosystems- freshwater and marine
6. Reinier Mann	Queensland Department of Environment and Science	20 years of experience in aquatic and terrestrial ecotoxicology, development of water quality guidelines and the Pesticide Risk Metric, environmental risk assessment	Contributor	Spatial and Temporal distributions of pesticides and risk.
7. Michael St. J. Warne	Universities of Queensland and Coventry	Aquatic and terrestrial ecotoxicology, water quality guidelines, environmental risk assessment and co-developer of the Pesticide Risk Metric. More than 30 years' experience researching in these fields.	Contributor	Contributing to writing and reviewing all sections of the report

Appendix 2: Additional figures and tables

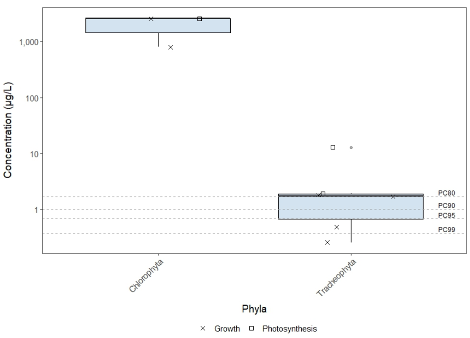
A: Fipronil freshwater



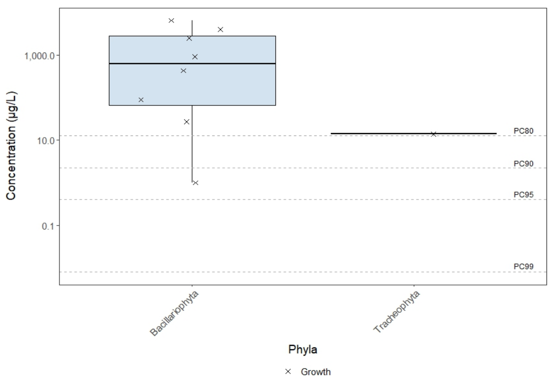
B: Imazapic freshwater



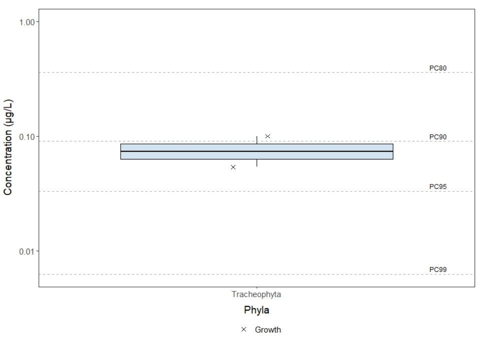
C: Isoxaflutole freshwater



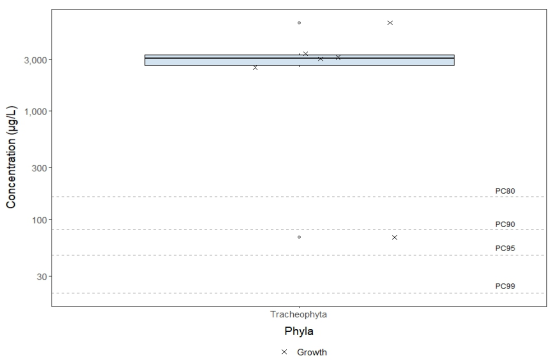
D: Metolachlor freshwater



E: Metsulfuron-methyl freshwater



F: Triclopyr freshwater



G: Imidacloprid freshwater

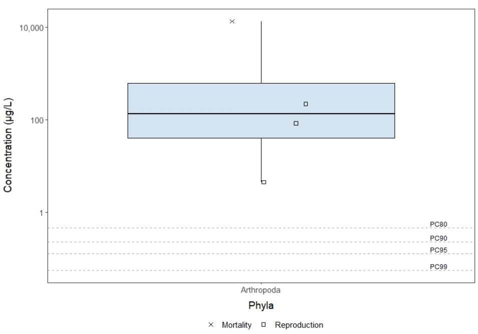


Figure A1. *Plots of toxicity data for freshwater GBR species exposed to A) fipronil, B) imazapic, C) isoxaflutole, D) metolachlor E) metsulfuron, F) triclopyr and G) imidacloprid against the GVs (PC99, PC95, PC90, PC80) obtained from Warne et al. (2020). The effect types include mortality, growth, reproduction, photosynthesis and bleaching for corals.*

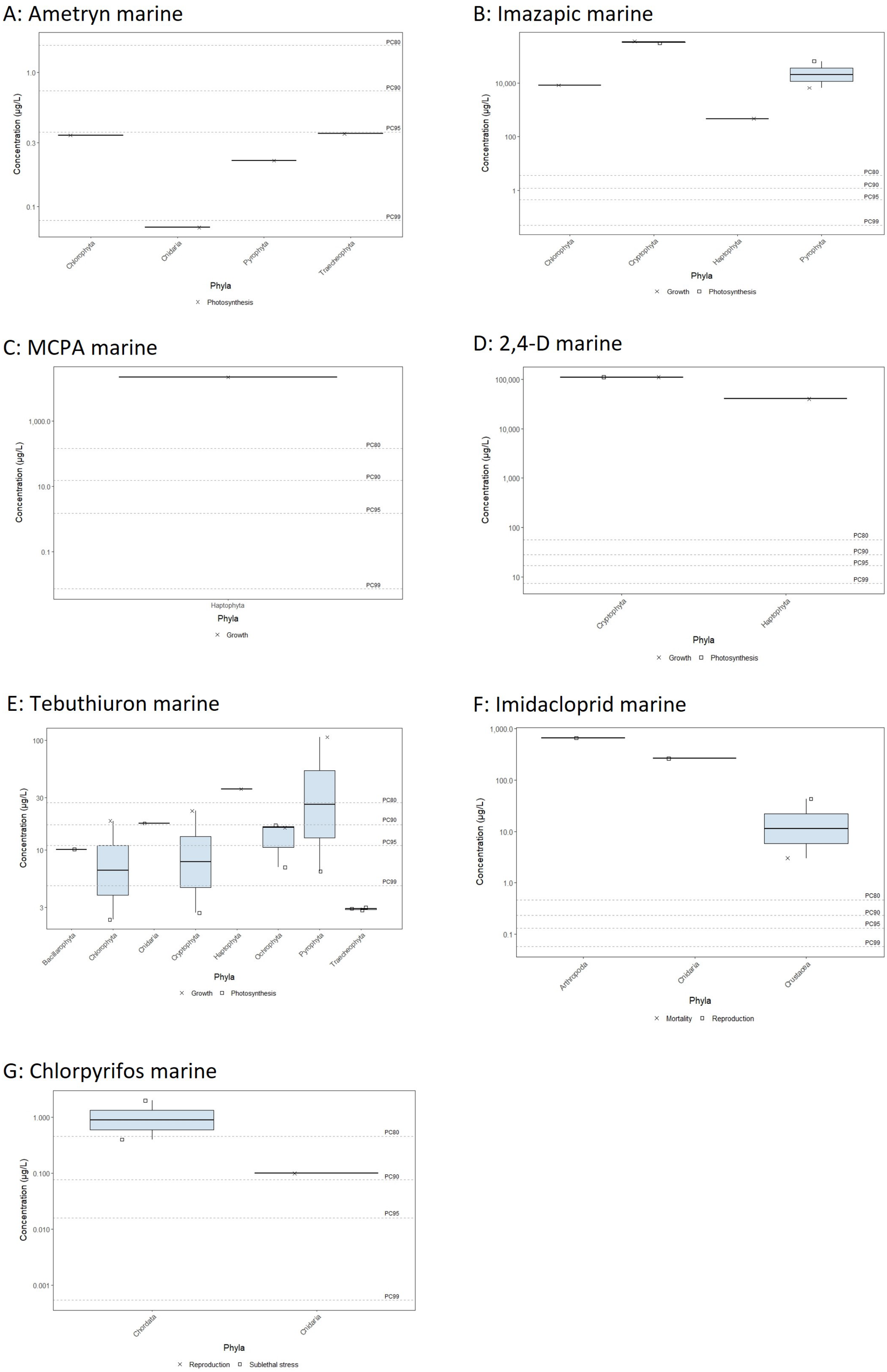


Figure A2. *Plots of toxicity data for marine GBR species exposed to A) ametryn, B) imazapic, C) MCPA, D) 2,4-D, E) tebuthiuron, F) imidacloprid and G) chlorpyrifos against the GVs (PC99, PC95, PC90, PC80) obtained from Warne et al. (2020). Cnidaria include corals and Tracheophyta includes seagrass. The effect types include mortality, growth, reproduction, photosynthesis and bleaching for corals.*

Table A1. *The contribution of atrazine, diuron, imidacloprid and metolachlor to annual wet season Pesticide Risk Metric values for the 12 focus waterways between 2016/17 and 2021/22. Data sourced from Water Quality & Investigations (2023b).*

Region	Catchment	Contributing pesticides	Proportional contribution to Pesticide Risk Metric (%)						
			2016/17	2017/18	2018/19	2019/20	2020/21	2021/22	Mean
Wet Tropics	Daintree River at Lower Daintree	diuron	ND	ND	30	32	3	54	**30**
		imidacloprid	ND	ND	64	0	0	1	**16**
	Russell River at East Russell	diuron	62	49	44	59	63	80	**60**
		imidacloprid	16	16	17	17	7	0	**12**
	Tully River at Euramo	diuron	36	47	38	48	55	75	**50**
		imidacloprid	48	40	52	25	28	3	**33**
Burdekin	Barratta Creek at Northcote	diuron	51	38	37	37	44	37	**40**
		atrazine	26	35	30	32	19	27	**28**
		isoxaflutole	2	0	3	4	13	7	**5**
	Haughton River at Powerline / Giru Weir Tailwater	diuron	24	12	25	19	16	27	**21**
		metolachlor	22	21	31	41	51	31	**33**
		atrazine	41	22	22	15	12	17	**21**
	Burdekin River at Home Hill Inkerman Bridge	diuron	0	0	13	1	1	16	**5**
		metolachlor	58	27	27	87	47	56	**50**
Mackay Whitsunday	O'Connell River at Caravan Park	diuron	21	37	30	29	39	21	**29**
		imidacloprid	53	34	31	31	33	30	**35**
	Sandy Creek at Homebush	diuron	40	46	43	40	37	34	**40**
		imidacloprid	25	23	26	26	32	26	**26**
		atrazine	12	9	10	9	9	11	**10**
		imazapic	6	9	8	8	8	8	**8**
	Plane Creek at Sucrogen Weir	diuron	ND	ND	50	33	8	2	**23**
		metsulfuron-methyl	ND	ND	8	40	56	30	**34**
		imidacloprid	ND	ND	0	2	11	34	**12**
Fitzroy	Fitzroy River at Rockhampton /Fitzroy River Water	metolachlor	76	83	88	87	96	84	**86**
Burnett Mary	Burnett River at Ben Anderson Barrage Headwater / Quay Street Bridge	diuron	4	17	11	12	12	4	**10**
		metolachlor	78	63	53	52	45	80	**62**
	Mary River at Home Park / Churchill Street	diuron	9	23	31	26	3	13	**18**
		metolachlor	40	40	42	60	68	51	**50**

Table A2. *The contribution of atrazine, diuron, imidacloprid and metolachlor to annual wet season Pesticide Risk Metric values for the 12 focus waterways between 2016/17 and 2021/22. Data sourced from Water Quality & Investigations (2023b).*

Region	Catchment	Proportional contribution of:	Proportional contribution to Pesticide Risk Metric (%)			
			2016/17	2017/18	2018/19	Mean
Wet Tropics	Low Isles	metolachlor	99	50	100	**83**
		MCPA	0	50	0	**17**
	High Island	metolachlor	43	92	47	**61**
		MCPA	56	0	53	**36**
	Normanby Island	metolachlor		59	88	**73**
		MCPA		41	0	**21**
	Dunk Island	metolachlor	98	42	84	**75**
		MCPA	0	33	0	**11**
	Lucinda	metolachlor	60	95	42	**66**
		MCPA	36	0	57	**31**
Burdekin	Barratta Creek	diuron	0	0	18	**6**
		MCPA	0	18	27	**15**
		metolachlor	99	47	45	**63**
		atrazine	1	32	8	**14**
Mackay Whitsunday	Repulse Bay	diuron	0	7	67	**25**
		metolachlor	98	48	12	**53**
		MCPA	0	28	7	**12**
	Sandy Creek	diuron	69	0	5	**25**
		metolachlor	22	54	38	**38**
		MCPA	0	45	35	**27**
		chlorpyrifos	0	0	20	**7**
	Sarina Inlet	diuron	58	44	73	**58**
		metolachlor	8	35	11	**18**
		MCPA	23	17	9	**16**
	Flat Top Island	diuron	78	79	76	**78**
Fitzroy	North Keppel Island	metolachlor	100	42	100	**81**
		MCPA	0	57	0	**19**