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The impact of pesticides on local waterways: a scoping review and method for identifying pesticides in local usage

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Abstract 1 (word count 361)

Pesticides used in agriculture are widely considered to be the most cost-effective way to reduce undesirable plants and animal pests and increase crop yields. However, these economic benefits should be evaluated against any deleterious impacts on the natural environment and human health. While a great deal of attention is paid to the impact of agricultural runoff, little is known about such impacts on local waterways. The aim of this study was to (i) develop a methodology to determine which pesticides were being used in local agriculture in the Byron Shire, Australia and (ii) search the literature for evidence of the impact of these chemicals on local waterways. After a comprehensive search involving multiple government databases, three pesticides with potentially high toxicity on the aquatic ecosystems and humans, which are used for the treatment of crops cultivated on the agricultural land in the Byron Shire, were selected for this review: bromoxynil, diquat and paraquat. In the systematic scoping review, two databases were searched (Scopus and Web of Science), including publications between January 2008 and April 2019; and from 160 obtained articles, 36 papers were identified for inclusion. The evidence of harmful effects at realistic concentrations (concentrations found in the environment) was found for all selected herbicides, but not on all organisms. In aquatic environments, diquat was found to be toxic to the snail, and bromoxynil to algae. The clearest and most consistent evidence was found for paraquat. At realistic concentrations, paraquat (i) severely inhibited healthy bacterial growth (*E. coli*), (ii) distorted tropical freshwater plankton communities and (iii) increased fish kills (common carp) three times more than the weed (water hyacinth) that it was employed to control. Of particular concern is that paraquat has been banned from sale in the European Union and many countries around the world but remains available in Australia and is likely in use in the Byron Shire. Further work is required to scope the extent of its use and the effectiveness of the regulations governing its use. This study provides a methodology that can be used to identify pesticides that are likely in local use and identify evidence of any negative impacts on the health of local waterways.

1. Introduction

Over one-third of the world's land surface and three-quarters of its freshwater resources are dedicated to crop or livestock production (Diaz et al., 2019). The expansion of the production of food, feed, fibre and bioenergy in recent decades has afforded economic prosperity for many developed countries. However, a panel of hundreds of world scientists have warned that these advances have come at a cost to nature, particularly soil, water and air quality, climate regulation and habitat provision (Diaz et al., 2019). The Global Assessment report has identified many anthropogenic drivers of unsustainable practices, including harmful policies that favour economic activity over environmental conservation. One industry named in the report is the agricultural industry, including the use of fertilizers and pesticides to enable the over-exploitation of natural resources.

Pesticides are a broad class of chemicals that are used to remove or reduce the presence of undesirable insects (insecticides), rodents (rodenticides), plants (herbicides), bacteria (bactericides), fungi (fungicides) and larvae (larvicides). In agriculture, herbicides are the main type of pesticides and are used to decrease the spread of weeds to achieve higher crop yields. Using pesticides is widely considered to be the most cost-effective way to achieve high crop production (Singh and Singh, 2016). The agricultural industry is a strong contributor to the Australian economy providing employment for over 1.6 million Australians and returning over $60 billion from farm production in 2016-17 (by National Farmers' Federation, 2018, https://www.nff.org.au/). However, the agriculture industry has also been identified as the greatest contributor to water pollution in terms of nutrient enrichment, particularly from high levels of nitrogen and phosphorus detected in freshwater (Foley et al., 2005). Indeed, land-based runoff has been identified as second only to climate change for its adverse impact on the waters surrounding the Great Barrier Reef (Tan & Humphries, 2018). In addition to nutrient, pesticide residues have been detected in water resources and sediments (Allinson et al., 2015; Landis et al., 2008) and in ground water (Dabrowski et al., 2014).

While much attention has focussed on the impacts of runoff on the Great Barrier Reef and the critical importance of its proper regulation (Hamman & Deane, 2018), little is known about the impact of residue pesticides and runoff on local waterways throughout regional Australia.. The aim of this systematic review was to determine whether there is any evidence in the literature of negative impacts of pesticides on local waterways.

2. Material and methods

2.1. Context

The study was undertaken within one 'local' area known as the Byron Shire, which is situated around the popular but small coastal town of Byron Bay, New South Wales (NSW), Australia. The Byron Shire Council Local Government Area (LGA) is located on the most easterly point of Australia, with tourism as its major industry, and agriculture and creative industries also major contributors to its economy (Lasky, 2019)While this review represents a case-study approach, the methodologies used in this study could readily be applied to any local area within Australia, and indeed around the world, to firstly identify what pesticides are likely to be in use in the local area, and then to find out whether there is any evidence for harmful effects on local waterways of those chemicals.

Located in the subtropical area, the Byron Shire has a rich agricultural industry including production of macadamias, avocados, bananas, coffee, pork, vegetables, dairy, beef, bush foods and flowers (https://www.byron.nsw.gov.au/Business/Business-in-Byron/Agriculture).

2.2.***Design***

This study consists of two parts: (1) A method of pesticide selection, which involved the development of a methodology to identify which pesticides are likely to be in use within the Bryon Shire and; (2) A systematic scoping review of the literature of the selected pesticides to identify whether there was any evidence for harmful effects of the selected pesticides on local waterways.

Part 1: Pesticides selection

The objective of part one of the review was to identify the most toxic agricultural pesticides used in the Byron Shire (Australia). However, information about the type and quantity of agricultural pesticides used in the local region (i.e. the Byron Shire) was not readily available or accessible in the public domain. Therefore, the following methodology, summarised in **Figure 1**, was applied to identify the pesticides most likely to be in use (based on the nature and extent of the most common of crops grown in the area):

1. The five largest (by area) agricultural land uses were identified (Figure 2);
2. The main chemicals likely to be applied to these land uses were determined by searching the Australian Pesticides and Veterinary Medicines Authority's (APVMA) online database and identifying the chemicals with the greatest number of product registrations (Australian Pesticides and Veterinary Medicines Authority, 2018);
3. A short list of chemicals were then subjected to two further stages of short listing using the hazard statements in the Material Safety Data Sheet. These were found using the online search tool on Safe Work Australia's website (Safe Work Australia, 2018). Selection of the pesticides was based on their Globally Harmonised System of Classification (GHS) hazard statement and their toxicity on the aquatic ecosystems and humans (**Table 1**).
    3.1. In the first stage the hazard statement for aquatic toxicity containing only chemicals classified as H410 (highly toxic to marine life with long-term effects*)* were short listed for the next stage (highlighted red in **Table 1**).
    3.2. In the second stage, the hazard statement for human toxicity containing only the chemicals that were found to be also the most highly toxic to humans (**Table 1**) were prioritised for the current review.
    3.3. Finally, additional background information would be sourced on the selected pesticides prior to the literature search. An overview of the physiochemical properties was obtained

from PubChem (https://pubchem.ncbi.nlm.nih.gov). The World Health Organisation (WHO) was used to source information on lethal dose and toxicity rating (WHO, 2015).

Part 2: Scoping review

Having identified a short list of chemical pesticides, the literature review was designed to address the question: are there any negative impacts on the local aquatic environments associated with their use. The literature review used the Preferred Reporting Items for Systematic Review and Meta-analysis (PRISMA) statement (Moher et al., 2009). A systematic scoping review was considered the most appropriate form of knowledge synthesis for the question, which was essentially to identify whether any such evidence exists and to examine the 'extent, range and nature' of the available evidence (Arksey & O'Malley, 2005). The framework for this scoping review was informed by Arksey and O'Malley (2005), with additional enhancements proposed by Levac, Colquhourn and O'Brien (Levac et al., 2010) and (Peters et al., 2015), as summarized in **Table 2**. The methodology was registered with Open Science Framework prior to the completion of the data analysis phase and can be accessed at https://osf.io/p5z9b.

2.3. Search strategy

The literature search strategy was designed in consultation with a librarian and is detailed in **Table 2**. Each chemical was searched separately to allow counting of articles. The search using the individual chemical name as a search term was combined with AND with the key search terms for the environmental impacts: 'toxicity', OR 'contamination' OR 'pollution' OR 'environment'. To focus on waterways and agriculture, the above search was combined with AND for the key search terms 'water' or 'aquatic'; plus AND for the search terms 'agriculture' OR horticulture' OR 'crop'). The search was limited to title, abstract and keywords, English language and publications between January 2008 and April 2019 to ensure currency of evidence. Two databases were searched (Scopus and Web of Science), each by two independent researchers. Reference lists of all identified papers were also searched for additional studies and reviews that were relevant.

2.4. Study Selection

Papers that met the following criteria were included: (i) scholarly journal articles, (ii) paper included reports of bromoxynil, diquat and/or paraquat, and (iii) papers that investigated impact of at least one of the chemicals on aquatic environments at realistic (within the range of use) concentrations. Papers were initially screened by title and abstract by two independent researchers. Studies that appeared to meet the inclusion criteria were further scrutinized through an evaluation of the full text article. Those studies whose full text met the study criterion were included in the review. During the process of the selection of relevant studies an iterative team approach was used, as proposed in a scoping review framework by Levac, Colquhoun and O'Brien (2010).

2.5. Data Extraction

Two reviewers independently extracted the following data into an *a priori* designed evidence table: first author's surname, year and country, title of paper, study design, feature of aquatic environment studied, location of data collection (in laboratory, in situ or other), effects on environment, and other comments/points of interest.

3. Results

3.1. Pesticide selection and toxicity

The three pesticides identified as having both the highest aquatic and human toxicity, in alphabetical order, were bromoxynil, diquat and paraquat (**Table 1**). Information on solubility, vapour pressure, half-life, and physical description for each of the chemicals is presented in **Table 3**. It should be noted that values varies considerably depending on environmental factors such as presence of oxygen, soil type, pH and microbial activity (Hanson et al., 2015).

All pesticides are characterised with a strong affinity to bind to soil particles with the half-life for soil and water presented in **Table 3** (https://pubchem.ncbi.nlm.nih.gov).

Preliminary information on toxicity for bromoxynil, diquat, and paraquat is presented in **Table 4**. Lethal dose (LD_{50}) of a chemical causes death of 50% of the animal test group. Although articles in the scoping review discussed LD_{50} of different species (Bouétard et al., 2013; Marvá et al., 2010; Thaimuangphol & Kasamesiri, 2015; Wast et al., 2016; Yarpuz-Bozdogan, 2016), none used the same species for all three chemicals. Therefore, to provide consistency between chemicals, LD_{50} of the rat was used, consistent with values listed on the World Health Organization (WHO) website.

3.2 Pesticide literature

Before specifying the specific names of herbicides an initial generic search resulted in 1800 papers in Scopus and 1805 from the Web of Science. After inclusion of the specific names of the selected pesticides (i.e. bromoxynil, diquat and paraquat), the search produced 160 records. Following removal of duplicates, 144 papers remained (**Table 2**). A further 102 were excluded as not meeting the study criteria after screening the titles and abstracts. The remaining 42 full-text articles were further scrutinized and 6 additional papers were excluded as their focus (e.g. monitoring soil quality and microbial degradation of pesticides) was not relevant to the objective of the scoping review. Data extraction to the table was checked for consistency between reviewers, with no evidence of significant discrepancies in the extraction results. The PRISMA flow of papers through the selection process is presented in **Figure 3**.

Study types included 28 original research and 8 of review articles. Original research included 12 laboratory experiments (Ansara-Ross et al., 2008; Botelho et al., 2012; Bouétard et al., 2013; Chusaksri et al., 2010; De Solla et al., 2012; Kim et al., 2009; Li et al., 2015; Li et al., 2017; Marvá et al., 2010; Nsibande & Forbes, 2016; Oh et al., 2014; Thaimuangphol & Kasamesiri, 2015); 11 sampling studies *in situ* (de Queiroz et al., 2018; Donald et al., 2018; Ismail et al., 2011; Kathiresan & Deivasigamani, 2015; Leboulanger et al., 2011; Love et al., 2011; Messing et al., 2011; Mottes et al., 2017; Siemering et al., 2008; Wast et al., 2016; Yarpuz-Bozdogan, 2016). There was one clinical study on humans (Konthonbut et al., 2018) and one epidemiologic study (Gatto et al., 2009). Two articles were computer model risk assessment (Dabrowski et al., 2014; Henning-De Jong et al., 2008). Review articles included 7 reviews (Fenner et al., 2013; Gebrehanna et al., 2014; Juraimi et al., 2013; Roberts et al., 2012; Sartori& Vidrio, 2018; Singh & Singh, 2016; Tsai, 2013) and one systematic review on the impact of pesticides on human health (Freire & Koifman, 2012). There was one case study (Tsai, 2013b). Aquatic environments from locations around the world ranged from drinking water, well water, surface water, ditches, reservoirs, ponds, wetlands, lakes, catchment areas, large watersheds and coastal ecosystems. Studies *in situ* included multiple locations in North America (De Solla et al., 2012; Donald et al., 2018; Gatto et al., 2009; Love et al., 2011; Messing et al., 2011; Mottes et al., 2017; Siemering et al., 2008), Europe (Leboulanger et al., 2011) and Asia (Ismail et al., 2011, Kathiresan & Deivasigamani, 2015, Wast et al., 2016, Yarpuz-Bozdogan, 2016).

Organisms explored in these studies included (Botelho, 2012), microalgae (Marvá, 2010; Simering, 2008), an aquatic plant (Kathiresan & Deivasigamani, 2015), phytoplankton (Leboulanger et al., 2011), crustaceans (Kim et al., 2009; Thaimuangphol & Kasamesiri 2015; Yarpuz-Bozdogan, 2016;), gastropods (Bouetard et al., 2013; Wast et al., 2016) and fish (Wast et al., 2016). Human studies involved a case-controlled study of farmers who had Parkinson's disease in the USA who had been exposed to pesticides, including paraquat, through contaminated drinking wells (Gatto et al., 2009), and paraquat residue found in the babies of women in Malaysia who had been exposed to pesticides through drinking wells during their pregnancy (Konthonbut et al., 2018).

Seven articles from 36 contained information on toxicity and effects of the pesticides at realistic concentrations on organisms found in the aquatic environment: *Escherichia coli* (Botelho et al., 2012), daphnia (Yarpuz-Bozdogan, 2016), plankton (Leboulanger et al., 2011), snails (Bouétard et al., 2013), shrimp (Thaimuangphol & Kasamesiri, 2015) and fish (Kathiresan & Deivasigamani, 2015; Siemering et al., 2008) and one modelling study (Ansara-Ross et al., 2008). These results are summarised in **Table 5**.

3.3 Bromoxynil

There was one relevant paper which modelled a probabilistic risk assessment of the harmful effects to aquatic species from bromoxynil (Ansara-Ross et al., 2008). Ansara-Ross et al. (2008) set out to determine the risk to aquatic environments on a number of chemicals including bromoxynil (**Table 5)**. Bromoxynil was classified as a chemical with possible risk. Further analysis using the PERPEST (Predicting the Ecological Risks of PESTicides, van den Brink et al., 2002) model indicated no clear effects of bromoxynil on fish, crustaceans, insects, or plankton, but demonstrated a low negative effect on periphyton communities.

3.4. Diquat

Two papers were identified that investigated the impacts of diquat on aquatic environments (Bouétard et al., 2013; Siemering et al., 2008) as presented in **Table 5**. A French team lead by Boutetard (Bouetard et al., 2013) investigated the toxicity pathways of exposure of ecologically realistic concentrations of diquat on the great pond snail *(Lymnaea stagnalis)*. The exposure level chosen was consistent with realistic field concentrations after aerial spraying. Three snails were measured after 5, 24 and 48 hours of exposure. The results indicated that exposure significantly stimulated gene transcription in the redox-cycling pathways, inducing oxidative stress, along with other stress-responsive pathways in the haemolymph and the gonado-digestive complex. This study demonstrated that: (i) diquat is capable of inducing toxicity in a non-target animal species, (ii) oxidative stress pathways could be used as a biomarker for diquat toxicity, and (iii) there is a risk of apoptosis (cell death) in haemocytes (lymph cells) in *L. stagnalis* at high concentrations of diquat, which could seriously compromise the snail immune system.

Siemering et al. (2008), developed and implemented a 3-year monitoring program in the state of California to determine the extent that aquatic herbicide impacts on the environment. The program developed a risk quotient for determining regulatory limits of certain pesticides. In locations at one hour post exposure to diquat, the risk quotient for diquat's effect on green algae (*Selenastrum*), duckweed (floating plants also known as bayroot) and fish (fathead minnow and delta smelt), had exceeded the Level of Concern as determined by the US Environental Protection Agency. The number of times that risk quotientsexceeded level of concern indicated that 'more extensive risk characterizations' are required to assess the risk of diquat to aquatic environments (Siemering et al., 2008).

3.5. Paraquat

There were four studies that reported evidence of the harmful effects of realistic concentrations of paraquat on aquatic environments (**Table 5**). In an *in vitro* laboratory study in Brazil, using a commercial formulation and recommended concentration of paraquat (200g/L), Botelho and colleagues (2012) measured the impact on aquatic micro-organisms using *E.coli* as a test organism. The study found that *E. coli* growth was completely inhibited for the first 300 minutes after exposure to paraquat. After this initial lack of growth, *E.coli* grew exponentially, but resulting in lower final concentration (based on the colony-forming units density (CFU) values) than when exposed to other herbicides. The results demonstrated extreme sensitivity of *E. coli* to paraquat exposure. This negative effect on *E. coli* growth is significant because the bacteria participate in organic decomposition, nutrient cycling and energy flow and thus the presence of *E. coli's* is commonly used as an indicator of water quality (Botelho, 2012).

A study in India on controlling water hyacinth (*Eichhornia crassipes*) found that paraquat increased mortality to the common carp (Kathiresan& Deivasigamani, 2015). This study measured the impact of using paraquat-treated water on crops post-germination. Along with water hyacinth biomass, three species of fish (common carp, mrigal, rohu) mortality were measured 32 days after sowing. Water hyacinth is a weed that forms a biomass that itself reduces water quality and causes mortality to fishes (control: 14.5% carp, 50.0% mrigal, 21.7% rohu). The paraquat-treated water (at 1.50 kg/ha) substantially worsened fish mortality for the common carp (42.0% carp), but not the mrigal or rohu

(50.6% and 25.0%, respectively). An examination of the tissue histopathology of the organs of affected fishes found extensive tissue damage in multiple organs after herbicide exposure, particularly the liver and gills (Kathiresan & Deivasigamani, 2015).

A microcosm study in Mozambique (Leboulanger et al., 2011) looked at the impact of herbicides, including paraquat, on two new human constructed freshwater reservoirs. All components of tropical plankton (bacterioplankton, phytoplankton, and zooplankton) were monitored for five days as a measure of the direct and indirect effects of herbicide exposure on the health of the trophic community. Herbicide exposure had an immediate inhibitory effect. Interestingly, paraquat decreased plankton diversity and overall biomass and green microalgae became dominant. Results from this study indicated that the aquatic species of a freshwater resevior with a simple trophic community are sensitive to the effects of paraquat exposure and an acute exposure could negatively impact the the system within days.

4. **Discussion**

There is evidence of harmful effects of three analysed herbicides on aquatic environments. At realistic concentrations, diquat was found to be toxic to the snail, and bromoxynil to algae (Siemering et al., 2008). The clearest and most consistent evidence of negative effects was found for paraquat. At realistic concentrations found in the environment (within the safty range), paraquat severely inhibited healthy bacterial growth of *E. coli* (Botelho et al., 2012), distorted tropical freshwater plankton communities (Leboulanger et al., 2011) and increased fish kills (common carp) three times more than the weed (water hyacinth) that it was employed to control (Kathiresan & Deivasigamani, 2015). In non-aquatic organisms like honey bees (Cousin et al., 2013) very low concentrations of paraquat in larvae food disruptied the normal growth of honey bee eggs and colony. Critically, these low concentrations were below the detection limit by most modern analytical methods. Thus, we do not know how widespread the exposure is to honey bees, and whether this extreme sensitivity to paraquat would be exacerbated by exposure to other pesticides.

4.1. Bromoxynil

Bromoxynil is a nitrite herbicide used to control broadleaf weeds by inhibiting photosynthesis. It is widely used for pests associated with maize, wheat, sorghum and onions (Ansara-Ross, 2008) and for the treatment of broad-leaved weeds (Topp et al., 1992). A number of studies have investigated the potential health effects of exposure to bromoxynil. It is also a possible human carcinogen (Toxnet Toxicology Data Network, 2012; US National Archives and Records Administration Office of Pesticides Programs - Health Effects Division Science Information Management Branch, 2006) and a moderate eye, skin and respiratory irritant (Krieger, 2001). Safety concerns have led to a number of studies on exposure, particularly of farmers who use the pesticide for their crops (Cessna & Grover, 2002). The general population may also be exposed via inhalation of ambient air and dermal contact with surface water in agricultural regions where the product is used. (Semchuk et al., 2003). However, a 5-year study monitoring bromoxynil level in 7 wetlands placed on organic farms and 16 wetlands located on minimum-tillage farms in Canada, have recently shown the levels below water quality guidelines (Donald et al., 2018).

4.2. Diquat

Diquat is classified as a bipyridyl class of pesticide. It is used to protect potato, banana, vine and other seed crops. It is also used in aquatic systems for control of submersed, floating and emerging weeds. Diquat is the third most widely used herbicide in the world (Li et al., 2017). The physical properties of diquat (like paraquat) are unusual among the herbicides as it is highly absorbent in water and binds very strongly to the soil-organic matter matrix (Florencio et al., 2004). In soil, diquat becomes isolated and protected from the soil microorganisms, which can irreversibly prevent or significantly delay its cellular breakdown (Ogram et al., 1985; Weber & Coble, 1968). Hence, its biodegradation is extremely slow, but it does not translocate and consequently, diquat is rarely observed in secondary sites (Fenner et al., 2013).

In aquatic environments, diquat has been shown to break down quickly and completely with exposure to ultraviolet light (Florencio et al., 2004; Funderburk & Bozarth, 1967). However, caution must be applied when interpreting results from lab-based studies that may not simulate natural environmental conditions. A recent review of the potential toxic effects of diquat on fish and aquatic invertebrates in natural environments concluded that there were only short term or negligible effects on fish and aquatic invertebrates, which were thought to be outweighed by the increase in the available body of water (Breckels & Kilgour, 2018).

The toxicity of diquat may vary depend on aquatic species tested. Snails (Bouétard et al., 2013) and daphnia (Siemering et al., 2008) were more sensitive to negative impacts of diquat exposure compared with, for example, some fish species (Siemering et al., 2008). However a study on continuous lethal doses of diquat on microalgae reported concerning findings. In a Spanish study on herbicide resistance in herbicide-polluted waters, Marva et al (2010) looked at the impact on the natural evolution of a species of freshwater microalgae after exposure to lethal doses of diquat (*Scenedesmus intermedius*). Specifically, they used a very rapid evolution model to investigate: (i) whether adaptation occurred at lethal doses, and (ii) whether this occurred through physiological adaptation (acclimatization) due to post-adaptive mutation after herbicide exposure; or from (iii) adaptation arising through rare spontaneous mutations before subsequent exposures. The result of this study, demonstrated that rare, pre-selective spontaneous mutations of the microalgae appeared before exposure to subsequent lethal doses, ensuring survival of the species but with unpredictable consequences. They concluded that human manufactured pollutants could cause the 'emergence of evolutionary novelties in aquatic environments'. These findings should be followed up due to potential mutagenic effects with long-term consequences on the aquatic environment.

4.3. Paraquat

Paraquat is a bipyridylium herbicide used to control weeds around rice crops (Ismail, 2011), cotton, tomatoes, beans, soybeans, potatoes, sunflowers, sugar cane (Tsai, 2013a), fruit orchards and mulberry forests (Kim et al., 2009). It is a chemical with characteristically strong adsorption to organic matter due to its binding to negatively-charged components in the soil (**Table 3**). This greatly reduces its mobility in soil through leaching or other processes, and it is not readily chemically or microbiologically degraded (Smith & Mayfield, 1978). In water, the persistence of paraquat seems to depend upon the quantity and quality of sediment present. In one study, 80% of applied paraquat persisted in river water 56 days post-application (Wang et al., 1994), while U.S. Environmental Protection Agency reported aproximate half life of 160 days (https://nepis.epa.gov).

In an early study in New Zealand (Burnet, 1972), the recommended concentration of paraquat was added to the Waimakariri River, Canterbury, to control aquatic weeds. This resulted in a massive kill of drift invertebrate fauna (amphipods) to 5% of pre-treatment levels within one month, demonstrating a profound immediate and prolonged toxic effect. Interestingly, paraquat exposure on six day old water flea (*Daphnia magna*) in the three different types of water-sediment systems (system A water-alone control; system B simulating a spray drift exposure and system C simulating the irrigation scenario), did not lead to acute affect on *D. magna.* This was explained by a quick reduction of paraquat in water after the introduction of sediment, which quickly adsorbs to it in a dose-dependent manner (80 - 90%) within 48 hours (Kim et al., 2009).

At very low concentrations, as low as ng/kg, paraquat was shown to induce damages in honey bees (Cousin et al., 2013). In a French study (Cousin et al., 2013), researchers randomly selected a sample of healthy hives to insert an empty comb, returning 24 hours later to collect the lava. This was taken back to the laboratory and exposed to graded concentrations of paraquat 0 (control), 0.001, 0.01, 0.1 and 1 μg/kg in the water used as part of their food preparation, along with royal jelly. Within 48 hours, paraquat had substantially and significantly decreased the size of the oenocyte cells, cytoplasm and nucleus in a dose-dependent manner. The most remarkable thing was that disruption occurred at every concentration level, with the lowest concentration being lower than the detection limit of the most mass spectrometry analysis. This suggests that the honey bees, and their oenocytes in particular, are highly sensitive to paraquat (Cousin et al., 2013). A recent review by Sartori and Vidrio (2018) provides an overview of research studies demonstrating high toxicity of paraquat to honeybees, fish, and other aquatic species including teratogenic effects in birds and amphibians.

4.4. Risk to humans

Of these three agricultural chemicals, paraquat appears to pose the most imminent threat to humans. Paraquat is classified by WHO as a class II pesticide or moderately hazardous to human health (**Table 4**). Due to its high toxicity and deleterious effects, this pesticide has been reportedly banned from use in over 50 countries including China, the 27 countries of the European Union, Cambodia, and Vietnam (Konthonbut et al., 2018).

The early literature documents many cases of children and young people being severely poisoned from accidently swallowing paraquat from unlabeled containers (Haley, 1979). Paraquat was found to be easily absorbed via skin, lungs and the gastrointestinal tract (Huang et al., 2012), with a high number of cases of harmful effects on humans particularly in Asia where this chemical was used for suicides especially in rural communities (Wu et al., 2013).

A review by the American Academy of Paediatrics listed paraquat and diquat as highly toxic chemicals (Roberts et al., 2012). Children are considered to be very vulnerable to adverse effects of pesticides because of developmental, dietary, and physiologic factors. However, ongoing exposure remains a part of life for many children. A longitudinal study from agricultural areas of Thailand where paraquat is known to be used (Konthonbut et al., 2018), showed that drinking from a community well during pregnancy was associated with significantly higher paraquat in the meconium of the neonate than those who did not drink from the well (geometric mean (standard deviation): 124.9 (3.35) ng/mL exposed versus 26.99 (4.37) ng/mL not exposed, $p = 0.012$). Similarly, living next to farmland where pesticides were sprayed (46.62 (4.79) exposed versus 19.70 (3.77) ng/mL, non-exposed, $p = 0.031$), and having household family members who are agriculturalists were associated with significantly higher paraquat in meconium (42.09 (5.10) versus non-agriculturalists household 16.81(2.47) ng/mL, $p = 0.016$). This study confirmed that paraquat can pass the placenta barrier and 55% of the newborn meconium samples had measurable paraquat concentrations. Although this study does not link increased levels of paraquat in biological tissue with direct harmful effects, it is very concerning in the context of all that is now known about paraquat toxicity. Another study investigated whether consumption of water from private wells located in areas with documented historical agricultural pesticide use was associated with an increased risk of Parkinson's desease (PD) among residents of the Central Valley of California (Gatto et al., 2009). While the authors concluded that the consumption of well water potentially contaminated with pesticides may play a role in the incidence of PD, no direct link could be made for exposure to paraquat alone as paraquate was not detected in well water. The authors did note that they were not expecting to detect paraquat, as it does not usually enter wells through ground water (Gatto et al., 2009), although recent findings confrmed increased risk for contamination of surface waters and groundwater when pesticides used were used in local coffee planations (de Queiroz et al., 2018).

4. 5. Limitations

The search strategy used in this study included only papers published in English within the previous 10 years. The publication dates limits was to ensure currency of information. However, there were highly relevant earlier studies on these chemicals that were not identified in the initial search but were found on searches of the references from papers identified in the initial search. The most relevant of these papers were then included in the discussion.

Environmental research outcomes vary according to the methodologies used, potential biases, seasonal variability in environmental conditions, the characteristics of analysed species and other contributing biotic and abiotic factors. The scope of our literature review was to assess whether or not there was evidence of harmful effects of chemicals used in agriculture entering the local waterways. Questions about how frequent and the concentrations of the chemicals that are likely to be in use were beyond the scope of the current project but should be addressed in future research. Also, an assessment on the propensity of the chemicals to persist in soil and water was also beyond the scope of the current study.

Our findings provide information about three agricultural herbicides identified as likely to be in current use in the Byron Shire (Australia). In this scoping review, we have collated the available scientific evidence on the toxicity of three agricultural pesticides acquired from laboratory controlled conditions, via *in situ* monitoring, computer modelling studies, risk assessments and epidemiological studies conducted in a number of countries around the globe (USA, Canada, Brazil, China, Korea, Malaysia, Taiwan, India, South Africa, Netherlands and France). This review found evidence of harmful effects on aquatic environments from all the three herbicides investigated: bromoxynil, diquat and paraquat, even when used at realistic (recommended) concentrations.

5. *Conclusions*

This scoping review identified bromoxynil, diquat and paraquat as three chemicals most likely to be in common use in the Byron Shire that were most toxic to aquatic ecosystems in the local waterways. Paraquat has been banned from sale in many countries because of its high toxicity potential but remains available in Australia. Further research is urgently required to scope the extent of its use and the effectiveness of regulations governing its use. This study provides a methodology that can be used in regional areas to identify pesticides that are likely in local use and identify evidence of any negative impact on the health of local waterways.

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