



**Investigating pesticide and heavy metal distribution from water and
sediments near expanding horticulture activities in the
Coffs Harbour NSW region**

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Executive Summary

Southern Cross University was successful in obtaining funding from Coffs Harbour City Council to perform pesticide and heavy metal analyses from water, soil and biota near expanding horticulture activities in the Coffs Harbour with funding from the Environmental Levy Program. However, biota such as molluscs were not found within the Hearnese Lake estuarine systems as was originally expected. Therefore we were unable to conduct analyses on these organisms as originally planned. To compensate, highly specialized sediment analyses were conducted on dated sediment cores throughout this coastal area which provide solid evidence as to why specific biota that are typically used for the analyse outlined in the project were not found in this area. The topics of concern are the pesticides and heavy metals entering the Solitary Islands Marine Park (SIMP), implications associated with the rapid expansion of agricultural and urban development.

Coastal development and agricultural practices are often located in catchments upstream of ecologically important aquatic systems. The eastern coast of Australia has an extensive history of development including intensive horticulture and associated pesticide use along its coastal regions. This type of expansion can lead to unintended negative impacts on local flora and fauna. Due to these types of concerns, this study aims to investigate the occurrence of pesticides and heavy metals along habitat-protected areas within the Solitary Islands Marine Park, Australia.

Water samples were collected along creeks within an estuarine transect during three sampling periods. Samples were analysed for 171 pesticide analytes, including organochlorines, organophosphates, herbicides, and fungicides. Five insecticides, two herbicides, and two fungicides were detected in coastal creeks. The neonicotinoid imidacloprid was detected at 5 out of 6 sites, with concentrations reaching $294 \mu\text{g L}^{-1}$, the highest yet detected in Australian waterways. Methomyl, an organophosphate insecticide, was also detected at 5 sites, and the organophosphate insecticide dimethoate was detected at 4 out of the 6 sites, which occurred at the 2nd highest detected concentration found in the study ($12.8 \mu\text{g L}^{-1}$). The presence of these pesticides in the aquatic environment downstream of horticulture in this and other regions may have serious implications for stream biota and ecologically important marine ecosystems.

In soils and subsequent dated sediments, arsenic accumulation rates were shown to have significantly increased in the past decade, up to $259.6 \text{ mg m}^{-2} \text{ year}^{-1}$ in 2020. Additionally,

methylmercury in sediments were found to range from 0.1 mg kg⁻¹ in 2017 to 0.2 mg kg⁻¹ in 2019. Methylmercury in surface sediments within estuaries are of concern, as this substance is known to bioaccumulate within aquatic ecosystems and is highly toxic to humans. This study highlights the importance in monitoring agriculture-derived pollutants discharged in catchments and provides a robust set of data that enables initiatives aiming to mitigate pesticides and heavy metals found within the Coffs Harbour region and the SIMP.

Part 1. Pesticide distribution along creeks flowing to the Solitary Islands Marine Park

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1.1 Introduction

With an increasing global population and subsequent food demand, agricultural practices are becoming more intense and expansive. To secure productivity and efficiency, the use of pesticides in agricultural practices has increased globally [1, 2]. In Australia, for example, over 8,000 pesticides and veterinary chemicals are currently registered for use [3] in a broad range of practices such as in cropping, livestock, horticulture, and domestic use. Australia uses over 80 active ingredients currently banned in the European Union; of these banned chemicals, 48 pesticides are considered endocrine disruptors, and 17 pesticides are likely to be carcinogens. Due to Australia's extensive history with pesticides, contamination of the aquatic environment by these chemicals may occur in intensive horticultural catchments [4-6].

Coastal agricultural practices are frequently situated upstream from estuaries and other important aquatic habitats [7-9]. Worldwide, coastal estuaries are some of the most endangered yet ecologically important habitats, providing critical nurseries and foraging grounds for various species of fish and invertebrates [10, 11]. Although coastal aquatic ecosystems face serious water quality issues [12-14], very little is understood in terms of pesticides concentration and flux levels that reach coastal waterways or how these contaminants may affect estuarine habitats [8, 9].

Pesticides and other contaminants can be transported into waterways via spray drift or water runoff during agricultural irrigation or rainfall events, often draining into surface waters or leaching into groundwater through soils [15]. The distribution and persistence of a pesticide in waterways and sediments depend on the individual pesticide's properties such as, but not limited to, hydrophobicity, concentration, lipophilicity, along with environmental conditions such as temperature, pH, and sediment characteristics [16]. As a result, downstream ecosystems frequently become a sink for many pesticides that bioaccumulate once entered in the food web or are buried in sediments [17]. Specific pesticides in aquatic systems can threaten drinking water systems [18], aquatic zooplankton and phytoplankton [19, 20], seagrass [21], coral reefs [3], oysters [22, 23] and higher trophic organisms such as amphibians [24], crustaceans [25, 26], as well as fish and their predators [27, 28]. Due to the Investigating pesticide and heavy metal distribution from water and sediments near expanding horticulture activities in the Coffs Harbour NSW region

threats directly related to pesticide pollution, investigations into the origin of site-specific agriculture areas are essential for the effective management of aquatic habitat health [29].

Non-point source pollutant monitoring is crucial to better understand the health of aquatic systems [30]. For instance, in a nationwide survey of pesticide contamination in important surface waterways and groundwater, the United States Geologic Survey found one or more pesticides in 90% of water samples from agricultural, urban, and mixed-land use streams [31]. Despite the widespread and intensive use of pesticides in Australia, only a few long-term studies have focused on pesticides in the waterways of New South Wales (NSW) [32], Queensland [33], and South Australia [30]. Lewis et al. (2009) detected off-site transport of insecticides and herbicides into important aquatic systems, such as wetlands and waterways, flowing to the Great Barrier Reef, a World Heritage listed, valuable and sensitive marine environment. Current monitoring programs of Australian waterways have often detected pesticide residues above Australian guidelines [3]. However, on a local scale, pesticide runoff in Australian waterways remains largely unknown. More knowledge is necessary to address the information deficit across agricultural catchments and detect changes in pesticide runoff over time.

Coffs Harbour, NSW, has been an agricultural hub since the 1950s. The region was well known for banana cultivation, with the industry established in the region in 1891, then expanding in the mid-1900s with pesticide usage to support increased productivity [34]. The blueberry industry has now replaced most banana cultivation in the area and coexists with increasing hothouse horticulture [35]. Blueberry horticulture production has doubled from 2013 to 2020, accounting for more than 90% of Australia's blueberries [13, 36]. A preliminary study in 2019 found six agricultural pesticides; boscalid, diuron, metolachlor, carbendazim, propiconazole and terbutryn, in drinking water tanks near horticulture, likely driven by spray drift (Hessey et al. 2019). Furthermore, Conrad et al. (2019) found a range of pesticides present in soil cores collected near agricultural practices, including propiconazole, diuron, dimethoate, carbendazim, methomyl.

Here, we investigate pesticide runoff in a horticultural catchment waterway, flowing into a subtropical estuary within the Solitary Islands Marine Park. Specifically, we assess: 1) the spatial distribution of 171 analytes, including organophosphates, thiocarbamates and carbamates, triazinone and triazine herbicides, and conazole and aminopyrimidine fungicides, along a gradient from just below potential horticultural sources to the headwaters

of an estuarine system; 2) the influence of rainfall on pesticide composition by comparison between periods of higher rainfall (January to April) and periods of lower rainfall (October), with the later collected before and after mild rainfall.

1.2. Materials and Methods

1.2.1 Study Site

Field sampling was conducted in Double Crossing Creek, a coastal waterway in the Sandy Beach and Woolgoolga catchment area in northern NSW, Australia (-30.1362, 153.1975; ~20km north of Coffs Harbour) that drains into Hearn's Lake estuary. Six sites were sampled over approximately 2.5km (Figure 1.1). Site 1 was positioned ~20m downstream from a covered tomato cropping practice and Site 6 was located downstream near the upstream entrance to Hearn's Lake estuary (Figure 1.1), which is zoned as habitat protected area within the Solitary Islands Marine Park (SIMP). The estuary is considered to be an intermittently closed and open lake or lagoon (ICOLL), being one in about 70 ICOLLs on the NSW coast [37]. ICOLLs are unique in their entrance dynamics, which can remain closed off to the ocean for extended periods of time [38]. The entrance of Hearn's estuary is variable, mostly being closed to the ocean by a sand barrier formed by longshore currents and opening to the Pacific ocean during times of intense rainfall [37]. The estuary, which has a history of pressure from intense agricultural use, may be subject to excess nutrients and agricultural chemicals [39, 40] mobilised from farm fertiliser applications and soil erosion, driven by irrigation and rainfall.

The whole catchment of Hearn's Lake, including other creeks other than the location of this study, is 6.8km² [41], of which approximately 1.09 km is currently used for horticulture (16%) [34]. The catchment land is steep, rising to approximately 269m above sea level in ~4km [34], and the mean annual rainfall of the area is 1685mm per year, with approximately 60% of rain occurring from January to May. The region experiences high agricultural productivity, which has rapidly grown in recent years. More than 90% of Australia's blueberries are produced here, with banana, cucumber, tomato, and avocado horticulture also prevalent in this region (Figure 1.1) (Regional Development Australia, 2017). Site 6 of our study captures one creek in the catchment (Double Crossing Creek), which is the main tributary that drains into Hearn's Lake. The sub-catchment area that is reflected in our study is 223.3 km² [41].

Figure 1.1. Location of study area on the east coast of Australia, sample sites, catchment boundary, current and abandoned agricultural practices, and waterways.

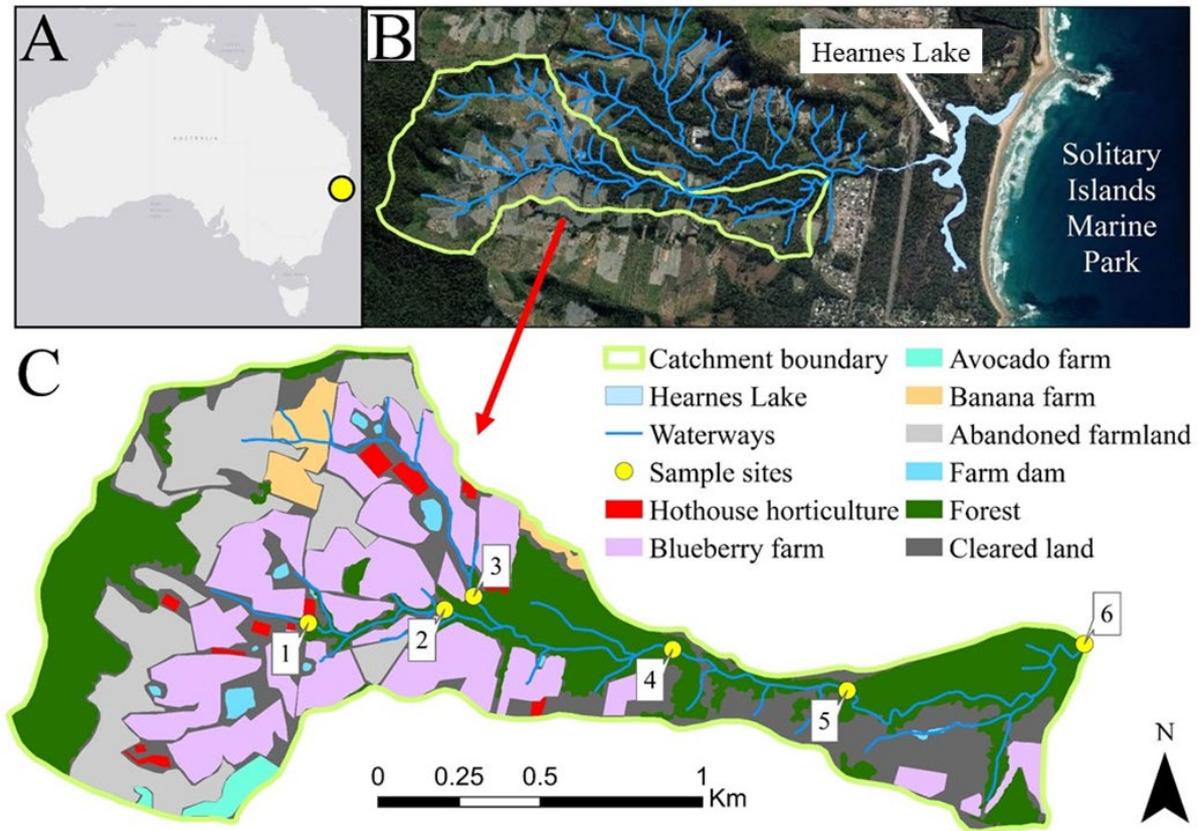


Table 1.1. Environmental data collected over the summer-autumn sampling period.

Values are averaged across all samples taken.

Site	Temperature average (°C)	pH average	DO (mg/L) average	DO (%) average	Salinity (ppt) average	Creek width (cm)	Creek depth (cm)	Creek area (m ²)	Flow rate (m s ⁻¹)	Turbidity (NTU)
1	25.95	7.41	8.372	102.925	2.1125	12.09 ± 11.9	3.38 ± 3.7	0.79 ± 1.92	0.13 ± 0.13	144.29 ± 92.93
2	22.76	6.82	3.052	35.4	0.24	134.97 ± 63.95	24.52 ± 11.11	37.58 ± 25.62	0.10 ± 0.06	17.45 ± 26.99
3	22.89	6.49	4.513	52.71	0.22	103.43 ± 40.24	9.44 ± 7.10	11.11 ± 11.14	0.15 ± 0.10	38.37 ± 94.50
4	22.15	7.3	6.369	73.39	0.2	55.49 ± 50.40	13.50 ± 2.34	7.02 ± 6.11	0.42 ± 0.21	3.93 ± 9.66
5	22.82	7.23	6.047	70.22	0.21	107.50 ± 78.12	10.12 ± 12.49	18.68 ± 29.19	0.19 ± 0.12	2.95 ± 2.92
6	22.55	7.44	4.744	54.17	0.2	146.36 ± 48.67	9.22 ± 4.40	14.59 ± 9.05	0.22 ± 0.13	7.50 ± 5.71

1.2.2. Sample Collection

Samples were collected from six sites in the Hearnese Lake catchment area (Figure 1.1) during three separate sampling periods based on precipitation patterns: 1) weekly over 14

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weeks from January to April 2019 (Australian summer - autumn), from here on referred to as "summer-autumn"; 2) before a single rain event on September 30th 2019 (Australian spring); from here on referred to as the "spring-before rain event" and 3) after a single rain event on October 1st 2019 from here on referred to as "spring-after rain event". Further sampling was prohibited due to COVID restrictions and to compensate a suite of analyses were conducted at every time interval of these sampling campaigns. Sampling was conducted during what was observed to be a particularly dry summer and autumn. Approximately 244mm of accumulated rainfall occurred over summer. The first rainfall event post dry period contributed approximately 30mm in one day. Then a secondary flush preceded a second large event that yielded >30mm in one day. Salinity, pH, DO (%), and temperature was recorded in the field during each sampling (Table 1.1). Flow rates were calculated during summer-autumn sampling, according to Conrad et al. (2019).

During summer-autumn, 10ml of unfiltered water was collected from each site once a week (n = 14 per site) then stored at 4°C and in the dark until processed. The samples from each site were then pooled across the 14 weeks to create a single composite sample prior to pesticide analysis, to account for short-term fluctuations. Due to the composite nature of these samples, chronic vs. acute concentrations are unknown. The turbidity of each individual pooled sample (n=6) was determined in the laboratory using a TN-100/T-100 turbidimeter. Pooled samples were filtered through a 0.45-micron filter paper using vacuum filtration to remove any sediments. The filtered samples were stored in amber vials before analysis.

During spring, a single unfiltered 5L water sample was collected per site (n=6) on 30/9/2020 and the following day after a mild rain event (17mm). All samples were stored at 4°C and in the dark until processed. Once turbidity was determined per site, samples were filtered and stored in 100ml amber vials to be sent for analysis.

1.2.3. Analytical Testing Methods

To examine the non-point source pollution of Double-Crossing Creek, water samples were analysed for the extended multi-residue pesticide suite of 171 analytes (water) (EP234), which included organophosphorus pesticides, thiocarbamates and carbamates, triazine herbicides, triazole fungicides, and more (See Appendix). Analysis was performed at ALS Global, Sydney using LC-MSMS with direct injection (40µl), using an in-house NATA accredited method. Every 20 samples produced were accompanied with a Method Blank, Lab Controlled Spike, 2x Duplicates, and a Matrix Spike. Only detections above limits of

reporting (LOR) were reported, and all values below the reliable detection limit based on analytical standards were given the value of "not-detected" (see Appendix). A quality control test using spiked samples at known concentrations was conducted to ensure method precision.

1.3. Results

1.3.1. Pesticide spatial and temporal patterns

A total of nine pesticides were detected in water samples during the summer-autumn sampling (Table 1.2), which was the highest number of detected pesticide residues out of the three sampling periods. They included 3 organophosphates (dimethoate: min: $0.02 \mu\text{g L}^{-1}$ max: $12.8 \mu\text{g L}^{-1}$, omethoate: $0.12 \mu\text{g L}^{-1}$, malathion: $0.47 \mu\text{g L}^{-1}$), 1 carbamate (methomyl: min: $0.02 \mu\text{g L}^{-1}$ max: $5.6 \mu\text{g L}^{-1}$), 2 triazine herbicides (terbutryn: min: $0.1 \mu\text{g L}^{-1}$ max: $0.46 \mu\text{g L}^{-1}$, terbuthylazine: min: $0.01 \mu\text{g L}^{-1}$ max: $0.03 \mu\text{g L}^{-1}$), 2 azole fungicides (pyrimethanil: $0.09 \mu\text{g L}^{-1}$, triadimenol: $1.5 \mu\text{g L}^{-1}$), and 1 neonicotinoid insecticide (imidacloprid: min: $0.02 \mu\text{g L}^{-1}$ max: $294 \mu\text{g L}^{-1}$). All detected pesticides were reported at Site 1, which was surrounded by the most intense horticultural activity, and this site had the highest concentration of pesticides out of the six sample sites. All detected pesticide concentrations decreased substantially from Site 1 to Site 2 and then generally fluctuated between the remaining sites (i.e. Imidacloprid: (S1) $294 \mu\text{g L}^{-1}$, (S2) $0.05 \mu\text{g L}^{-1}$; Dimethoate: (S1) $12.8 \mu\text{g L}^{-1}$, (S2) <LOR; Malathion: (S1) $0.47 \mu\text{g L}^{-1}$, (S2) <LOR) (Figure 1.3). Only two out of the nine pesticides, imidacloprid and dimethoate, were detected during the spring sampling period pre- and post-rainfall event (Table 1.2) (Pre-rainfall imidacloprid: (S1) 0.61 and (S3) $0.07 \mu\text{g L}^{-1}$, Dimethoate: 0.07 (S3) $\mu\text{g L}^{-1}$; Post-rainfall imidacloprid: (S1) 0.04 and (S3) $0.04 \mu\text{g L}^{-1}$, Dimethoate: (S5) $0.02 \mu\text{g L}^{-1}$).

Imidacloprid was detected the most frequently (five out of six study sites) and at the highest concentration of any single pesticide found during this study (Table 1.2). During the summer-autumn sampling, imidacloprid peaked at Site 1 ($294 \mu\text{g L}^{-1}$) and then decreased substantially at Site 2 ($0.05 \mu\text{g L}^{-1}$). The imidacloprid concentration at Site 3, which is located on a separate creek from Sites 1 and 2, was $0.24 \mu\text{g L}^{-1}$. Imidacloprid was not detected at Site 4 ($<0.01 \mu\text{g L}^{-1}$) but was then detected again at Sites 5 and 6 (0.06 and $0.02 \mu\text{g L}^{-1}$, respectively) (Figure 1.3, Figure 1.4). During the spring sampling, imidacloprid was detected above the LOR ($<0.01 \mu\text{g L}^{-1}$) at Sites 1 and 3 before the single rain event ($0.61 \mu\text{g}$

L⁻¹ and 0.07 µg L⁻¹, respectively), and then detected again at Sites 1 and 3 after the single rain event (0.04 µg L⁻¹ 0.04 µg L⁻¹, respectively) (Figure 1.2).

Dimethoate was detected as the pesticide with the second-highest concentration (12.8 µg L⁻¹ at site 1) and occurred above the LOR (<0.02 µg L⁻¹) at 4 out of 6 sites during the summer-autumn sampling period (Table 1.1). It was not found above its limit of detection (<0.02 µg L⁻¹) at Site 2 and 3 but was found again 0.02 µg L⁻¹ at Sites 4, 5, and 6 (Figure 1.3). During the spring, dimethoate was detected above the LOR (<0.02 µg L⁻¹) solely at site 2 (0.02 µg L⁻¹) before the rain event, and then solely at Site 5 after the rain event (0.02 µg L⁻¹).

Methomyl, a carbamate insecticide, was detected at five out of six sites during the summer-autumn sampling period. Methomyl was detected at its highest concentration at Site 1 during the summer-autumn (5.6 µg L⁻¹) and was also detected at Sites 3, 4, 5 and 6 (0.08 µg L⁻¹, 0.02 µg L⁻¹, 0.02 µg L⁻¹, 0.02 µg L⁻¹, respectively) during the summer-autumn (Figure 1.3).

Terbutryn was detected at 50% of sites during summer-autumn (Figure 1.3), with the highest concentration at Site 1 (0.46 µg L⁻¹) and also above detection limits at Sites 4 and 5 (0.19 µg L⁻¹ and 0.10 µg L⁻¹, respectively). Terbutylazine was found at 66% of sites with only slight variation between sites (Site 1: 0.02 µg L⁻¹, Site 2: 0.03 µg L⁻¹, Site 3: 0.02 µg L⁻¹, Site 4: 0.01 µg L⁻¹)(Figure 1.3). Triadimenol, omethoate, malathion, and pyrimethanil were found exclusively at Site 1 (1.5 µg L⁻¹, 0.12 µg L⁻¹, 0.47 µg L⁻¹, and 0.09 respectively) during the summer-autumn sampling period, and therefore not detected above the LOR at any of the other sample sites or during the other sampling periods (Figure 1.3).

Table 1.2. Detected pesticides from Hearnes Lake across three different study periods: wet season (summer-autumn), dry season before rain (spring), and dry season after rain (spring). Values are taken from known concentrations (>LOR) (µg L). I= Insecticide, F=Fungicide, H= Herbicide; Minimum, maximum, and average values taken from known concentrations (above LOR). *Stream discharge rates as in White et al., 2021. The pesticide load (flux per area, per time) was calculated using the equation: $F = CMQ/A$. Where F is the flux of nutrients (kg ha day⁻¹), C is the concentration of nutrient (uM), M is the molecular weight of the element (g mol⁻¹), Q is discharge (m³ day⁻¹) and A is catchment area (ha). Unit conversions were used where appropriate.

Name	Type	Water solubility	Half life in water (river conditions)	Bioaccumulation potential (log K_{ow})	LOR ($\mu\text{g L}^{-1}$)	Number of detections	FOD (%)	Average ($\mu\text{g L}^{-1}$)	Min ($\mu\text{g L}^{-1}$)	Max ($\mu\text{g L}^{-1}$)	Flux* ($\mu\text{g m}^{-2} \text{ day}^{-1}$)
Wet season	Dimethoate	I	25,000 (mg L^{-1}) at 20 °C ^a	43 days (at 22 °C) ^o	0.78 ^g	4	67	3.22 ± 5.21	0.02	12.8	0.247
	Imidacloprid	I	6100 (mg L^{-1}) at 20 °C ^a	33–44 days ^h	0.57 ^p	5	83	58.87 ± 103.91	0.02	294	4.498
	Malathion	I	143 (mg L^{-1}) at 20 °C ^c	0.2 weeks (pH 6) to 21 weeks (pH 8) ⁱ	2.36 ^q	1	17	0.47 ± -0	-	-	0.035
	Methomyl	I	58,000 ($\text{g } 100 \text{ mL}^{-1}$) at 25 °C ^a	73, 205, and 194 days (pH 5, 7, and 9, respectively) ^{k, j}	0.60 ^q	5	83	1.15 ± 2.49	0.02	5.6	0.112
	Omethoate	I	500,000 ($\text{g } 100 \text{ mL}^{-1}$) at 20 °C ^b	26 days (at 24 °C & pH 7) ^m	-0.74 ^d	1	17	0.12 ± 0	-	-	0.009
	Pyrimethanil	F	121 ($\text{g } 100 \text{ mL}^{-1}$) at 25 °C ^d	14 days ^{e, l}	2.84 ^d	1	17	0.09 ± 0	-	-	0.007
	Terbuthylazine	H	5 ($\text{g } 100 \text{ mL}^{-1}$) at 20 °C ^e	50 days ^l	3.40 ^e	4	67	0.02 ± 0	0.01	0.03	0.033
	Terbutryn	H	25 ($\text{g } 100 \text{ mL}^{-1}$) at 20 °C ^f	6.9 to 30 days (pond water) ^k	3.74 ^e	3	50	0.25 ± 0.19	0.1	0.46	0.052
	Triadimenol	F	120 ($\text{g } 100 \text{ mL}^{-1}$) at 20 °C ^g	River water value unknown (110–375 days absorbed to sediment in pond water) ^o	2.90 ^e	1	17	1.5 ± 0	-	-	0.112
	Dimethoate	I	2.5 ($\text{g } 100 \text{ mL}^{-1}$) at 21 °C ^a	43 days (at 22 °C) ^m	0.78 ^o	1	17	0.02 ± 0	-	-	0.005
Dry season (Before rain)	Imidacloprid	I	00.61 ($\text{g } 100 \text{ mL}^{-1}$) at 20 °C ^a	33–44 days ^h	0.57 ^p	2	33	0.34 ± 0.38	0.07	0.61	0.014
	Dimethoate	I	2.5 ($\text{g } 100 \text{ mL}^{-1}$) at 21 °C ^a	43 days (at 22 °C) ^m	0.78 ^q	1	17	0.02 ± 0	-	-	0.001
	Imidacloprid	I	00.61 ($\text{g } 100 \text{ mL}^{-1}$) at 20 °C ^a	33–44 days ^h	0.57 ^p	2	33	0.04 ± 0	-	-	0.024

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a ICSC database (2004). b University of Hertfordshire (2021). PPDB: Pesticide Properties Database. Omethoate. Retrieved from: <http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/492.htm> c Bowman, BT & Sans, WW (1983) Retrieved from: <https://go.drugbank.com/drugs/DB00772> d Tomlin, C.D.S. (ed.). The Pesticide Manual - World Compendium, 11 th ed., British Crop Protection Council, Surrey,England 1997 (Hazardous Substances Database). e He, Y., Jain, P., & Yalkowsky, S. H. (2010). Handbook of aqueous solubility data. CRC press. f Yalkowsky, S. H., & He, Y. (2003). An extensive compilation of aqueous solubility data for organic compounds extracted from the AQUASOL database. Handbook of Aqueous Solubility Data, 377. g O'Neill, M. J. (2006). The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. Whitehouse Station, New Jersey: Merck Research Laboratories, Division of Merck and Co. h Sarkar, M. A., Biswas, P. K., Roy, S., Kole, R. K., & Chowdhury, A. N. D. A. (1999). Effect of pH and type of formulation on the persistence of imidacloprid in water. Bulletin of Environmental Contamination and Toxicology, 63(5), 604–609. i Worthing, C.R. and S.B. Walker (eds.). The Pesticide Manual - A World Compendium. 8th ed. Thornton Heath, UK: The British Crop Protection Council, 1987., p. 298. j Worthing, C.R. and S.B. Walker (eds.). The Pesticide Manual - A World Compendium. 8th ed. Thornton Heath, UK: The British Crop Protection Council, 1987., p. 778. k D. C. Muir, M. Pitze, A. P. Blouw and W. L. Lockhart, Weed Res., 1981, 21, 59–70. l Chambon, P. (1998). Terbutylazine (TBA) in Drinking-water. World Health Organization, Geneva. m Hartley D et al.; The Agrochemicals Handbook; Old Woking Surrey,England; Unwin Bros Ltd. (1983). n Lartiges SB, Garrigues PP; Environ Sci Technol 29:1246–54 (1995). o Gao JP et al.; Water Res 31: 2811–19 (1997). p C. D. S. Tomlin, “The e-Pesticides Manual,” Version 3.0, 13th ed., BCPC (British Crop Protection Council)(2004). q Hansch, C., Leo, A. and Hoekman, D. (1995) Exploring QSAR: Hydrophobic, electronic, steric constants. ACS, Washington, DC. r MacBean C, ed.; e-Pesticide Manual. 15th ed., ver. 5.1, Alton, UK; British Crop Protection Council. Terbutylazine (5915-41-3) (2008–2010). s Baker EA et al.; Pestic Sci 34: 167–82 (1992).

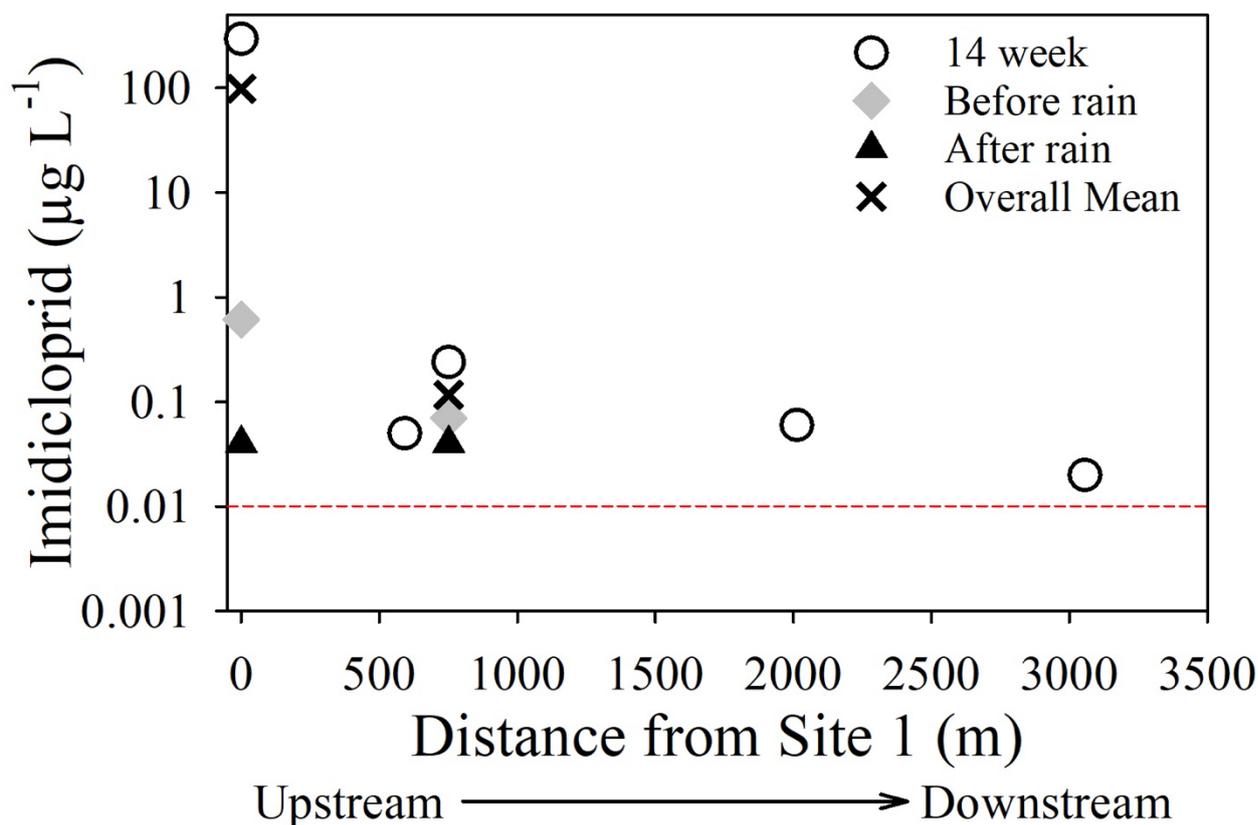


Figure 1.2. Imidacloprid concentrations ($\mu\text{g L}^{-1}$) at each study site throughout all three sampling periods (summer-autumn, spring-before rain event, and spring-after rain event).

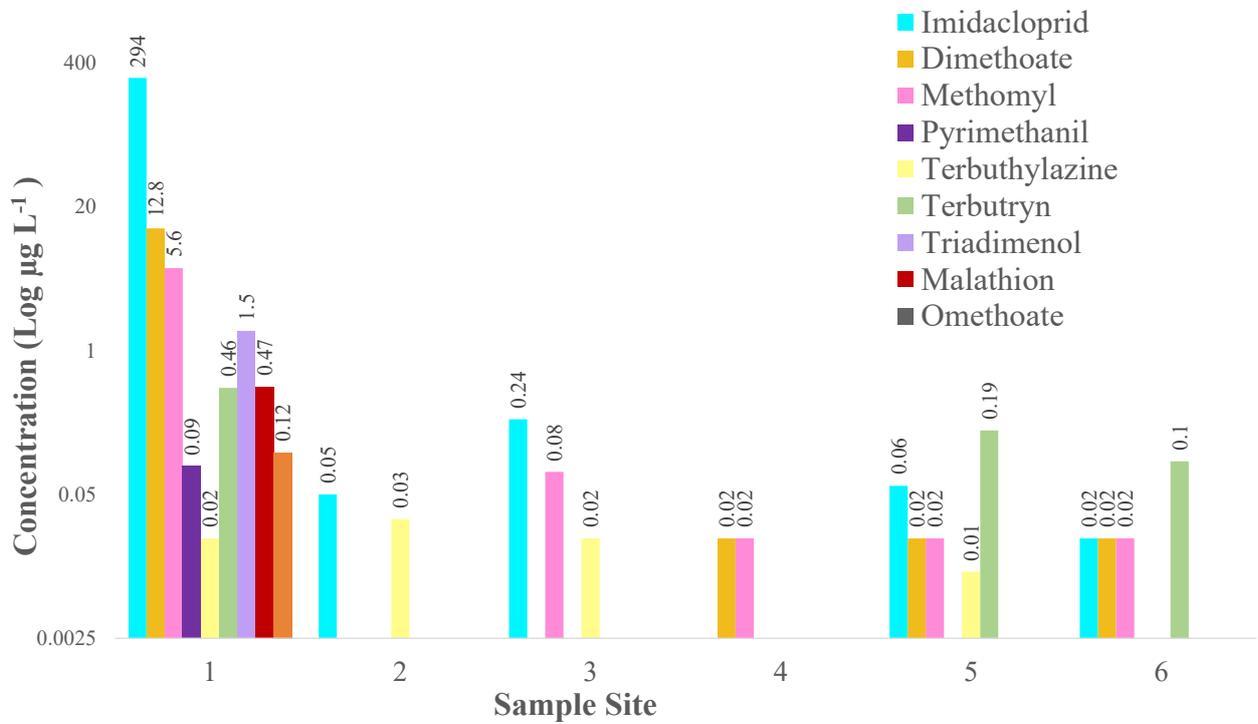


Figure 1.3. Pesticide concentrations ($\mu\text{g L}^{-1}$) detected at each sampling site along Double Crossing Creek during the summer-autumn sampling period in 2019.

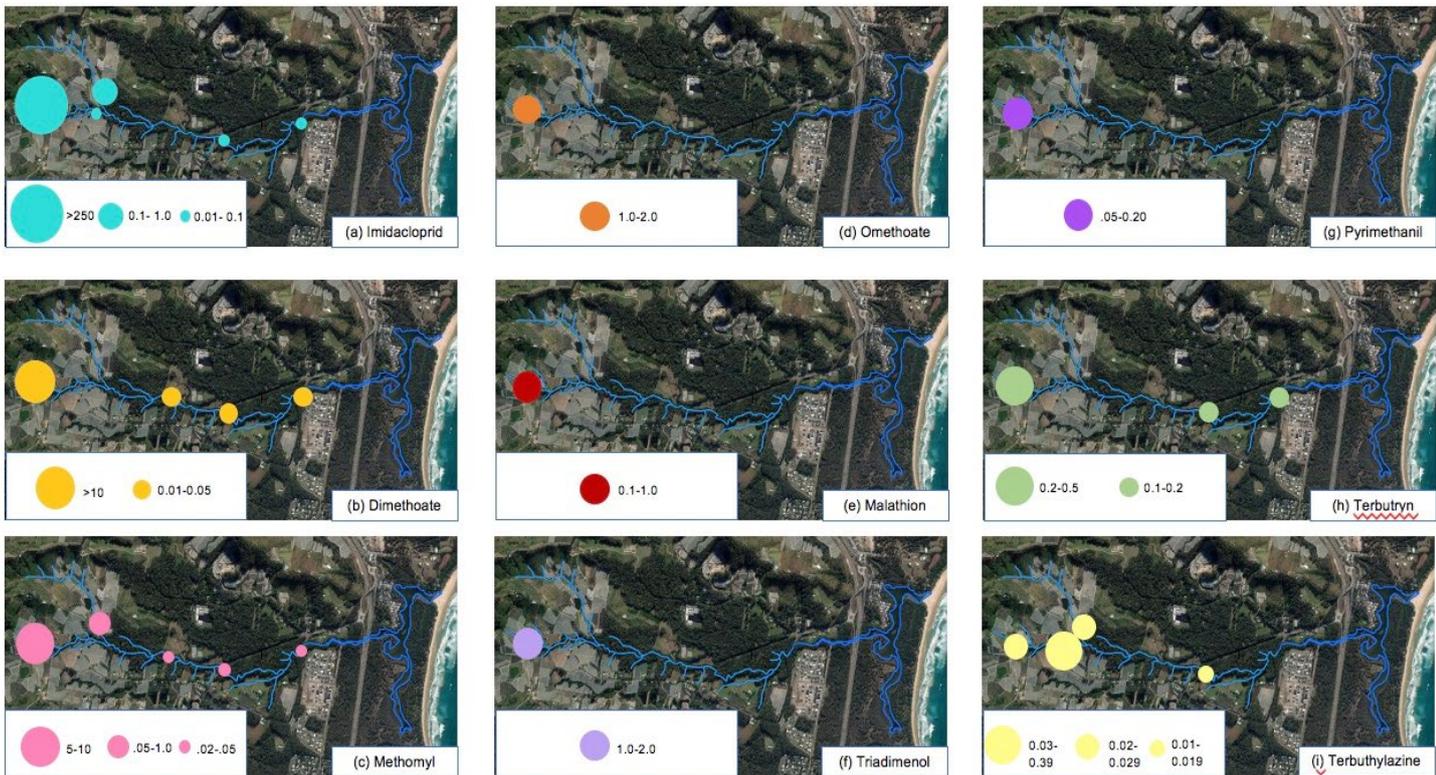


Figure 1.4. Spatial distribution of pesticide concentrations ($\mu\text{g L}^{-1}$) (a-i) along Double Crossing Creek in the Hearnes Creek estuary catchment during the summer-autumn sampling period in 2019.

1.3.2 Turbidity and pesticide relationships

Turbidity averages displayed a similar trend to that observed for total pesticide concentrations from Sites 1 to 4 (Figure 1.5). Turbidity values (NTU) taken from Site 1 during the summer-autumn sampling period were substantially higher (144.3 ± 28 NTU) than values observed at any of the other sites during the sampling period (17.4 ± 7.2 (S2), 38.4 ± 25.3 (S3), 3.9 ± 2.6 (S4), 3 ± 0.8 (S5), 7.5 ± 1.5 (S6) NTU) (Figure 1.5). A potential relationship between turbidity and pesticide concentrations was observed for imidacloprid and methomyl ($R^2 > 0.95$) (See Appendix). No linear correlations were observed for other pesticides detected.

1.4. Discussion

This study highlights pesticide contamination in the waterways that flow into Hearn's Estuary, which is located within the Solitary Island Marine Park, Australia. Nine pesticides were detected, two of which were persistent in all three sampling periods. There was a spatial gradient in pesticide concentrations with the highest levels recorded at an upstream site, nearest to the agriculture activity and generally dissipating downstream towards the coast (Figure 1.4). Turbidity was observed as a potential indicator of pesticide concentrations, with a possible relationship with concentrations in two of the detected pesticides, imidacloprid, and methomyl (See Appendix).

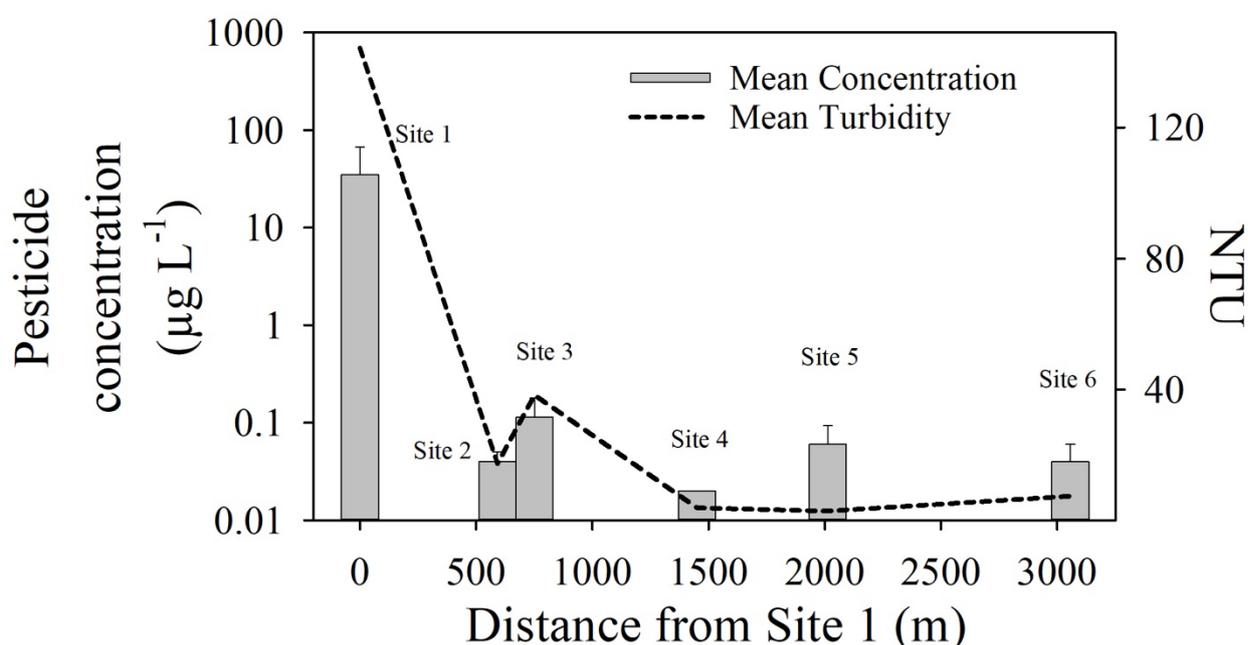


Figure 1.5. Total and average pesticide concentration during summer-autumn sampling period graphed on the left y-axis. The average turbidity of each site is graphed on the right y-axis.

The neonicotinoid insecticide imidacloprid was the dominant pesticide found with high concentrations detected during the summer-autumn sampling period and low-level persistence both before and after a mild rain event during the spring sampling. The concentrations of this water-soluble pesticide recorded at site 1 during summer-autumn ($294 \mu\text{g L}^{-1}$) was substantially higher than all other imidacloprid concentrations found in this study (e.g. $0.24 \mu\text{g L}^{-1}$, $0.06 \mu\text{g L}^{-1}$, $0.02 \mu\text{g L}^{-1}$) and is in the high range of previously detected concentrations from waterways in Australia (0.2 - $4.6 \mu\text{g L}^{-1}$) [42, 43] and globally (e.g. $320 \mu\text{g L}^{-1}$ in the Netherlands [44]; $3.29 \mu\text{g L}^{-1}$ in California [45]; $15 \mu\text{g L}^{-1}$ in Sweden [46]; and

11.9 $\mu\text{g L}^{-1}$ in eastern Canada [47]). These high concentrations indicate that imidacloprid is currently being used in the agricultural catchment particularly during the Australian summer season. The correlation between imidacloprid concentrations with water turbidity indicates that this pesticide is potentially entering the waterways as runoff and dissipating along the creek.

Imidacloprid is water soluble (6,100 mg/L) (Table 1.2), but has low bioaccumulation potential (K_{ow}) (0.57), and therefore can be adsorbed but is not predicted to bioaccumulate in organisms [48]. Contrarily, other studies have examined rapid uptake and some accumulation above water concentration by some species of prawns and oysters, although it can depart from the flesh when flushed with seawater [22, 49]. Previous studies have demonstrated that imidacloprid can negatively impact local estuarine species, including the eastern school prawn, *Metapenaeus macleayi* [50], the black tiger prawn *Penaeus monodon* [26], and the Sydney rock oyster *Saccostrea glomerata* [22, 23]. Although imidacloprid is registered for use in all of Australia, the use of this neonicotinoid pesticide has been severely restricted in the European Union due to environmental impacts on non-target species [51, 52]. Currently, there is no ANZECC water quality guideline for imidacloprid in Australia, although the Australian Pesticides and Veterinary Medicines Authority have plans to review this (APVMA 2019).

There was substantial spatial and temporal variation in the concentrations of imidacloprid detected in this study. The detection of neonicotinoid insecticides in the environment can be affected by a number of factors such as light, water depth, and the presence of sediment and organic materials, all of which can accelerate degradation and reduce concentrations in the water (e.g. shallow water depth with greater light penetration will increase photodegradation) [53]. Regardless, concentrations were most likely due to proximity to sites where imidacloprid was used and the frequency/intensity of use. Previous studies have demonstrated that neonicotinoids peak in concentration after 24 hours post application when entering surface waters, after which dissipation rapidly occurs [54]. Field studies investigating imidacloprid degradation have examined rice paddy water in which losses of imidacloprid have been suggested through several pathways including dilution, infiltration, plant uptake, microbial degradation, photolysis, and sorption to soil and sediment [54]. The use of composite samples over 14 weeks from January to April (summer-autumn) has likely increased the chance of detecting this pesticide but could also lead to an underestimate of peak concentrations in the waterways due to dilution in weeks with lower use

and/or runoff. The imidacloprid concentrations detected in the pooled sample from Site 1 during summer-autumn ($294 \mu\text{g L}^{-1}$) are similar to that reported following intense rainfall events in the Netherlands ($320 \mu\text{g L}^{-1}$) [44]. The transport and persistence of imidacloprid following rainfall is likely to result in pulses of elevated concentrations followed by chronic exposure, as confirmed by the lower concentrations detected during the spring sampling in downstream sites. Notably, sublethal effects on estuarine prawns, shrimp, and oysters were detected as low as $1.4 \mu\text{g L}^{-1}$ [50], $5 \mu\text{g L}^{-1}$ [26], and $\geq 10 \mu\text{g L}^{-1}$ [23], respectively. This highlights the significant risk of chronic exposure to neonicotinoids in non-target marine and estuarine species within the Solitary Islands Marine Park.

Three organophosphates (OP) were detected in our study; dimethoate, malathion, and omethoate. Historically, the global use of organophosphate insecticides increased as they were seen as replacements for organochlorine pesticides due to their affordability, increased productivity at a high efficacy, low environmental half-life, and shorter environmental persistence compared to organochlorine pesticides [55, 56]. The use of OPs has declined in the European Union due to evidence of adverse effects; however, the continued and extensive use of OPs has led to their accumulation in the environment at levels that are toxic for non-target organisms and could impact human's health [56]. The use of two OP pesticides detected in this study, dimethoate, and omethoate, is restricted in the European Union due to residue toxicity to humans but remains registered for use in New South Wales (European Commission 2019; APVMA, 2018).

Dimethoate was detected at the second-highest concentration in this study ($12.8 \mu\text{g L}^{-1}$, Site 1, summer-autumn) and was one of the two pesticides detected in all three sampling periods. Dimethoate is a systemic organophosphate insecticide with a low soil persistence and is highly water-soluble ($25,000 \text{ mg/L}$) compared to other organophosphate insecticides (Shadegan & Banaee, 2018). Therefore, dimethoate can reach surface waters and aquatic systems during runoff events. The environmental mobility of dimethoate is a possible factor contributing to the high concentration detected at site 1 during the wet season (summer-autumn). Globally, dimethoate has been detected in aquatic systems that are considered to be highly polluted, at concentrations as high as $11.31 \mu\text{g L}^{-1}$ in California, USA [57] and $2.6 \mu\text{g L}^{-1}$ in the Yellow River, China [58]. Following a comprehensive review of the toxicity of dimethoate for the European Commission and European Food Safety Authority, this pesticide (EFSA, 2018) was not approved for re-registration and banned for use in 2019 (The Commission Implementing Regulation 2019/1090). Prior to the ban of its use in aquatic

systems, dimethoate was found at low concentrations ($0.27 \mu\text{g L}^{-1}$, [59], 1999; $0.10 \mu\text{g L}^{-1}$, [60]). The results from these studies indicate that the dimethoate concentration detected in this study is high compared to global values. Despite dimethoate's high water solubility and low bioaccumulation potential (0.78), previous studies have demonstrated adverse effects on aquatic organisms, such as rotifers [61, 62], freshwater and saltwater crustaceans [55, 63], and freshwater fish and snails [64]. For instance, in the Sarno River, Italy was found to receive agricultural runoff, dimethoate was only detected at 0.00177 to $0.00623 \mu\text{g L}$ [56]. For this reason, further research of this aquatic system should investigate the transportation of dimethoate during intense runoff events, as well as consideration of the consequent food web impacts.

Omethoate, a systemic and contact organophosphate insecticide, was found solely at site 1 during the wet season sampling period ($0.12 \mu\text{g L}^{-1}$). This OP is used in horticulture to control insects and mites but can also occur in the environment as a toxic degradation-product of dimethoate post-application [65]. Although omethoate has been reported to break down in the environment within two weeks, the insecticide has proven to be approximately ten times more toxic than dimethoate and a more vigorous cholinesterase inhibitor (CDC, 2017). As of December 2018, omethoate use was banned in Victoria, Australia, but remains registered for use in New South Wales. Omethoate has been reported to be highly toxic when exposed to non-target organisms; acute 48-hour median effective concentration (EC50) for aquatic invertebrates (such as *Daphnia magna* which is used to determine toxicity to aquatic organisms) has been reported at $22 \mu\text{g L}^{-1}$ and the chronic 21-day No Observed Effect Concentration (NOEC) for aquatic invertebrates (unknown species) has been reported to be as low as $0.004 \mu\text{g L}^{-1}$ (PPDB, 2019). The omethoate concentration detected at site 1 was higher than this value, and the analytical limit of detection for omethoate did not detect concentrations lower than $0.01 \mu\text{g L}^{-1}$.

Malathion, the final organophosphate insecticide detected in this study, was also only detected above the LOR ($>0.02 \mu\text{g L}^{-1}$) at site 1 during summer-autumn ($0.47 \mu\text{g L}^{-1}$). Malathion has a low sorption coefficient (1.12 L g^{-1} , [66]) and has moderate to relatively high solubility, which enables it to easily reach surface waters through runoff [67]. Studies have indicated rapid degradation of malathion in freshwater aquatic environments ($t_{1/2}=12 \text{ d}$), which is accelerated in saltwater ($t_{1/2}= 9.3 \text{ d}$), but acute exposure through pulses of highly contaminated runoff has negative impacts on certain aquatic species such as *Danio rerio*, Zebrafish [68], and *Daphnia magna* [69]. Although malathion was solely detected above the

LOR at Site 1 during summer-autumn, this does not eliminate the absence of exposure potential. The sampling regime during the summer-autumn was not conducted every hour during peak flows, therefore it is likely that peak concentrations were missed. Also, due to the grouping of samples for each site, it is possible that individual samples had high concentrations that were missed due to dilution.

Methomyl, which was detected at five out of six sites during the summer-autumn sampling, is an environmental estrogen and can potentially disrupt the endocrine system of non-target organisms, resulting in negative impacts on reproductive health [70]. This carbamate insecticide is classified as a highly toxic compound, according to the WHO, EPA, and European Commission, and poses high toxicity risk to a range of aquatic [71] [72], as well as several amphibian species [73-75]. Methomyl is highly water-soluble with low persistence in sediment and therefore could contaminate groundwater and seawater. The half-life of methomyl is estimated at six days in surface waters and 14 days in sediment [76], although the actual half-life of methomyl in this particular waterway may vary from that predicted in other literature and is a worthy area for research.

The herbicides terbutryn and terbuthylazine were detected during the summer-autumn sampling period. Terbutryn, which occurred at Sites 1, 5, and 6 ($0.46 \mu\text{g L}^{-1}$, $0.19 \mu\text{g L}^{-1}$, $0.10 \mu\text{g L}^{-1}$, respectively), has been recognised as a threat to aquatic life and has been categorised as a priority substance in the EU since 2013 [77]. Terbuthylazine occurred at Sites 1, 2, 3, and 5 ($0.02 \mu\text{g L}^{-1}$, $0.03 \mu\text{g L}^{-1}$, $0.02 \mu\text{g L}^{-1}$, $0.01 \mu\text{g L}^{-1}$, respectively) with little variability in concentration levels between sites. Several previous studies have demonstrated the ability of terbuthylazine to contaminate groundwater, drinking water, and surface water [78, 79]. The United States EPA (1995) have classified terbuthylazine as toxic to aquatic species, including crayfish [80], carp [79, 81], and rainbow trout [82], and has also specifically outlined high toxicity to estuarine and marine invertebrates from acute exposures. In addition, terbuthylazine is potentially phytotoxic to aquatic plants and dissipates slowly in the environment (EPA, 1995). Terbuthylazine concentrations detected in this study are below the reported acute ecotoxicity thresholds for fish and aquatic invertebrates but could threaten aquatic organisms by sublethal effects from chronic exposure (Fish chronic 21-d NOEC = 0.09mg L^{-1} , Aquatic invertebrates chronic 21-d NOEC = 0.019mg L^{-1}) (PPDB, 2019).

The triazine herbicides, terbutryn, and terbuthylazine are photosynthetic inhibitors (PS II inhibitors) used globally for weed control in agriculture [83, 84]. Due to their efficient

ability to interfere with photosynthesis, PSII inhibitors can impact non-target photosynthetic organisms, such as seagrass [85], microalgae [86], coralline algae [87], or zooxanthellae, the endosymbionts of corals [33, 88]. Continued photosynthetic inhibition and therefore decreased algal production caused by PSII herbicides can eventually lead to coral bleaching, which can also occur due to increased temperatures, metals, and ocean acidification [89]. Research has demonstrated the additive behaviour and toxicity of PSII herbicides when it comes to photosynthesis inhibition in microalgae [90] and seagrass [91], potentially leading to higher toxicity to reef organisms than with individual concentrations [92]. Additionally, recent research in south Africa has observed the potential for PSII herbicides to accumulate at high concentrations within coral tissues, potentially increasing chronic toxicological effects [92].

The fungicides detected in this study above the LOR were pyrimethanil and triadimenol (See Appendix); both were detected at Site 1 during the summer-autumn ($1.5 \mu\text{g L}^{-1}$ and $0.09 \mu\text{g L}^{-1}$, respectively). Triadimenol is a triazole fungicide that can persist in the environment and is considered highly toxic [93]; and is a possible human carcinogen (US EPA, 2006). Triadimenol is also classified by the US EPA (2016) as moderately toxic to saltwater invertebrates and slightly toxic to freshwater fish on an acute basis. Zhang et al. (2018) reported that exposure of tadpoles to triadimenol caused oxidative stress at all concentrations tested, causing inhibitory effects on the development of the brain and disrupted thyroid hormone signalling (0.1, 1 and 10 mg/L). Adverse effects have also been observed in medaka fish (*Oryzias latipes*) when exposed in early life stages to environmentally relevant concentrations (3-30 $\mu\text{g/L}$ and 300 $\mu\text{g/L}$), such as altered ovary development and altered hormone balance [93]. It is important to note that although triadimenol was only detected above the LOR at Site 1 during summer-autumn ($1.5 \mu\text{g L}^{-1}$), the LOR for triadimenol was higher than most other pesticides detected in this study (LOR $<0.1 \mu\text{g L}^{-1}$).

Pyrimethanil, an aminopyrimidine fungicide, has been reported to exhibit moderate toxicity and delayed negative impacts to macrophyte and algal photosynthesis [94] and can also lead to negative impacts on aquatic invertebrates [95]. Pyrimethanil degradation in sediment-water systems can take up to 80 days (DT50-degradation half-life) (PPDB, 2019), with other factors such as temperature, photolysis, and sediment adsorption affecting degradation rates [94, 96]. Further research to investigate the occurrence of fungicides in Australian aquatic environments is necessary.

As agricultural practices expand along coastal regions globally to meet the needs of an exponentially increasing human population, it is important to understand the environmental effects potentially resulting from agricultural pollution. Much of the world's estuaries and other protected coastal systems are under threat from pesticide runoff. Figure 6 shows the imidacloprid flow rates ($\mu\text{g m}^{-2} \text{ day}^{-1}$) from near the agricultural activity to the estuarine system within the Solitary Island Marine Park. Even though the creek appears to attenuate some of the imidacloprid flow, this data suggests that a substantial amount of imidacloprid reaches the estuarine system. If this creek is representative of other creeks in this region of Australia, it is concerning as imidacloprid can negatively impact prawns [26, 50] and oysters [22, 23]. Imidacloprid is restricted in many regions of the world as a result of impacts on non-target organisms [51, 52].

The 100-1000-fold decrease in imidacloprid at downstream sites (Figure 1.6) suggests that riparian vegetation may assist in the attenuation of imidacloprid flow. However, the simultaneous occurrence of other herbicides in the waterway may negatively impact the vegetation over time. For this and other reasons, our study shows that it is important to obtain information on a range of pesticides and assess their synergistic and accumulative effects. Each type of pesticide may negatively affect different aspects of the natural environment and reduce ecosystem resilience, for example, by impacting the ability of these environments to attenuate pollutants. Therefore, in-depth monitoring of pesticide occurrence and persistence in such environments is necessary to ensure effective management of these systems, along with improved regulatory control of use and mitigation strategies to reduce the input in coastal waterways.

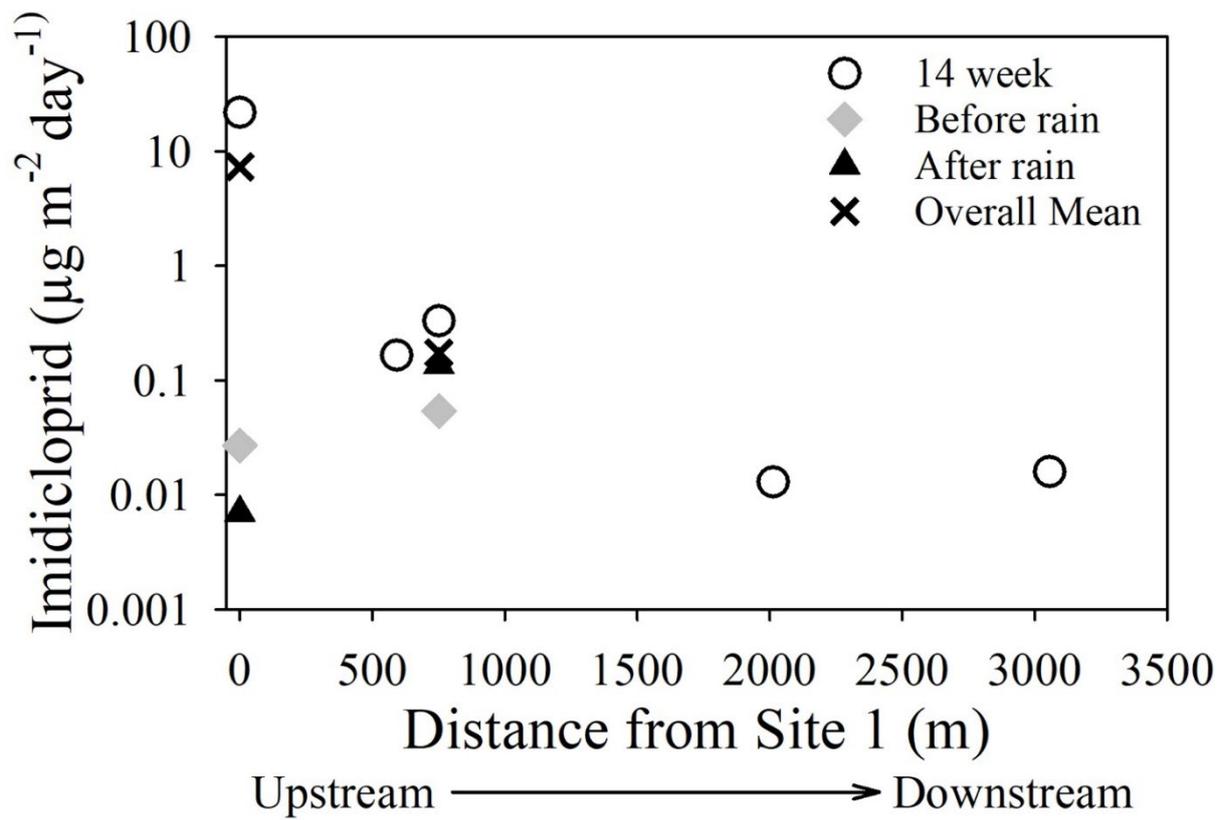


Figure 1.6. Imidacloprid flux ($\mu\text{g m}^{-2} \text{day}^{-1}$) at each study site throughout all three sampling periods (summer-autumn, spring-before rain event, and spring-after rain event).

Part 2. Historical behaviour of toxins in an agriculturally impacted estuarine sediments.

Melanie Taylor, Shane A. White, Tiago Passos, Christian J. Sanders

2.1 Introduction

Estuarine environments are highly dynamic and versatile systems that provide a range of critical ecosystem functions [97]. However, toxicant discharge from developed and disturbed catchments may affect these functions. Anthropogenic activities such as urban and agriculture expansion release pollutants and nutrients to downstream coastal habitats [98-100]. For instance, surface runoff and groundwater discharge from urban activities and agriculture-derived residues have been reported as a primary source of nutrient, pesticide, and trace metal (TM) contamination to estuarine ecosystems [101, 102]. This is because soluble pollutants from coastal catchments can bind to fine sediments or organic matter and be discharged into the ocean [100, 103]. Subsequently, intertidal coastal ecosystems can intercept and sequester these sorbed pollutants, limiting transport to the broader marine environment [98-100]. As a result, intertidal coastal ecosystems that accumulate sediments, such as mangroves, thus provide critical ecosystem services including, carbon, nutrient, TM and pesticide sequestration [104].

Accurately quantifying historical TM and pesticide accumulation rates recorded in sediment profiles can provide evidence for the source of contaminants in mangrove environments, as well as evaluate their behaviour under different environmental conditions [99, 105, 106]. Environmental contamination by toxicants such as arsenic (As), methylmercury (MeHg), and conazole fungicides has been linked to rising ecological and worldwide public health concerns [107]. Due to an exponential surge in their use in many industrial, agricultural, household, and technical applications, human exposure has increased significantly [108]. Many metals are necessary for a variety of biochemical and physiological processes, including cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), and zinc (Zn). However, elements such as mercury can be highly bioavailable and toxic to many species. The bioavailability and toxicity of TMs are determined through differing biogeochemical characteristics, with soluble metals being the most mobile, bioavailable, and more toxic form [105, 109].

The transformation of contaminants via bioecological process can result in compounds exhibiting a higher toxicity, and greater mobility than the original chemical

pollutant [110, 111]. One of these processes includes the decomposition of organic matter deposited amongst sediment which may accelerate methylation, for instance. Under anoxic conditions microorganisms transform inorganic Hg into the more toxic MeHg, which can then remobilise within the aquatic environment (Al-Sulaiti et al., 2022). Methylmercury creates lethal, sublethal and reproductive impacts on marine species at environmentally relevant exposure levels [112]. Another biogeochemical process resulting in enhanced toxicity is related to arsenic which may be found in two different oxidation states, As(III) and As(V). Microbial oxidation of As(III) to As(V) within sediment occurs under aerobic conditions while respiratory reduction of As(V) to As(III) favours anoxic environments [113]. The decomposition of organic material can accelerate reduction, and subsequent remobilisation of As(III) [114].

Accurately quantifying historical TM and pesticide accumulation rates recorded in sediment profiles can provide evidence for the source of contaminants in estuarine systems, as well as evaluate their behaviour under different environmental conditions [99, 105, 106]. Here, we investigate historical contamination based on sediment deposition fluxes from ^{210}Pb dated sediment cores. From these well-established geo-chronologies, we examine TM accumulation rates, metal speciation, historical pesticide contamination and their impact on a protected marine setting. This research aims to identify the links between accretion rates, sediment sources and specific pollutants potentially discharged into a protected estuarine ecosystems.

2.2 Methods

2.2.1 Study Site

Hearnes Lake is located between an agricultural catchment and a marine protected area on the north coast of New South Wales, periodically feeding into the adjacent Pacific Ocean [37]. The site is located within the Solitary Islands Marine Park (SIMP) classified as a protected area for marine wildlife under the *Marine Parks Act 1997*. Hearnes lake catchment is 6.8 km², with catchment hydrology driven by surface flows from Double Crossing Creek in combination with saline and fresh groundwater reserves [13]. The catchment geology consists of Palaeozoic sandstone overlain with mudstone, with the upper reaches predominately comprised of red kandosols, and humic gley hydrosol found around waterways [39]. Brown and yellow podzolic kurosols dominate the south-eastern boundaries of the catchment, with highly saline solonchak podosols characteristic of salt marshes and

mangrove communities surrounding Hearn's Lake [39]. Agricultural enterprise accounts for ~25% of the catchment, with land use change increasing [104] (Figure 2.1). Accelerated disturbance within the catchment is hypothesised to be contributing to sediment deposition within Hearn's Lake [104, 115].

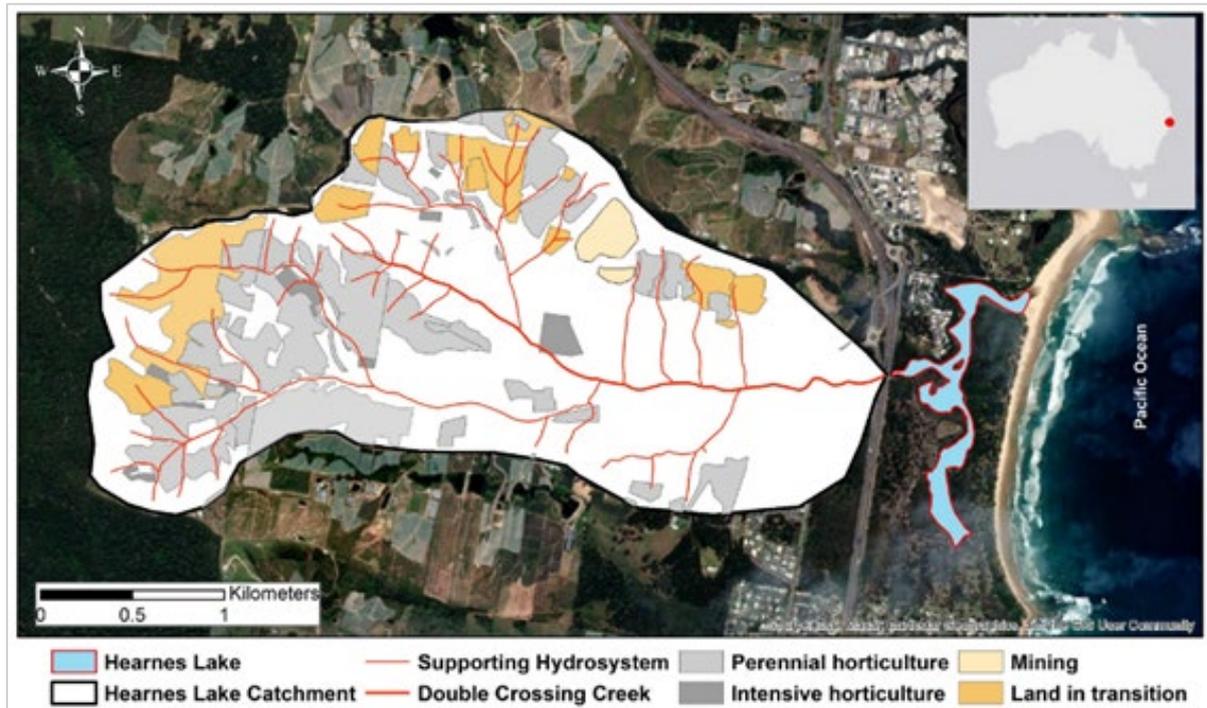


Figure 2.1. Map of the study site location including Hearn's Lake catchment and agriculture areas in the region, NSW, Australia (Source: ESRI ArcGIS).

2.2.2 Sample collection

Ten sediment cores were collected to a depth of approximately 60cm from various locations around Hearn's Lake (Figure 2.2). Cores were segmented at 2cm intervals, subsamples were freeze-dried and weighed to acquire sediment dry weight. Dry bulk density (DBD) was obtained by dividing dry weight by subsection volume as per methods outlined by Ravichandran et al. (1995). Subsamples were subject to ^{210}Pb and ^{226}Ra analysis to determine age and mass accumulation rates (MAR).

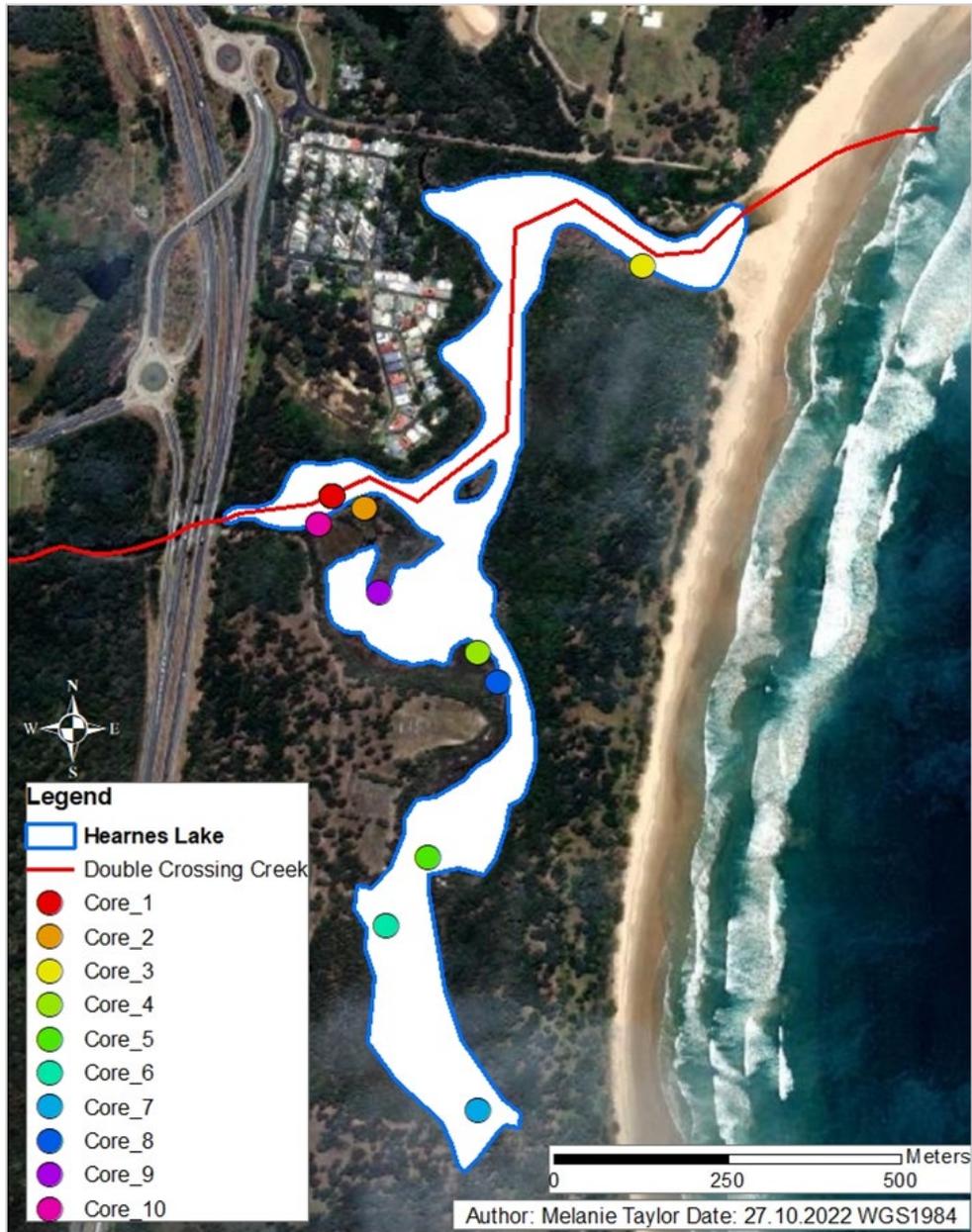


Figure 2.2. Core sample locations, Hearn's Lake NSW.

2.2.3 ^{210}Pb analysis and dating

Approximately 5g of homogenised material per core subsample were packed into gamma vials, sealed with epoxy, and left for 21 days for ^{222}Rn to achieve secular equilibrium between ^{226}Ra and ^{214}Pb [103]. Aliquots were processed in a high-purity germanium (HPGe) gamma detector. ^{210}Pb activity was determined by the 46.5 KeV gamma peak, and ^{226}Ra activity by averaging peaks (295.2 KeV, 351.9 KeV, and 609.3 KeV) from ^{214}Bi and ^{214}Pb activity [117]. Counts per minute were multiplied by a correction factor based on gamma-ray intensity and well detector proficiency to determine the ^{210}Pb and ^{226}Ra activities to determine the excess ^{210}Pb [34]. Data formulated by the gamma detector were subject to

correlation analysis to identify cores with undisturbed geochronology. Excess ^{210}Pb was utilised to calculate age and sediment accumulation rate (SAR) following the Constant Rate of Supply (CRS) and Constant Initial Concentration (CIC) methods [118]. Two cores were selected to undergo grain size, stable isotope, and historical contaminant loading analysis.

2.2.4 Grain-size analysis

Sediment aliquots for each depth interval were treated with 8.8M hydrogen peroxide (H_2O_2) to remove organic material content. Deflocculation of clay aggregates was achieved by adding 5% sodium hexametaphosphate ($(\text{NaPO}_3)_6$) and rotating for 24 hrs on an end-over-end mixer [119]. Samples were analysed on a Malvern Mastersizer 3000 laser diffraction particle analyser. Descriptive statistics were formulated by Gradistat version 8 and utilised to determine clay, silt, fine sand, and coarse sand mineral grain size fractions [120].

2.2.5 Carbon and nitrogen stable isotopes

Sediment aliquots for each depth interval were homogenised and weighed out to 15 mg in high-grade tin and silver pellets to analyse total organic carbon (TOC), total nitrogen (TN), stable carbon isotopic ratio ($\delta^{13}\text{C}$), and stable nitrogen isotopic ratio ($\delta^{15}\text{N}$), similar to Passos et al. (2022). Silver pellets were treated with 15M hydrochloric acid (HCl) to remove carbonate content (CaCO_3) prior to $\delta^{13}\text{C}$ and total organic carbon (TOC) analysis. Pellets were subject to combustion before analysis in a Thermo Finnigan Model Delta Plus XP, following methods outlined by Naidu et al. (2000), to determine TOC, $\delta^{13}\text{C}$, TN, and $\delta^{15}\text{N}$.

2.2.6 Trace metal analyses

Homogenised aliquots were weighed out to approximately 0.4g and digested on a hot block for 1hr at 120°C with nitro-hydrochloric acid ($3\text{HCl}:\text{HNO}_3$), following Conrad et al. (2019). Samples were processed by a Perkin Elmer NexION 350D Inductively Coupled plasma mass spectrometer (ICPMS), to identify total Silver (Ag), Arsenic (As), Lead (Pb), Cadmium (Cd), Chromium (Cr), Copper (Cu), Manganese (Mn), Nickel (Ni), Selenium (Se), Zinc (Zn), Mercury (Hg), Iron (Fe), Aluminium (Al), Beryllium (Be), Boron (B), & Cobalt (Co). Samples for speciation analysis underwent acid digestion, aliquots for As species were treated with dilute nitric acid extraction, Hg species to mercaptoethanol extraction, and Cr species to EDTA acid extraction, before analysis via liquid chromatography. Trace metal fluxes were determined from DBD, sediment accumulation rate (SAR), and metal concentrations, similar to Sanders et al. (2014), using Equation 1.

Equation 1

$$DBD \times SAR \times TM \text{ concentration} = TM \text{ flux (mg m}^{-2}\text{yr}^{-1}\text{)}$$

Background TM concentrations were calculated by averaging sediment TM concentrations below the depth of ²¹⁰Pb excess depletion. The Contamination factor (CF) was calculated using Equation 2 and applied to total TM and TM flux data.

Equation 2

$$\text{Contamination Factor} = TM \text{ concentration (mg kg}^{-1}\text{)} / TM \text{ background (mg kg}^{-1}\text{)}$$

2.3 Results and Discussion

2.3.1. Chronology

Radionuclide activity identified that many cores had been subject to physiological or biological mixing. Estuarine environments are highly dynamic systems, bio-turbidity, rainfall, opening and closures of the lake, along with anthropological influences, can promote mixing, and disturb the sediment interface [123]. Statistical analysis identified two cores displaying a relatively undisturbed geochronology (Figure 2.3).

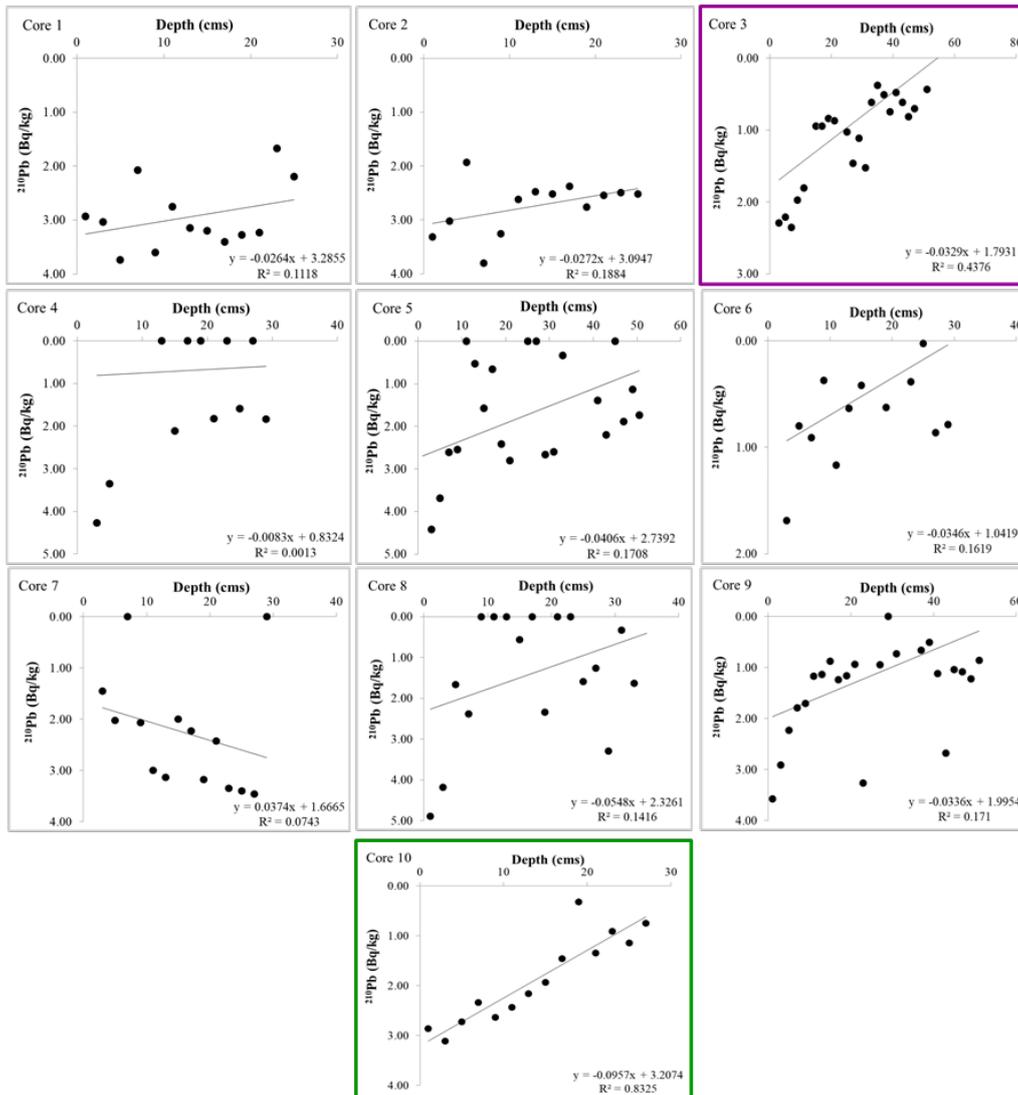


Figure 2.3. Natural log of excess ^{210}Pb ($\text{LN } ^{210}\text{Pb}$ excess) decay, Hearnese Lake Core samples.

Core 3 is located near the ICOLL mouth (Figure 2.4). The site is subject to tidal sand deposition from longshore currents [13], with biogeochemical processes influenced by tidal intrusion [124]. Remnant mangrove populations are evident around the location. Core ten is located near the headwater, Double Crossing Creek, a hydrological mixing zone, potentially impacting TM distribution [125]. The site is located within 100m of the Pacific Highway, the primary transport artery for the NSW North coast and an area that has been through significant development since 2015. The section of highway adjacent to Hearnese Lake underwent major upgrade and development work from 2015 to 2020.



Figure 2.4. Location of Hearn's Lake core samples, including core subject to physiological mixing, and cores 3 and 10, displaying undisturbed geochronological profiles.

2.3.2. Sedimentation rates

Both sediment cores show a relatively undisturbed geochronology, with ^{210}Pb excess found to be reach background values at 50 cm for Core 3 and 30 cm for Core 10. Comparing the results using the constant initial concentration (CIC) and constant rate of supply (CRS) methods suggest that there was variation in accumulation rates between core depths. Mass accumulation rates (MAR) as determined by the CIC model ranged from 0.5 g cm^{-2} in 2017 to 1.1 g cm^{-2} in 1989 for Core 3, and from 0.18 g cm^{-2} in 1992 to 0.3 g cm^{-2} in 1930 for Core 10. The CRS model reported MAR to vary from 0.2 g cm^{-2} in 1907 to 9.6 g cm^{-2} per year in 2018 for Core 3, and from 0.3 g cm^{-2} in 1930 to 3.3 g cm^{-2} in 2020 for core 10. Lack of vegetation cover in combination with the slope of the catchment is suspected to be

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exacerbating soil erosion during rain events [115]. Conrad et al. (2020) found runoff to increase TM export at Double Crossing Creek, with rainfall accounting for between 31% and 70% of total TM loading. The acceleration of sediment deposition within Hearnes Lake could potentially result in infilling, replacing the coastal contaminant sink with a channel transporting toxicants directly into the protected Solitary Island Marine Park.

There are several possibilities for increased sedimentation. Firstly, the Pacific Highway upgrade road works occurring between 2015 and 2020, in combination with high-intensity rainfall events, may have eroded sediment from the works site. Due to the timeline of the roadwork, it was initially suspected that the disturbance might be the reason behind the steady increase in sediment accumulation at the site of core 10 during the same period. However, the SAR continued to increase after the Pacific Highway project was completed, so other sediment sources are also likely to have contributed to the relatively large sediment deposition in recent times. The sustained shift in sediment material source indicates an ongoing disturbance factor accelerating deposition around the Double Crossing Creek outlet. The second possible sediment source is land use change in the upper agricultural catchment along with housing development, occurring consistently throughout the catchment from 2000 until present. Farmers have changed land uses from bananas to blueberries and, more recently, flattened large areas of the hilly landscape to construct protected cropping structures such as hothouses [34].

Catchment size has been associated with increased sedimentation rates in agriculturally impacted coastal systems [115]. For example, Heathcote et al., (2013), found agricultural land use to account for $986 \text{ g m}^{-2} \text{ yr}^{-1}$ deposition in United States watersheds, a six-fold increase since 1850. Furthermore, Moustakim et al., (2022), recorded substantial acceleration in deposition in an agriculturally impacted Moroccan catchment. Derakhshan-Babaei et al., (2022) found elevated erosion and subsequent deposition in the Kan watershed was due to low density vegetation, physiographic elevation changes, and grazing of livestock.

2.3.3. Grain-size analysis

Grain size analysis shows that both Cores 3 and 10 contain a high percentage of coarse and fine-grained sands (Figure 2.5). Core 3 recorded less than 1% clay and an average (n=30) of 1.7% silt throughout the sediment profile. Core 10 reported no significant changes in the clay and silt fractions over time. Average (n=15) core mineral grain-size fraction for clay was 4.6 %, and silt 13.9 %. The coarse grain sand fraction increased from 10.7 % in

1930 to 26.82 % in 2020. Dry bulk density (DBD) shows trends in the fine sand mineral grain size fraction and is strongly influenced by porosity [103]. Core 10 recorded a substantial decrease in DBD from 2011 in response to the displacement of the fine sand fraction.

The differences in mineral grain size observed between cores are likely attributed to core location. Core 3, located near the ICOLL mouth, has sand continuously being delivered to the site via longshore currents [13, 37]. Forecasted sea level rise associated with climate change is predicted to globally accelerate sand deposition in coastal catchments [128], resulting in the landward migration of coarse-grained sediments [129].

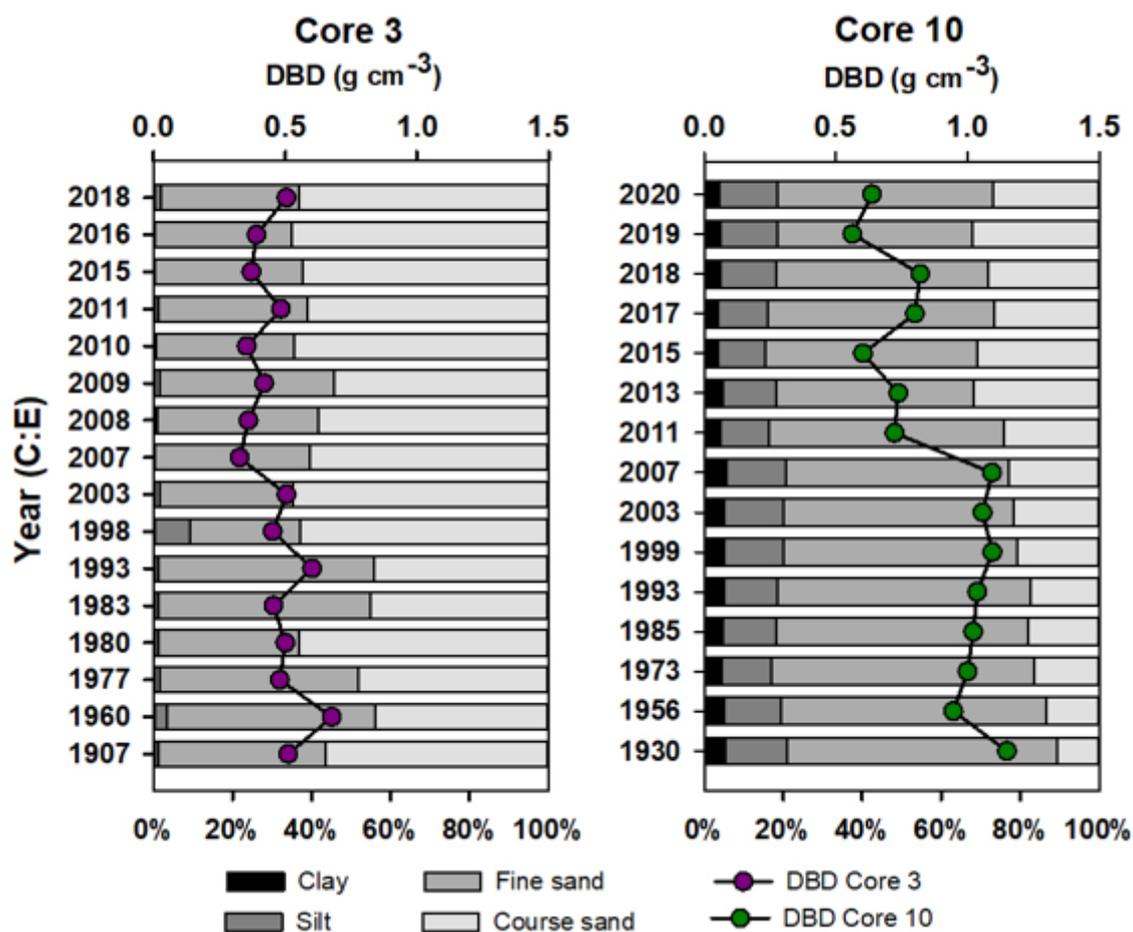


Figure 2.5. Mineral grain size fraction (%) and Dry Bulk Density (g/cm^3) of core samples 3 and 10 (Hearnes Lake, NSW) dated using the constant rate of supply model.

2.3.4. Stable Carbon and Nitrogen Isotopes

TOC:TN ratios plotted against $\delta^{13}\text{C}$ indicate that the organic matter source is mixed (Figure 2.6); however, primarily from C_3 terrestrial plants, with a great marine influence

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along Core 3 as expected [130-132]. However, the decreasing $\delta^{13}\text{C}$ values in more recent sediments are likely related to increased terrestrial sources in both sediment cores, thus, likely related to deforestation within the catchment [122, 133]. A shift of $\delta^{15}\text{N}$ can be observed between soils with different land-use and regimes, since the isotopic ratio depends on nitrogen inputs, including land management practices [98, 134], and the processing of nitrogen in the water column, i.e., nitrification and denitrification. For instance, measured $\delta^{15}\text{N}$ levels on cultivated agricultural soils can be higher than those supporting native vegetation, as fertiliser application can increase $\delta^{15}\text{N}$ abundance through fractionation processes [134].

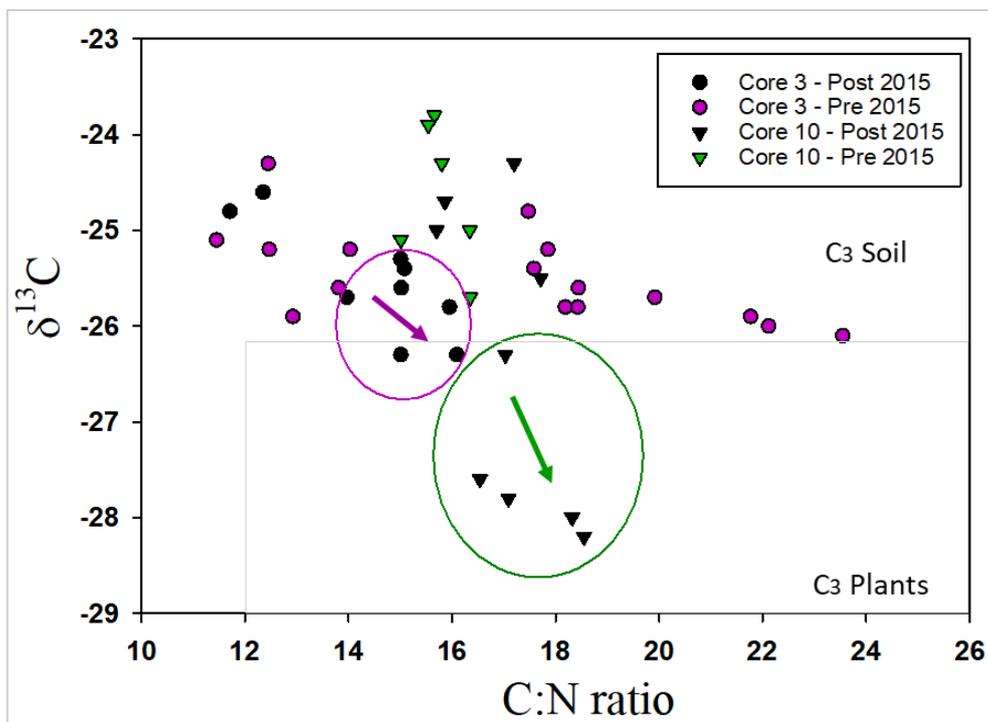


Figure 2.6. TOC:TN ratios plotted against $\delta^{13}\text{C}$, Cores 3 and 10, Hearnese Lake, NSW. Circled areas indicate sediment layers post 2015, with arrows highlighting increasing $\delta^{13}\text{C}$ in more recent sediments.

2.3.5. Total metals and metal fluxes

Core 10 recorded higher concentrations for all analysed trace metals (Table 2.1). Total As, Pb, Cu, Co, Mn, Ni, Se, Al., Be, B, Fe, and Hg, recorded maximum concentrations in the most recent sediments from core 3, and total As, Pb, Mn, Zn, Fe, and Co, in most recent layers from core 10. All metals fell within recommended ANZECC (Australian & New Zealand Environmental Conservation Council) default guidelines for contaminant concentrations in sediments, though it should be noted guidelines for Co, Mn, Se, Be, and B

are unavailable due to gaps in the literature. Cd and Ag were below detectable limits. However, the total As in surface sediments from Core 10 (12.38 mg kg⁻¹) were higher than larger, anthropologically impacted, catchments in Spain (9.3 mg kg⁻¹), Russia (7.15 mg kg⁻¹), and Iraq (6.13 mg kg⁻¹) [135, 136]. Total Mn has increased by 295% for core 3 and 228% for core 10 since the year 2000, however total concentration was found to be lower than many sites globally [135, 137]. Total Ni was recorded at 4.8 mg kg⁻¹, one of the lowest results reported in comparison to the literature on global estimates.

Table 2.1.

Total trace metals (mg kg⁻¹): min, max, mean, and standard deviation for Core 3 (n=25) and Core 10 (n=15), Hearn's Lake, NSW.

Total metals mg kg ⁻¹									
Core 3				Core 10					
	Min	Max	Mean	SD		Min	Max	Mean	SD
As	1.89	5.16	3.22	0.73	As	4.06	12.38	6.79	2.22
Pb	0.68	7.47	2.62	1.99	Pb	16.47	25.81	19.91	2.80
Cr	2.16	4.86	3.11	0.73	Cr	7.30	10.58	8.92	0.81
Cu	0.27	3.82	0.88	0.82	Cu	9.98	19.63	14.67	2.61
Mn	6.53	29.31	10.88	4.94	Mn	18.95	79.59	44.69	18.58
Ni	0.50	1.92	0.95	0.36	Ni	2.37	4.80	3.46	0.66
Se	0.50	0.76	0.51	0.05	Se	0.50	1.00	0.67	0.31
Zn	1.87	14.17	5.46	3.55	Zn	11.47	40.31	23.44	7.74
Hg	0.01	0.06	0.02	0.02	Hg	0.03	0.13	0.09	0.03
Fe	1624	4901	2110	674	Fe	3972	16356	6959	3137
Al	591	3548	1405	901	Al	10183	15056	13587	1310
Be	0.10	0.11	0.10	0.00	Be	0.30	0.67	0.43	0.12
B	5.00	12.21	6.23	1.96	B	9.68	17.53	12.54	2.49
Co	0.15	0.73	0.37	0.13	Co	0.69	2.28	1.20	0.46

From 2007-2015 metal deposition within the catchment was seen to decline, however, from 2015 to present TM deposition has increased substantially (Figure 2.7). Highest metal deposition is noted in the most recent sediment layers for all analysed metals except for Hg. Overall, metals deposition along this estuary has increased between 5-50-fold since human occupation, with highest acceleration seen in the order: Mn > Fe > Zn > As > Co. Manganese fluxes have increased from 9.29 and 70.57 mg m⁻² year respectively in oldest sedimentary layers to 368.6 and 1668.85 mg m⁻² year in most recent layers. Iron loading at the site of core 10 has increased from 14794 mg m⁻² in 1930 to 342931 mg m⁻² in 2020. Zinc deposition increased 45-fold around core 3 and 20-fold around core 10 since the 1930s, with current deposition rates at 251 and 845 mg m⁻² year⁻¹. Arsenic deposition was recorded at 114 mg m⁻² for core 1 and 260 mg m⁻² for core 10 in newly deposited sediments. Co deposition has

increased every year from 2017 around core 10, current deposition is estimated at $48 \text{ mg m}^{-2} \text{ year}^{-1}$. Chromium fluxes have increased to 145 and $175 \text{ mg m}^{-2} \text{ year}^{-1}$ for both cores, respectively.

Core 3 recorded the highest contamination factors for Mn (6.6), Zn (4.8), As (3.8), Ni (3.4), Fe (3.3), and Co (2.1), in the most recent sediment layer. From 2018 to present, contamination factor increases in As, Cu, Mn, Ni, Se, Zn, Fe, Be, and Co. Boron was the only TM to exhibit a decrease in contamination factor, declining 37% post human occupation. The contamination factor, based on TM deposition fluxes, was found in many results to be higher than contamination factor based on total TM concentrations. Highest contamination for core 3 was in 2018 for all analysed metals. The deposition event that occurred during this period substantially increased the contamination factor, with all reported values falling between 21.4 and 115.7, respectively. Core 10 reported a steady increase in contamination factor for all TMs from 2015 to the present. The highest contamination was seen in Mn at 32.01, followed by Zn (23.1), As (18.37), Ni (16.3), and Fe (15.9). Contamination based on metal depositional fluxes is largely under-reported in scientific literature due to efforts need to date sediment deposition. However, the result here suggested that trace metal deposition fluxes significantly influence contamination, as concentrations may not be telling the entire story. For instance, high sediment discharge from catchments may dilute pollutant deposition and as a result concentration would be reduced. Accumulation rates more accurately show the amount of pollutants entering a catchment based on area and time, which may highlight issues that may occur as a result of specific pollutants entire the system.

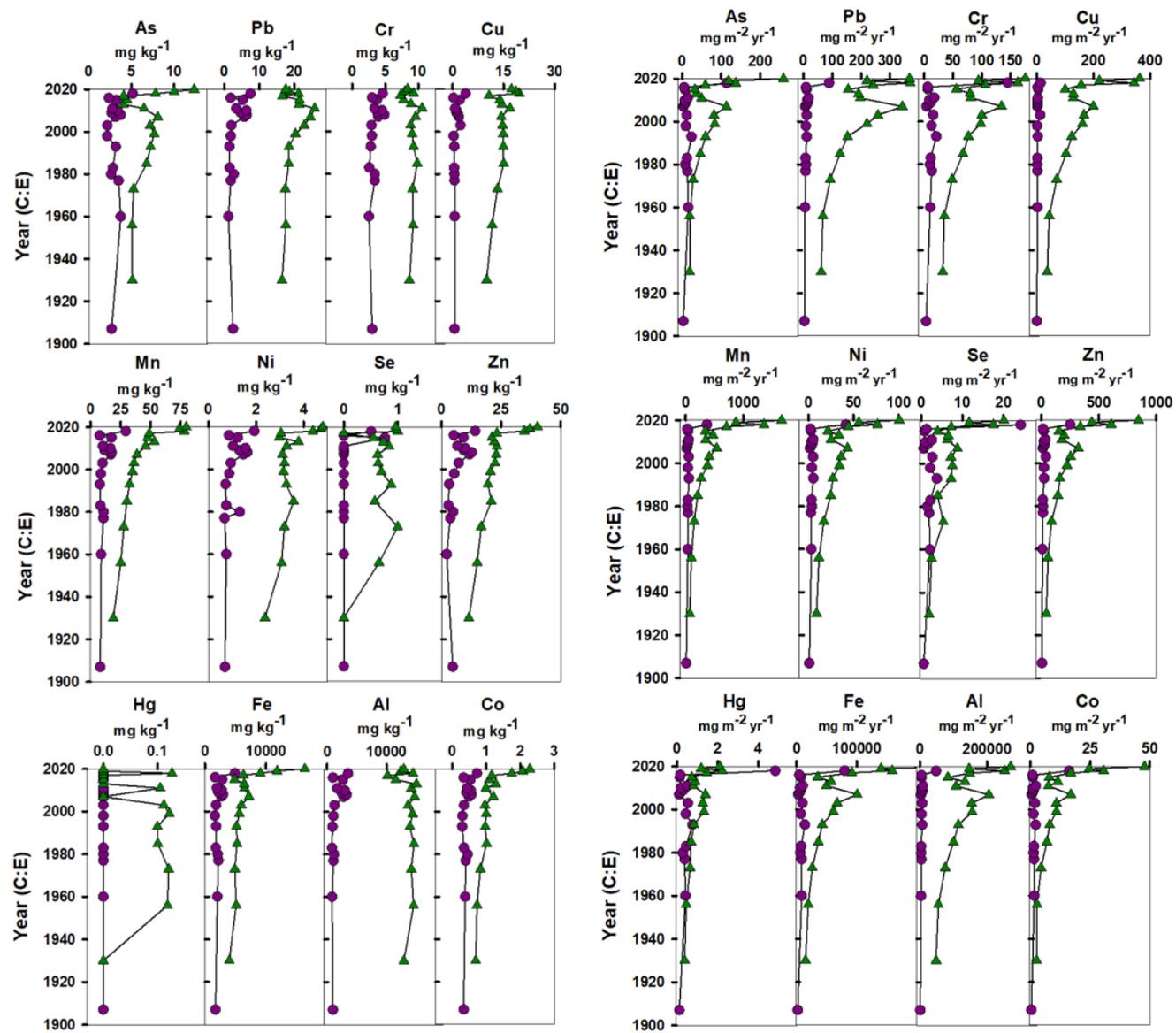


Figure 2.7. Total trace metal (mg kg^{-1}) and trace metal fluxes ($\text{mg m}^{-2} \text{ year}^{-1}$), Hearnes Lake sediment core 3 and 10. Investigating pesticide and heavy metal distribution from water and sediments near expanding horticulture activities in the Coffs Harbour NSW region

2.3.6. Speciated metals

Total Cr was Cr(III) in both soluble and insoluble forms. Insoluble Cr(III) was found to dominate in both sediment profiles (Figure 2.8). Core 10 recorded higher total Cr concentrations. Soluble Cr(III) recorded minimum levels of 0.27 mg kg^{-1} in 1953 for core 3 and 0.41 mg kg^{-1} in 1956 for core 10. Maximum concentrations were reported between 2010-2015 for both cores at 0.77 and 0.79 mg kg^{-1} . Cr loading at Hearnes Lake has remained relatively stable; however, contamination factor scores indicate high deposition events strongly influence Cr pollution levels.

Mercury loading fluctuated throughout both sediment profiles. Total Hg was highest in the most recent sediment layer (0.06 mg kg^{-1}) for core 3, and maximum concentrations for core 10 were recorded at 0.13 mg kg^{-1} in 1999 followed by 0.12 mg kg^{-1} in 2018. Prior to 2015, Hg loading at Hearnes Lake was represented solely by the mercuric cation (Hg^{2+}). The appearance of MeHg is of concern due to Hearnes Lake location within the highly protected SIMP.

Mercury methylation is influenced by redox processes, pH, temperature, dissolved oxygen (DO), and microbial interactions [138]. The decomposition of organic matter deposited amongst sediment accelerates methylation, under anoxic conditions microorganisms transform inorganic Hg into the more toxic MeHg, which can then remobilise within the aquatic environment [139]. Mercury compounds were found to be toxic at levels below that of recommended environmental guidelines [140]. Methylmercury is considered a toxicant of highest concern globally due to the high mobility, impact on diversity and ecosystem functioning, bioaccumulation patterns, and transferability to the trophic chain [141].

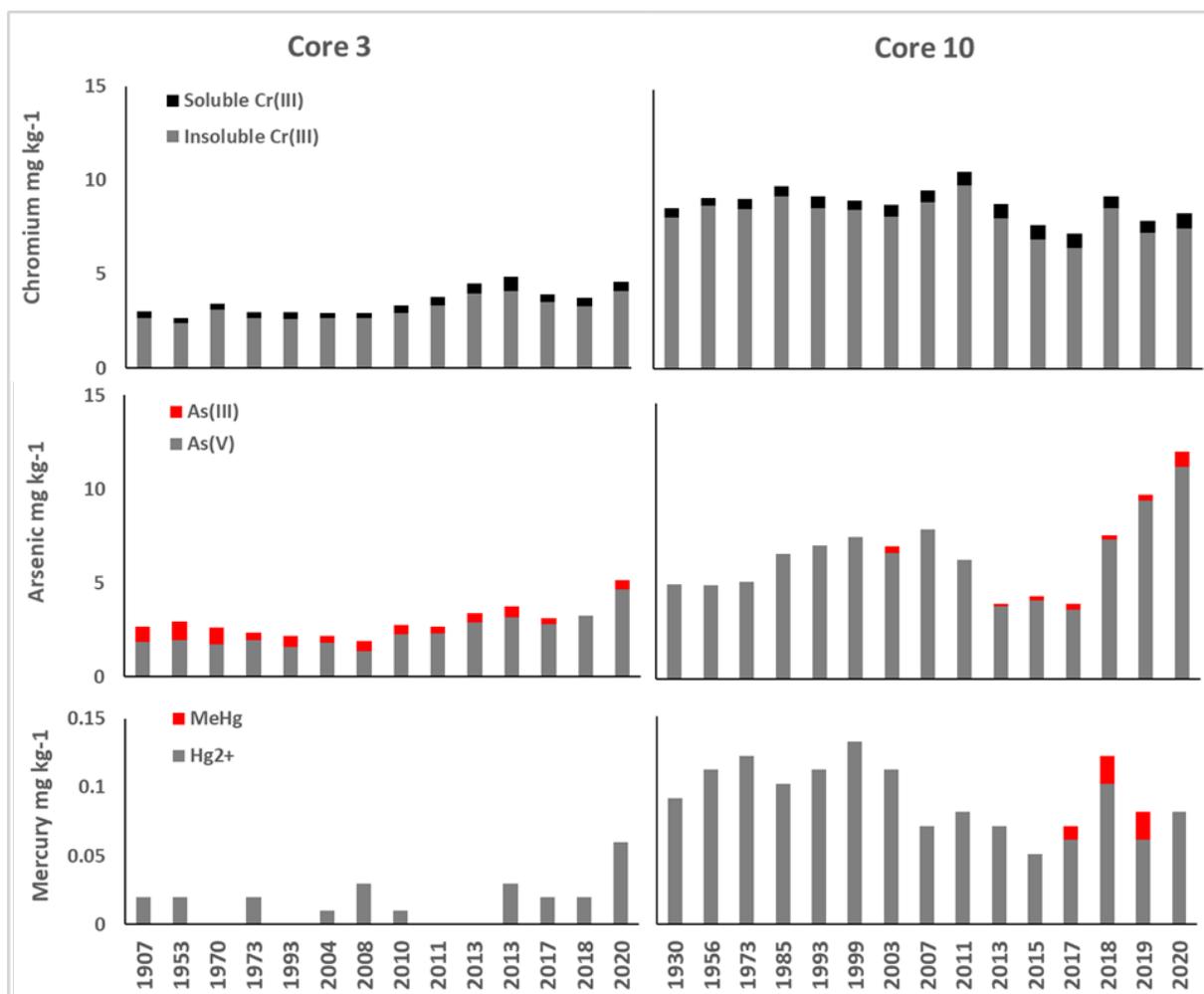


Figure 2.8. Speciated chromium (soluble and soluble trivalent fractions), arsenic (trivalent and pentavalent fractions), and mercury (inorganic (Hg_2^+) and methylated (MeHg) fractions) (mg kg^{-1}).

Core 10 recorded 140% higher total As concentrations throughout the sediment profile than core 3. Core 3 contained higher overall As(III) though concentrations in core ten increase from 2015 to the present. Trivalent As (As(III)) was found throughout the sediment profile of core 3, recording the highest concentrations (0.99 mg kg^{-1}) in ~1953. Sediment layers dated to 2018 were absent of As(III) in this core. Core 10 reported no trace As(III) prior to the year 2000 and recorded the highest levels (0.83 mg kg^{-1}) in newly deposited sediments. Microbial oxidation of As(III) to As(V) within sediment occurs under aerobic conditions while respiratory reduction of As(V) to As(III) favours anoxic environments [113]. The decomposition of organic material can accelerate reduction, and subsequent remobilisation of As(III) [114].

Pentavalent As (As(V)) recorded the highest concentrations for both cores (Core 3, 4.66 mg kg⁻¹ and Core 10, 11.55 mg kg⁻¹) in the most recent sediment layers. Contamination factor₂ based on fluxes₂ found enrichment of total As to have increased substantially for both cores at 21.4 and 18.37₂ respectively. These results indicate that even though As concentrations fell within ANZECC sediment quality guidelines, As pollution has increased considerably.

2.3.7. Pesticides

Pesticide analysis found traces of propiconazole (0.01 mg kg⁻¹) and tebuconazole (0.002 mg kg⁻¹) within the sediment profile of core 10. Propiconazole was found in the most recent sediment layer, while tebuconazole was found throughout the core down to layers dated to 1957. Core 3, taken within a region more influenced by marine sediments, recorded no trace pesticides. Propiconazole and tebuconazole are from the conazole family of fungicides and have been linked to a range of health issues in terrestrial and marine biota [142, 143]. These pesticides are currently under review in New Zealand and banned in the United Kingdom.

Conazole fungicides are prone to bioaccumulate in soils and exhibit low to moderate solubility in estuarine waters [142]. Propiconazole and tebuconazole were detected in surface water from nearby sites within the SIMP [144]. This suggests the fungicides accumulate in catchment topsoils and are transported to the hydro-system as suspended solids in runoff events [145]. Soluble contaminants can potentially remobilise, moving up or down the sediment profile [146]. Pesticide suites identified by Laicher et al. (2022), were not detected in the sediments of this study, highlighting the different behaviours of each pesticide and to the medium to where they may be found. High sand mineral grain fractions inhibit toxicant adsorption capacity [103, 129], resulting in percolation down the sediment profile and possible accumulation in groundwater reserves [97].

Tebuconazole has been linked to endocrine, reproduction, and metabolism disruption, hepatotoxicity, and cancers [142], as well as osmoregulation and respiratory disorders, impaired development, and neurotoxicity in marine species [143]. Pesticide contamination can detrimentally impact microbial communities in groundwater at exceptionally low environmental concentrations [97]. Tebuconazole exacerbates cyanobacterial blooms by causing mortality in parasitic chytrids that prey on cyanobacteria populations [145]. Degraded carbon uptake was displayed by algae in response to propiconazole exposure at an

estimated environmental concentration (EEC) of 0.08 mg L⁻¹ [140]. The transformation of pesticide compounds by biogeochemical redox pathways can lead to the mobilisation of contaminants that are more toxic, and bioavailable for uptake by marine organisms [147]. Studies by Peterson et al., (1994) found freshwater and marine phytoplankton to exhibit pesticide sensitivity at concentrations much lower than indicated by water quality standards.

Implications

This research reports that Hearnes Lake, NSW, is a highly impacted catchment, subject to a wide range of anthropological disturbance factors. Pesticide transport [144], and TM loading [34, 104], combined with some of the highest dissolved nutrient input recorded in literature [13], have resulted in environmental conditions representative of a eutrophic hydrological system, unlikely to sustain higher marine organisms. While these results indicate that total TMs are unlikely to be the reason behind the lack of diversity at Hearnes Lake, the results from this study suggest that the microbial transformation of TMs into compounds exhibiting a higher degree of toxicity and availability for trophic uptake, such as methylmercury, should be taken into consideration.

Toxicant enrichment factors were shown here to increase in response to TM fluxes and were indicative of a highly polluted system. The substantial differences in contamination factor reported by TM fluxes highlights the importance of research into historical contaminant loading in impacted coastal environments. Toxicant fluxes and contamination factors are rarely studied or reported in the literature. Results of this study raise concerns that contamination factors and subsequent pollution ratings in coastal ecosystems could be vastly understated in literature.

The sedimentation rates in this estuary have shown to be increasing (Figure 2.9), in pace with agriculturally impacted catchments worldwide [34, 115]. Preliminary modelling indicates that Hearnes Lake is slowly infilling and could potentially be replaced by a channel feeding toxicants directly into the broader SIMP. This scenario will detrimentally impact carbon and toxicant sequestration potential, ecosystem functioning, and recreational capacity, of the Hearnes Lake catchment, and has the potential to severely impact biota protected under the Marine Parks Act (1997). Depth profiling and further deposition analysis across differing estuaries within the region would be required to provide an accurate forecast model on how Hearnes Lake relates to other systems impacted by Agricultural expansion in Australia and

around the globe. Therefore, it is suggested that further research be applied to formulate enhanced pollution modelling methodology.

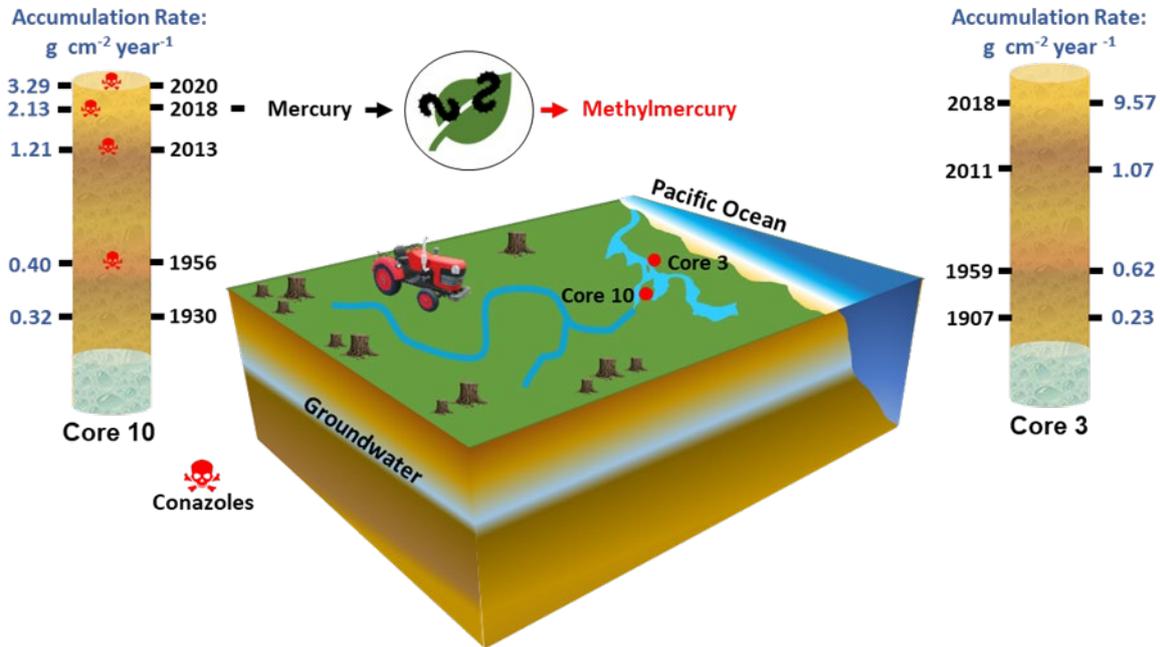


Figure 2.9. Original schematic outlining the results of contaminants found in dated sediments. 16

RECOMMENDATIONS

The agricultural industry in Australia relies on the application of fertilisers and pesticides to continue to provide integral food resources [148]. However, there is limited information available to guide farm owners on environmentally sustainable selection of pesticides. The continued use of toxic compounds banned overseas due to adverse health response in humans suggest that current guidelines on agrochemical applications may be insufficient in ensuring the long-term sustainability of Australian resources. This is particularly true in the Coffs Harbour area, and as a result two broad recommendations are provided based on the results of this study: Firstly, the prevention of the mobilisation and transport of agrochemicals derived from mercury compounds to freshwater and subsequent marine resources is recommended [140]. Secondly, a reduction in application rate/frequency of agrochemicals could potentially improve soil, surface water, and groundwater quality along estuaries within the Coffs Coast regions. The collaboration between key stakeholders could lead to the implementation of enhanced environmental management plans in this region along with bioremediation practices, protecting valuable ecosystem services, and supporting agriculture endeavours integral to food security [105, 149].

CONCLUSION

The combination of analyses in this study showed that toxicant contamination factors increased in response to development in the region, indicative of highly polluted systems. The substantial differences in contamination factors reported for differing pesticide in creeks and metal fluxes highlight the importance of research into historical contaminant loading in developing coastal environments.

Several pesticides were detected in the studied catchment, which discharges into the Solitary Islands Marine Park. Many of these pesticides have been banned or severely restricted for use in the European Union due to their ecotoxicity but remain registered for use in this region of Australia (dimethoate, omethoate, imidacloprid, terbutryn, triadimenol, and methomyl). In addition, the two pesticides with the highest concentrations in this study, imidacloprid and dimethoate, were detected at relatively high concentrations compared to global values found in polluted aquatic environments.

Furthermore, toxicant contamination factors increased in more recent sediments of estuarine habitat in the Coffs Harbour region, indicative of highly polluted systems. This conclusion is based on the ^{210}Pb dated sediment cores which showed increasing heavy metal deposition in more recent sediments, along with the highly toxic and bioavailable methylmercury and pesticide accumulation. Pesticide transport and metal loading combined with high dissolved nutrient input in this marine protected region will likely result in eutrophic conditions, unlikely to sustain a healthy environment for higher marine organisms. Regulatory measures are suggested to improve the management of pesticides and heavy metals in coastal agricultural catchments along this region of Coffs Harbour.

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Appendix (Part 1).

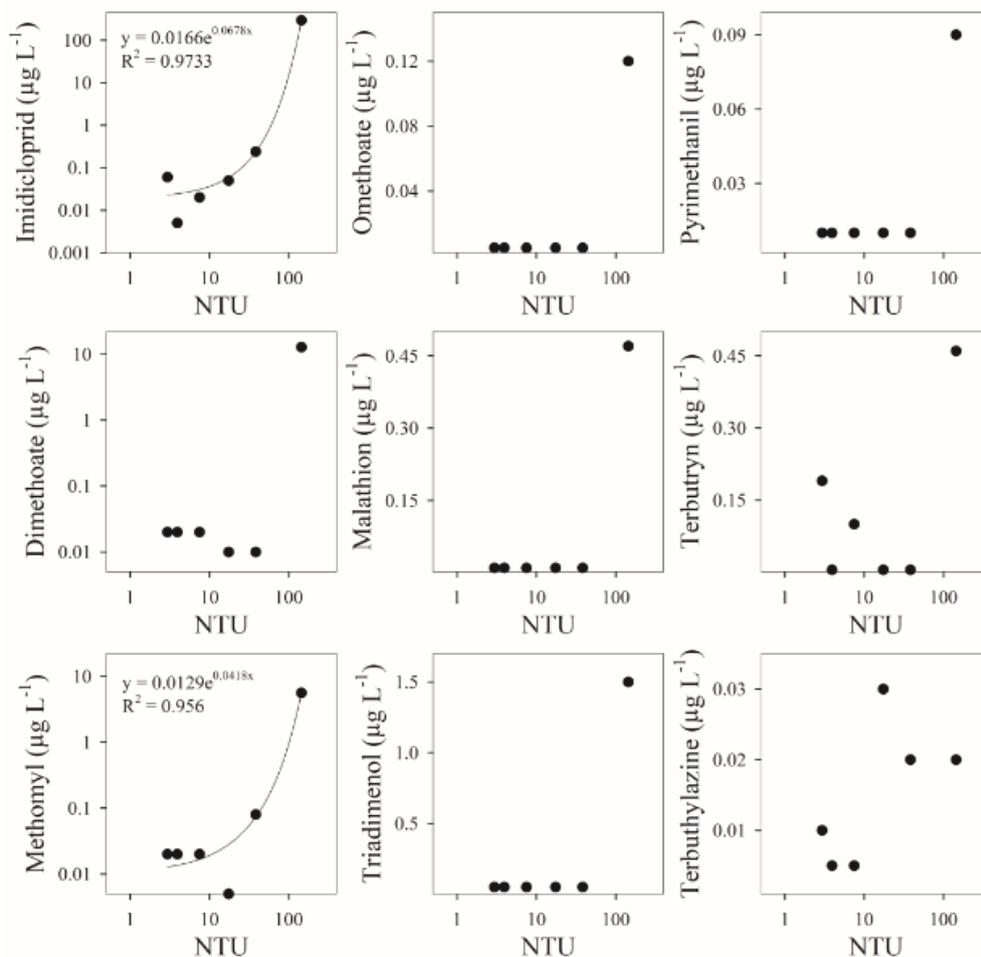


Fig 1. Relationship between turbidity (NTU) and concentration values ($\mu\text{g L}^{-1}$) of detected pesticides (a)-(i) from the summer-autumn samples collected at Double Crossing Creek

Table 1. Wet Season Sampling Period, Water Samples

**All measurements are in $\mu\text{g L}^{-1}$*

January to April 2019 (14-weeks) Summer to Autumn							
EP234: Multiresidue Pesticides							
Analyte grouping/Analyte	LOR	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
3-Hydroxy Carbofuran	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
4OH-TPN as Chlorothalonil	2	<2	<2	<2	<2	<2	<2
Abamectin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Acephate	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Alachlor	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Aldicarb	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ametryn	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Aminopyralid	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Amitraz	100	<100	<100	<100	<100	<100	<100
Asulam	2	<2	<2	<2	<2	<2	<2
Atrazine	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Atrazine-desethyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Atrazine-desisopropyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Azinphos-ethyl	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Azinphos-methyl	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Azoxystrobin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bendiocarb	0.1	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Benomyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bensulfuron methyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bensulide	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boscalid	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Brodifacoum	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Bromacil	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Bromophos-ethyl	0.1	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Bromoxynil	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Butachlor	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Carbaryl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Carbendazim (Thiophanate methyl)	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Carbofenthoion	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Carbofuran	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Carboxin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Carfentrazone-ethyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chlorantraniliprole	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

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Chlorfenvinphos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Chloroxuron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chlorpyrifos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Chlorpyrifos-methyl	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chlorsulfuron	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Coumaphos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cyanazine	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cyproconazole	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cyprodinil	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cyromazine	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Demeton-O	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Demeton-O & Demeton-S	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Demeton-S	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Demeton-S-methyl	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Diazinon	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Dichlobenil	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dichlorprop-P	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dichlorvos	0.2	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Diclofop-methyl	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Dicofol	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Difenoconazole	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Diflubenzuron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Diflufenican	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Dimethoate	0.02	12.8	<0.02	<0.02	0.02	0.02	0.02
Diphenamid	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Disulfoton	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Diuron	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Endothal	1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
EPN	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
EPTC	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ethion	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ethoprophos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Etridiazole	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Fenamiphos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fenarimol	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Fenchlorphos (Ronnell)	10	<10	<10	<10	<10	<10	<10
Fenitrothion	2	<2	<2	<2	<2	<2	<2
Fenoxycarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fensulfothion	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

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Fenthion	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Fipronil	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Flamprop methyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fluometuron	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Flupropanate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Flusilazole	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Formothion	20	<20	<20	<20	<20	<20	<20
Fosetyl Aluminium	10	<10	<10	<10	<10	<10	<10
Haloxyfop	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Hexaconazole	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Hexaflurate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Hexazinone	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Imazapyr	10	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0
Imidacloprid	0.01	294	0.05	0.24	<0.01	0.06	0.02
Indoxacarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Iodosulfuron methyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Iprodione	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Irgarol	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Isoproturon	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Malathion	0.02	0.47	<0.02	<0.02	<0.02	<0.02	<0.02
Metalaxyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Metalaxyl-M	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Metaldehyde	10	<10	<10	<10	<10	<10	<10
Methidathion	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Methiocarb	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Methomyl	0.01	5.6	<0.01	0.08	0.02	0.02	0.02
Metolachlor	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Metribuzin	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mevinphos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Molinate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Monocrotophos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Myclobutanil	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Naftalofos	1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Napropamide	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Nicarbazin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Nitralin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Norflurazon	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Novaluron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Omethoate	0.01	0.12	<0.01	<0.01	<0.01	<0.01	<0.01

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Oryzalin	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Oxamyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Oxyfluorfen	1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Paclobutrazole	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Parathion	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Parathion-methyl	2	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Pebulate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Penconazole	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pendimethalin	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Phorate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pirimicarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pirimiphos-ethyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pirimiphos-methyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Prochloraz	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Profenofos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Promecarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Prometryn	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Propachlor	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Propamocarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Propanil	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Propargite	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Propazine	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Propiconazole	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Propyzamide	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Prothiofos	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyraclostrobin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyrasulfatole	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyrazophos	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyrimethanil	0.02	0.09	<0.02	<0.02	<0.02	<0.02	<0.02
Pyriproxyfen	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyroxsulam	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Quinclorac	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Rimsulfuron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Siduron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Simazine	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Spirotetramat	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sulfotep	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Sulprofos	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Tebuconazole	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Tebuthiuron	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Temephos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Terbacil	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Terbufos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Terbuthylazine	0.01	0.02	0.03	0.02	<0.01	0.01	<0.01
Terbutryn	0.01	0.46	<0.01	<0.01	<0.01	0.19	0.1
Tetrachlorvinphos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tetraconazole	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Thiamethoxam	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Thiobencarb	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Thiodicarb	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Thiometon	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Toltrazuril	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Triadimefon	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Triadimenol	0.1	1.5	<0.1	<0.1	<0.1	<0.1	<0.1
Triazophos	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Trichlorfon	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Trichloronate	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Trifloxystrobin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Trifloxysulfuron-sodium	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Trifluralin	10	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0
Trinexapac Ethyl	1	<1	<1	<1	<1	<1	<1
Vernolate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 2. Before Rain Sampling Event, Water Samples

**All measurements are in $\mu\text{g L}^{-1}$*

Before Rain Event							
EP234: Multiresidue Pesticides							
Analyte grouping/Analyte	LOR	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
3-Hydroxy Carbofuran	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
4OH-TPN as Chlorothalonil	2	<2	<2	<2	<2	<2	<2
Abamectin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Acephate	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Alachlor	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Aldicarb	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ametryn	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Aminopyralid	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Amitraz	100	<100	<100	<100	<100	<100	<100
Asulam	2	<2	<2	<2	<2	<2	<2
Atrazine	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Atrazine-desethyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Atrazine-desisopropyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Azinphos-ethyl	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Azinphos-methyl	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Azoxystrobin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bendiocarb	0.1	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Benomyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bensulfuron methyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bensulide	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boscalid	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Brodifacoum	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Bromacil	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Bromophos-ethyl	0.1	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Bromoxynil	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Butachlor	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Carbaryl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Carbendazim (Thiophanate methyl)	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Carbophenothion	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Carbofuran	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Carboxin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Carfentrazone-ethyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chlorantraniliprole	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chlorfenvinphos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Chloroxuron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chlorpyrifos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Chlorpyrifos-methyl	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chlorsulfuron	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Coumaphos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cyanazine	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cyproconazole	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cyprodinil	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cyromazine	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Demeton-O	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Demeton-O & Demeton-S	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Demeton-S	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Demeton-S-methyl	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Diazinon	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Dichlobenil	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dichlorprop-P	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dichlorvos	0.2	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Dicofop-methyl	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Dicofol	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Difenoconazole	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Diflubenzuron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Diflufenican	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Dimethoate	0.02	<0.02	0.02	<0.02	<0.02	<0.02	<0.02
Diphenamid	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Disulfoton	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Diuron	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Endothal	1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
EPN	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
EPTC	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ethion	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ethoprophos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Etridiazole	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Fenamiphos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fenarimol	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Fenchlorphos (Ronnell)	10	<10	<10	<10	<10	<10	<10
Fenitrothion	2	<2	<2	<2	<2	<2	<2
Fenoxycarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fensulfthion	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fenthion	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

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Fipronil	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Flamprop methyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fluometuron	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Flupropanate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Flusilazole	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Formothion	20	<20	<20	<20	<20	<20	<20
Fosetyl Aluminium	10	<10	<10	<10	<10	<10	<10
Haloxyfop	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Hexaconazole	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Hexaflurate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Hexazinone	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Imazapyr	10	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0
Imidacloprid	0.01	0.61	<0.01	0.07	<0.01	<0.01	<0.01
Indoxacarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Iodosulfuron methyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Iprodione	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Irgarol	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Isoproturon	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Malathion	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Metalaxyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Metalaxyl-M	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Metaldehyde	10	<10	<10	<10	<10	<10	<10
Methidathion	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Methiocarb	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Methomyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Metolachlor	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Metribuzin	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mevinphos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Molinate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Monocrotophos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Myclobutanil	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Naftalofos	1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Napropamide	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Nicarbazin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Nitralin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Norflurazon	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Novaluron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Omethoate	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Oryzalin	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Oxamyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Oxyfluorfen	1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Paclobutrazole	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

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Parathion	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Parathion-methyl	2	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Pebulate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Penconazole	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pendimethalin	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Phorate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pirimicarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pirimiphos-ethyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pirimiphos-methyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Prochloraz	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Profenofos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Promecarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Prometryn	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Propachlor	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Propamocarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Propanil	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Propargite	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Propazine	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Propiconazole	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Propyzamide	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Prothiofos	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyraclostrobin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyrasulfatole	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyrazophos	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyrimethanil	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pyriproxyfen	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyroxsulam	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Quinclorac	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Rimsulfuron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Siduron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Simazine	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Spirotetramat	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sulfotep	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Sulprofos	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Tebuconazole	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tebuthiuron	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Temphos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Terbacil	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Terbufos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Terbuthylazine	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Terbutryn	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tetrachlorvinphos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

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Tetraconazole	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Thiamethoxam	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Thiobencarb	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Thiodicarb	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Thiometon	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Toltrazuril	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Triadimefon	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Triadimenol	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Triazophos	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Trichlorfon	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Trichloronate	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Trifloxystrobin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Trifloxysulfuron-sodium	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Trifluralin	10	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0
Trinexapac Ethyl	1	<1	<1	<1	<1	<1	<1
Vernolate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 3. - After Rain Sampling Event, Water Samples*All measurements are in $\mu\text{g L}^{-1}$

After Rain Event							
EP234: Multiresidue Pesticides							
Analyte grouping/Analyte	LOR	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
3-Hydroxy Carbofuran	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
4OH-TPN as Chlorothalonil	2	<2	<2	<2	<2	<2	<2
Abamectin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Acephate	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Alachlor	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Aldicarb	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ametryn	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Aminopyralid	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Amitraz	100	<100	<100	<100	<100	<100	<100
Asulam	2	<2	<2	<2	<2	<2	<2
Atrazine	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Atrazine-desethyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Atrazine-desisopropyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Azinphos-ethyl	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Azinphos-methyl	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Azoxystrobin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bendiocarb	0.1	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Benomyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bensulfuron methyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bensulide	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boscalid	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Brodifacoum	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Bromacil	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Bromophos-ethyl	0.1	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Bromoxynil	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Butachlor	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Carbaryl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Carbendazim (Thiophanate methyl)	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Carbofenothion	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Carbofuran	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Carboxin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Carfentrazone-ethyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chlorantraniliprole	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chlorfenvinphos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

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Chloroxuron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chlorpyrifos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Chlorpyrifos-methyl	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chlorsulfuron	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Coumaphos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cyanazine	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cyproconazole	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cyprodinil	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cyromazine	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Demeton-O	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Demeton-O & Demeton-S	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Demeton-S	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Demeton-S-methyl	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Diazinon	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Dichlobenil	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dichlorprop-P	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dichlorvos	0.2	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Diclofop-methyl	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Dicofol	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Difenoconazole	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Diflubenzuron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Diflufenican	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Dimethoate	0.02	<0.02	<0.02	<0.02	<0.02	0.02	<0.02
Diphenamid	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Disulfoton	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Diuron	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Endothal	1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
EPN	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
EPTC	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ethion	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ethoprophos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Etridiazole	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Fenamiphos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fenarimol	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Fenchlorphos (Ronnell)	10	<10	<10	<10	<10	<10	<10
Fenitrothion	2	<2	<2	<2	<2	<2	<2
Fenoxycarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fensulfothion	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fenthion	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Fipronil	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Flamprop methyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fluometuron	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

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Flupropanate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Flusilazole	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Formothion	20	<20	<20	<20	<20	<20	<20
Fosetyl Aluminium	10	<10	<10	<10	<10	<10	<10
Haloxifop	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Hexaconazole	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Hexaflurate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Hexazinone	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Imazapyr	10	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0
Imidacloprid	0.01	0.04	<0.01	0.04	<0.01	<0.01	<0.01
Indoxacarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Iodosulfuron methyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Iprodione	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Irgarol	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Isoproturon	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Malathion	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Metalaxyl	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Metalaxyl-M	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Metaldehyde	10	<10	<10	<10	<10	<10	<10
Methidathion	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Methiocarb	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Methomyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Metolachlor	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Metribuzin	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mevinphos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Molinate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Monocrotophos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Myclobutanil	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Naftalofos	1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Napropamide	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Nicarbazin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Nitralin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Norflurazon	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Novaluron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Omethoate	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Oryzalin	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Oxamyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Oxyfluorfen	1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Paclobutrazole	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Parathion	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Parathion-methyl	2	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Pebulate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

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Penconazole	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pendimethalin	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Phorate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pirimicarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pirimiphos-ethyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pirimiphos-methyl	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Prochloraz	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Profenofos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Promecarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Prometryn	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Propachlor	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Propamocarb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Propanil	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Propargite	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Propazine	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Propiconazole	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Propyzamide	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Prothiofos	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyraclostrobin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyrasulfatole	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyrazophos	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyrimethanil	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pyriproxyfen	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyroxsulam	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Quinclorac	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Rimsulfuron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Siduron	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Simazine	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Spirotetramat	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sulfotep	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Sulprofos	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Tebuconazole	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tebuthiuron	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Temphos	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Terbacil	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Terbufos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Terbuthylazine	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Terbutryn	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tetrachlorvinphos	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tetraconazole	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Thiamethoxam	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Thiobencarb	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Thiodicarb	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Thiometon	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Toltrazuril	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Triadimefon	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Triadimenol	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Triazophos	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Trichlorfon	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Trichloronate	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Trifloxystrobin	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Trifloxysulfuron-sodium	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Trifluralin	10	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0
Trinexapac Ethyl	1	<1	<1	<1	<1	<1	<1
Vernolate	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Appendix (Part 2).

Contamination Factor: total trace metals and trace metal fluxes in estuarine sediments.

	As	Pb	Cr	Cu	Mn	Ni	Se	Zn	Hg	Fe	Al	Be	B	Co
Core 3 Total														
2018	0.62	2.22	1.38	1.29	1.13	2.25	1.00	3.36	1.00	1.02	1.66	1.00	1.11	1.81
2016	0.86	6.38	1.73	9.41	2.59	3.22	1.52	5.96	1.00	1.75	4.43	1.11	1.65	2.90
2011	0.74	4.07	1.55	3.36	1.53	2.69	1.00	4.30	1.00	1.21	2.86	1.00	1.00	2.35
2010	3.44	7.61	2.01	5.12	6.40	4.06	1.00	6.39	1.00	1.71	4.97	1.00	1.92	2.91
2009	0.71	5.68	1.75	5.03	1.71	3.40	1.00	6.03	1.00	1.35	4.04	1.00	1.00	2.24
2008	0.99	7.76	2.24	7.55	2.59	4.27	1.00	8.23	1.00	1.84	5.50	1.00	2.24	3.08
2007	0.83	6.88	1.81	8.41	2.50	3.80	1.00	7.54	1.00	1.65	4.64	1.00	1.24	2.65
2003	0.58	2.46	1.34	10.38	1.48	2.45	1.00	4.66	1.00	1.13	2.08	1.00	1.45	1.86
2003	0.50	2.39	1.34	1.76	1.51	1.53	1.00	2.77	1.00	1.01	1.87	1.00	1.21	0.12
1998	0.58	2.24	1.37	1.42	1.26	2.27	1.00	3.44	1.00	1.01	1.78	1.00	1.00	1.60
1993	0.84	1.78	1.29	2.26	1.14	1.87	1.00	2.06	1.00	1.14	1.52	1.00	1.00	1.57
1983	0.75	1.88	1.19	2.03	1.22	1.94	1.00	1.89	1.00	1.10	1.39	1.00	1.00	1.86
1980	0.70	3.28	1.57	2.47	1.61	3.43	1.00	3.16	1.00	1.29	1.98	1.00	1.00	2.43
1977	0.93	2.25	1.58	2.61	1.58	1.77	1.00	2.36	1.00	1.36	1.79	1.00	1.48	2.13
1960	1.00	1.41	1.17	2.69	1.31	1.96	1.00	1.41	1.00	1.25	1.42	1.00	1.20	2.06
1907	0.71	3.01	1.39	2.60	1.19	1.81	1.00	3.04	1.00	1.06	1.64	1.00	1.00	1.82
Core 10 Total														
2020	3.78	1.30	1.54	2.40	6.60	3.37	1.85	4.79	2.47	3.29	1.42	2.39	0.45	2.11
2019	3.06	1.38	1.47	2.58	6.12	3.31	1.90	4.41	2.47	2.38	1.37	2.45	0.41	1.93
2018	2.39	1.57	1.71	2.72	6.48	3.08	1.94	4.14	3.14	1.82	1.59	2.51	0.53	1.63
2017	1.25	1.23	1.34	1.48	4.05	2.13	0.97	2.77	2.47	1.27	1.12	1.66	0.39	1.07
2015	1.37	1.59	1.43	1.92	3.94	2.08	1.06	2.52	2.47	0.97	1.27	1.33	0.42	1.01
2013	1.24	1.58	1.64	2.00	4.40	2.65	1.41	2.63	2.47	1.29	1.66	1.12	0.48	1.19
2011	1.98	1.91	1.95	2.34	3.80	2.30	1.62	2.76	2.60	1.30	1.56	1.33	0.50	0.92
2007	2.47	1.82	1.77	1.98	3.20	2.17	1.21	2.73	2.47	1.45	1.62	1.47	0.39	1.12
2003	2.19	1.69	1.63	2.03	3.00	2.24	1.23	2.67	2.77	1.19	1.50	1.65	0.49	0.89
1999	2.35	1.50	1.67	2.06	2.89	2.21	1.34	2.44	3.02	1.13	1.58	1.21	0.40	0.93
1993	2.21	1.37	1.71	2.07	2.69	2.29	1.69	2.32	2.47	1.03	1.53	1.16	0.63	0.90
1985	2.07	1.36	1.81	2.08	2.50	2.51	1.11	2.48	2.49	1.06	1.61	1.43	0.53	0.94
1973	1.60	1.29	1.68	1.83	2.29	2.24	1.93	1.98	2.99	0.98	1.56	1.41	0.58	0.77
1956	1.55	1.30	1.69	1.61	2.08	2.15	1.26	1.78	2.94	1.02	1.60	1.45	0.68	0.68
1930	1.56	1.22	1.59	1.38	1.57	1.66	0.97	1.36	2.47	0.80	1.42	1.39	0.71	0.64
Core 3 Flux														
2018	21.40	77.62	47.39	44.17	38.73	77.19	34.31	115.69	34.31	35.12	56.76	34.31	38.19	62.05
2016	1.00	7.54	2.01	10.93	2.99	3.74	1.77	6.95	1.16	2.03	5.13	1.29	1.92	3.36
2015	1.37	9.20	2.12	17.31	4.33	5.03	1.01	9.16	1.00	3.03	5.87	1.12	2.44	3.93
2011	2.71	15.23	5.68	12.34	5.58	9.87	3.67	15.85	3.67	4.43	10.50	3.67	3.67	8.62
2010	1.29	11.05	2.96	7.31	3.49	5.80	1.43	9.16	1.43	2.44	7.08	1.43	2.73	4.16
2009	1.58	12.94	3.92	11.27	3.81	7.61	2.24	13.55	2.24	3.02	9.04	2.24	2.24	5.02
2008	1.20	9.58	2.72	9.17	3.12	5.18	1.21	10.02	1.21	2.23	6.66	1.21	2.71	3.73
2007	0.62	5.22	1.35	6.27	1.85	2.83	0.74	5.64	0.74	1.23	3.45	0.74	0.92	1.98
2003	2.22	9.59	5.16	39.85	5.65	9.38	3.83	17.94	3.83	4.34	7.98	3.83	5.55	7.14
2003	1.74	8.46	4.68	6.14	5.25	5.33	3.48	9.69	3.48	3.51	6.50	3.48	4.21	6.42
1998	1.75	6.94	4.17	4.33	3.82	6.90	3.04	10.50	3.04	3.06	5.41	3.04	3.04	4.87
1993	4.52	9.70	6.91	12.14	6.10	10.02	5.36	11.08	5.36	6.12	8.15	5.36	5.36	8.42
1983	2.34	6.00	3.73	6.36	3.80	6.07	3.13	5.93	3.13	3.44	4.33	3.13	3.13	5.82
1980	1.44	6.90	3.25	5.11	3.31	7.09	2.07	6.55	2.07	2.66	4.08	2.07	2.07	5.03
1977	2.51	6.19	4.27	7.06	4.26	4.79	2.70	6.42	2.70	3.67	4.82	2.70	3.99	5.76
1960	2.95	4.25	3.46	7.96	3.85	5.79	2.96	4.18	2.96	3.71	4.18	2.96	3.55	6.11
1907	0.58	2.51	1.14	2.14	0.98	1.48	0.82	2.51	0.82	0.87	1.35	0.82	0.82	1.49
Core 10 Flux														
2020	18.37	6.25	7.45	11.59	32.01	16.32	6.80	23.10	4.51	15.92	6.88	11.61	2.18	10.25
2019	8.40	3.74	4.01	7.05	16.75	9.06	3.94	12.00	2.55	6.50	3.73	6.74	1.11	5.28
2018	9.71	6.30	6.90	10.96	26.17	12.43	5.93	16.63	4.77	7.36	6.43	10.19	2.13	6.57
2017	4.22	4.11	4.51	4.98	13.63	7.18	2.46	9.27	3.13	4.26	3.76	5.59	1.30	3.61
2015	2.30	2.63	2.38	3.20	6.59	3.48	1.34	4.18	1.55	1.62	2.12	2.23	0.69	1.69
2013	2.56	3.24	3.37	4.12	9.10	5.48	2.22	5.41	1.92	2.66	3.42	2.33	0.99	2.45
2011	3.49	3.34	3.42	4.11	6.70	4.06	2.16	4.85	1.73	2.29	2.74	2.34	0.88	1.61
2007	8.02	5.83	5.70	6.38	10.33	7.03	2.97	8.78	3.01	4.67	5.23	4.76	1.26	3.63
2003	5.76	4.39	4.25	5.31	7.84	5.86	2.44	6.95	2.72	3.12	3.92	4.34	1.27	2.33
1999	5.90	3.74	4.17	5.15	7.25	5.54	2.55	6.10	2.85	2.83	3.96	3.05	0.99	2.32
1993	4.24	2.59	3.25	3.94	5.14	4.38	2.45	4.40	1.78	1.97	2.92	2.23	1.20	1.72
1985	3.30	2.15	2.87	3.30	3.98	3.98	1.34	3.92	1.49	1.68	2.55	2.27	0.83	1.49
1973	1.97	1.57	2.06	2.24	2.82	2.75	1.80	2.43	1.38	1.21	1.91	1.74	0.70	0.94
1956	1.36	1.13	1.48	1.41	1.82	1.89	0.84	1.56	0.97	0.90	1.40	1.27	0.59	0.59
1930	1.35	1.04	1.37	1.19	1.35	1.43	0.63	1.17	0.80	0.69	1.22	1.21	0.60	0.55

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