Investigating soil chemistry on intensive horticulture sites and in associated dam sediments

Final Report - Coffs Harbour City Council Environmental Levy Program

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Contents

List of Figures

List of Tables

Executive Summary

Southern Cross University performed soil and sediment quality investigations on farms with various land use histories, including blueberry and banana cultivation, with funding from the Coffs Harbour City Council's Environmental Levy program.

Terrestrial soils from chemical mixing sheds, crop production areas (fields), drainage areas, and bottom sediments from retention reservoirs (dams) were sampled from three different sites in the Coffs Harbour local government area. Sites 1 and 2 were in the Sandy Beach catchment, while Site 3 was in the Bucca Bucca Creek catchment. All three sites are currently used for blueberry cultivation.

Terrestrial soil cores were analysed for 97 different pesticide residues of different classes (herbicides, insecticides, fungicides). Additionally, terrestrial soil and dam sediment cores were analysed for trace metal contents.

Spatial distributions of pesticides and trace metals in terrestrial soils and sediments were analysed to identify contaminated sites. Comparisons to the Australia and New Zealand Environment and Conservation Council (ANZECC) and other soil quality guidelines (SQG) and enrichment factors (anthropogenic vs. naturally occurring portions) were used to assess contamination of trace metals.

The farm in the Bucca Bucca catchment (Site 3) had the greatest degree of contamination with pesticides. Fifty percent of the detectable pesticide residues were from two cores at this site. Ninety-eight percent of the total detected pesticide mass was observed in the chemical mixing shed core from Site 3. The fungicides propiconazole and cyprodinil were the most abundant pesticides from this core. Soil contents of these fungicides should decline as they degrade via natural processes, however propiconazole and cyprodinil can persist in the environment while bound to soil organic material. Degradation rates remain uncertain. Additionally, toxicity of propiconazole and cyprodinil degradation products may be greater than their parent compounds.

14 of 26 subsamples of terrestrial soil and dam sediment cores from Site 2 in Sandy Beach had arsenic contents over the SQG low value (20 mg kg^{-1}). One of these samples exceeded the SQG high range value (70 mg kg^{-1}). Arsenic is suspected to be from pesticide application which occurred during previous land use (banana cultivation).

Subsamples from dam sediment cores at all three sites had mercury (Hg) contents over the SQG low value (150 µg kg^{-1}). Mean contents of Hg from dam sediments (141 ± 15.5 µg kg^{-1}) were greater than terrestrial soils (78 ± 6.5 µg kg^{-1}) suggesting mobility of Hg from terrestrial soils and retention in nearby sediments.

Overall, based on their environmental toxicity, distribution, persistence, and mobility we identified the herbicide diuron, trace metals cadmium (Cd) and (Hg), and the fertiliser nutrient phosphorus (P) as contaminants of high concern. Using international pesticide toxicity standards from the Globally Harmonised System of classification and labelling of chemicals, we classified all other detected pesticides as contaminants of potential concern.

We highlight that our sampling was spatially restricted and suggest more sampling of farm soils to increase confidence in identifying contaminants of concern.

1. Introduction

Residues of agricultural treatment products such as fertilizers, herbicides, fungicides, and insecticides (or more broadly termed pesticides) may not undergo rapid degradation and are able to become persistent environmental pollutants. Accumulation and overexposure of pesticides within the natural environment can cause ecosystem and human health complications (Hernández et al. 2011, Schäfer et al. 2012).

Example pesticides include dieldrin, DDT, chlorpyrifos, paraquat, atrazine, propiconazole, diuron, and many others. In addition to pesticides, some naturally occurring elements, for example, trace metals such as lead (Pb), mercury (Hg), and arsenic (As) and excess nutrients from fertilizers such as nitrogen (N) and phosphorus (P) are associated with agricultural treatment products. These contaminants, whether of artificial (pesticides) or natural (trace metals and excess nutrients) origins, can disrupt normal ecosystem functioning via eutrophication and alteration of trophic interactions leading to decreased biomass and biodiversity (Tilman 1999, Bennett et al. 2001, He et al. 2005).

Contaminants are introduced and transported within the environment in various ways. Application methods used on farms include sprays (Aeolian transport), irrigation treatments (hydrological transport), or applied directly over top of crops in solid form (terrestrial transport with sediment erosion). Some contaminants such as N and certain organophosphate pesticides, may exhibit affinity to remain dissolved in water (Heathwaite and Johnes 1996, Ragnarsdottir 2000), while many others (trace metals and lipophilic pesticide molecules) may react with clay mineral particles and become bound to soil particles in the terrestrial setting (on the farm) or suspended in the water column (Kreuger et al. 1999).

As agricultural contaminants are often applied directly to the crops and because many contaminants exhibit the affinity to rapidly bind to soil particles, the accumulation of contaminants occurs in the soil underlying the crops. Indeed, agricultural fields are often sites of increased nutrient, metal, and pesticide accumulation (Haynes and Naidu 1998, He et al. 2005, Fang et al. 2007). While agricultural soils may be the predominant (or first) major sink for anthropogenic contaminants, these substances may be transported away from agricultural lands under changing environmental conditions. Rainfall leaches contaminants from the soils to surface or ground waters and increases soil erosion from agricultural landscapes (Brodie and Mitchell 2005, Santos et al. 2011). Areas receiving sediment downstream of agricultural lands, such as engineered dams or estuaries, can also become sinks of agricultural runoff (Kreuger et al. 1999, Conrad et al. 2019). Sampling crop production areas and adjacent waterways can provide better understanding of the extent of environmental impact from agricultural treatment products.

Vertical profiles of the soil/sediment column can also be useful when assessing the extent of contamination, especially associated with a particular land use history. Indeed, sediment core profiles can provide evidence of historical contamination by a particular industry or activity, especially when sediments are dated with radionuclides, such as ^{210}Pb (Machado et al. 2016, Conrad et al. 2017). Additionally, the depths at which contaminants are found in the soil/sediment column could be indicative of mobility within the sediment column, with potential implications for groundwater (Farooq et al. 2010). Using a multiple lines of evidence approach, such as dated sediments combined with contaminant quantification in

different soil/sediment types and from various land uses allows for better understanding of different agricultural activities contributions to environmental contamination.

The objectives of this work were to quantify contaminant levels in various soil and sediment types in catchments with different land use histories and to identify contaminants of concern. We analysed sediment cores for nutrient, trace metal, and select pesticide residues from different use areas of three farms in the Coffs Harbour local government area (LGA) that are currently used for blueberry cultivation, but have varying land use histories. This report focuses on the upper catchment very close to active farming operations, building on our earlier report (Conrad et al. 2019), which discussed sediment contamination in the downstream coastal areas (estuary and mangroves).

2. Materials and Methods

2.1 Study Site

The history of Coffs Harbour includes timber collection, dairy farming, gold mining, and other industries, however Coffs Harbour is most known for its history of banana farming. Cultivation of bananas began in 1891, with extensive plantations being developed by the 1920s. In the 1980's there was evidence of health effects of banana farm pesticide use including higher than average birth defect and cancer rates (Short 1994). Budd (1995) reported blood borne concentrations of organochlorine (OC) pesticides in Coffs Harbour children were higher than other more populous cities in Australia and other nations. However, data on the extent of environmental contamination from nearly a century of banana cultivation is lacking. Conrad et al. (2017) reported sediment enrichments with copper (Cu) which coincided with the beginning of aerial spraying of fungicides in 1956 (Hedditch 2014). Loughran et al. (1993) used Cesium-137 (^{137}Cs) radionuclides to estimate no net sediment erosion from banana farms in the Coffs Harbour region.

More recent times have seen a change in the primary horticultural industry of the Coffs Harbour LGA. Since the year 2000, there has been a > 400 % increase in blueberry farms in the area (White et al. 2018), with large scale land use change from banana to blueberry farms (demonstrated by Figure 1). Many uncertainties remain regarding the environmental impact of blueberry farms. Our recent studies identified high levels of dissolved N in waters leaving blueberry farms (White et al. 2018, White 2018). Conrad et al. (2019) identified increased erosion from land use conversion from banana to blueberry cultivation has led to trace metal and P sediment enrichment in an estuary downstream of an intensive horticultural basin (Hearnes Lake estuary). Here we sample soil and sediment cores from blueberry farms in the Coffs Harbour LGA to better understand the accumulation of agricultural contaminants nearer to their source of potential of introduction.

2.2 Sample collection

We sampled three separate farms (hereby referred to as Sites 1, 2, and 3) with varying land use history. Sites 1 and 2 are located in Sandy Beach, within the Hearnes Lake catchment (Figure 2), and have a history of banana cultivation since the 1940s, however are now both currently used for blueberries (blueberry cultivation beginning ~ 2002). Site 3 is located further inland in the Bucca Bucca creek catchment (Figure 2). Previous land use here was for

cattle grazing. A blueberry farm was established after 2012 (personal communication with land owner).

In order to better understand the effects of specific farming activities on terrestrial soil contaminant accumulation, we sampled various locations used for different purposes at each of the three sites. NSW state regulations require that all agricultural chemicals be properly contained in a lockable indoor area (Browne 2016). This means NSW farms typically have a shed that contains agricultural chemicals and a nearby area specially designated for the mixing of chemicals. Due to the increased chemical exposure at these 'mixing sheds', greater accumulation of contaminants can be expected here. For this reason, we sampled 30 cm soil core from the soils near chemical mix sheds at each site (which we hereby term 'mix shed' cores). Additionally, in order to assess the soil quality in crop production areas and to gain insight into what contaminants were being applied to crops, we took 30 cm sediment cores from crop production areas (hereby termed 'field' cores). Lastly, at Site 2, we sampled a 30 cm sediment core from a steeply sloping ditch which drained a mixing shed that was previously used during banana cultivation, but has been retired since 1980 (personal communication with land owner). This core we have named 'Site 2 drainage ditch'. All terrestrial soil cores were taken with a 10 cm diameter metal or PVC tube. A total of 7 terrestrial soil cores were taken on 4 and 6 March 2019 (Figure 2).

In addition to sampling terrestrial soils, we assessed sediment quality in waterways capturing runoff from the farms. We elected to sample from water retention areas (dams) which hold and recycle water to be used for crop irrigation. Construction of dams at Sites 1 and 2 was completed in 1976 and Site 3 was constructed in 2013 (personal communication with land owners). Three cores were collected from dam bottom sediments (Figure 2) on 4 March 2019 using a 6.8 cm inner diameter Aquatic Research Instruments Universal weighted gravity corer. Dam cores were collected from depths between 4.0 to 4.2 m. Maximum depths of the dams were ~ 6 m.
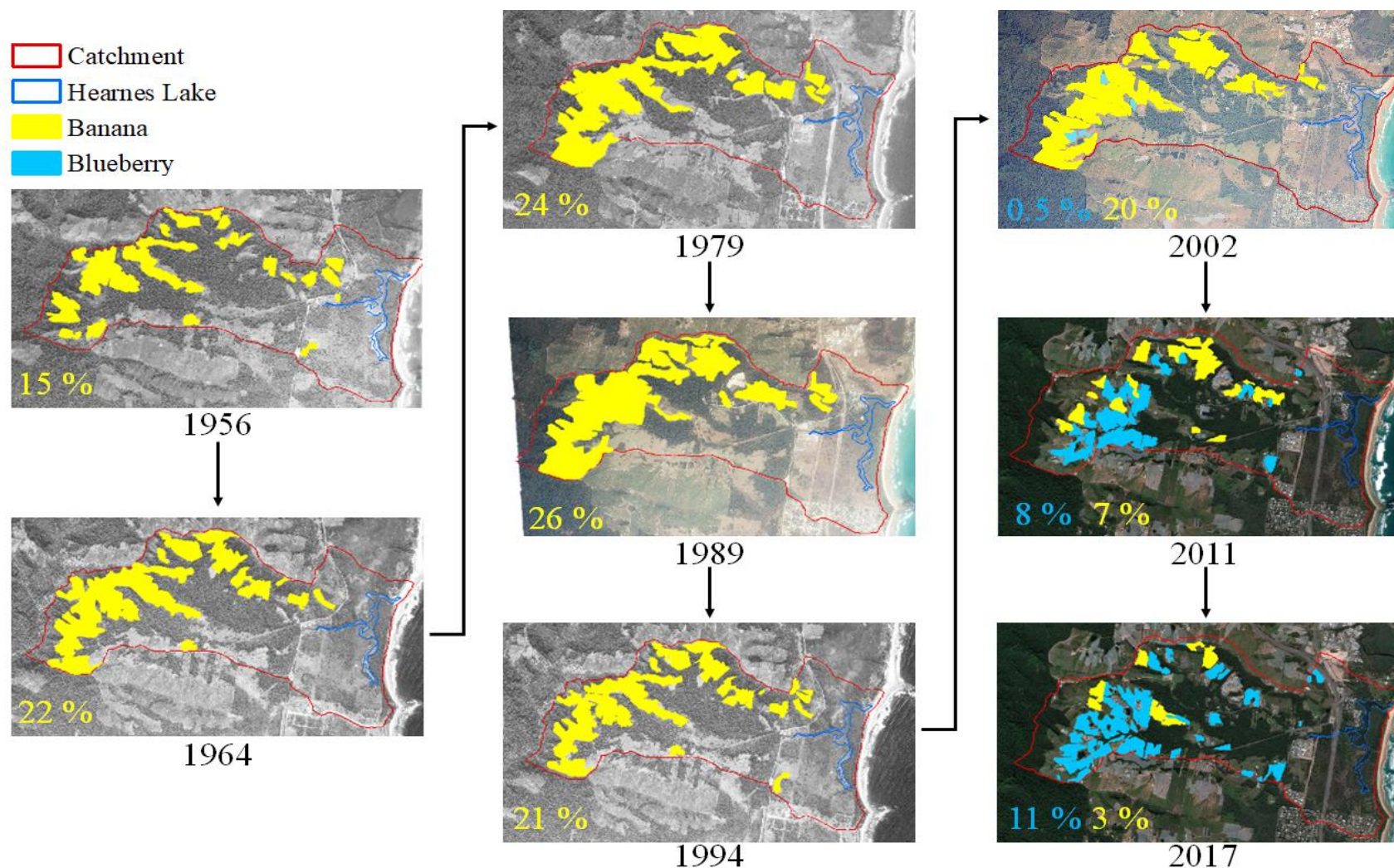
Figure 1. Aerial photography time series of the Sandy Beach catchment (red line, near Woolgoolga, NSW) demonstrating land use change in Northern NSW agricultural lands between 1956 and 2017. ArcGIS software used to quantify land uses. Banana farms: yellow polygons and percentages; blueberry farms: blue polygons and percentages. Images provided by NSW DPI.
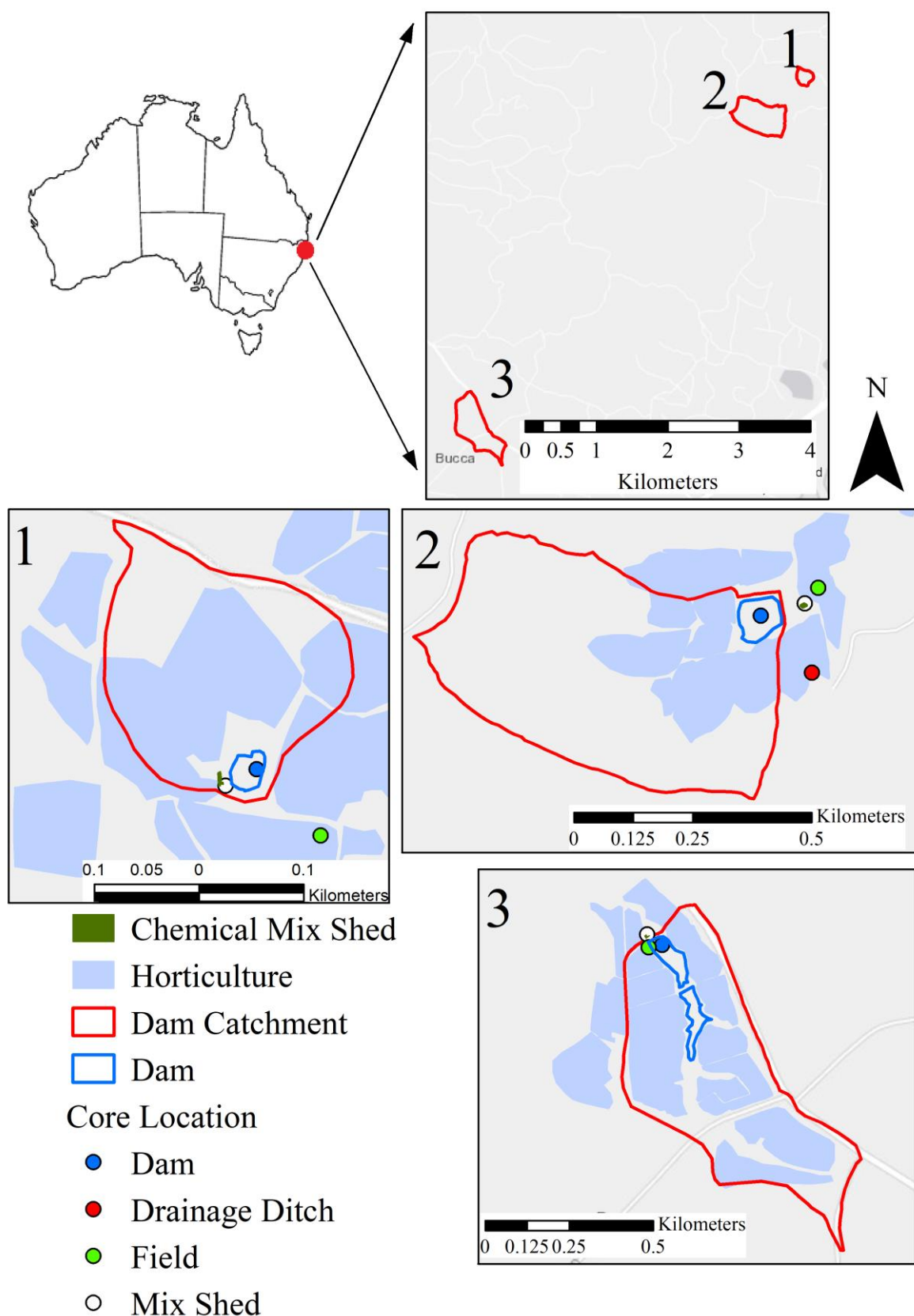
Figure 2. Locations of dam sediment cores (blue dots), mix shed (white dots), drainage ditch (Site 2 only, red dot), and field (green dots) soil cores in the Sandy Beach (Sites 1 and 2, black numbers) and Bucca Bucca (Site 3) farms near Coffs Harbour, NSW. Chemical mixing sheds (dark green outline), horticultural land (light blue outline), and dam catchments (red outline) presented.

2.3 Sample processing and chemical analyses

2.3.1 Terrestrial core pesticide analysis

For the terrestrial soil cores, we followed the NSW Environmental Protection Authority's (EPA) "Guidelines for Assessing Banana Plantation Sites" protocol (EPA 1997) for sampling pesticide residues and trace metals at areas of localised contamination (hotspots). Terrestrial soil cores were sectioned into intervals from 0 to 7.5 cm, 7.5 to 15 cm, and 15 to 30 cm depths (EPA 1997). Each subsection was frozen until the pesticide or trace metal analysis. Soils were dried at 105° C prior to analysis.

To determine soil organochlorine (OC) pesticide content, 10 g of sample was transferred to a tumbler bottle. Anhydrous sodium sulphate (Na_2SO_4) was added until the mixture was free flowing. To assess soil matrix effects on contaminant recovery, each sample was spiked with a universal pesticide surrogate (dibromo-DDE). Next, 30 mL of 1:1 dichloromethane (DCM): acetone solution was added. Bottles were tumbled for 1 hour. The resulting extract was concentrated under N_2 gas to 1 mL and placed into 1.5 mL vial. Samples were run on an Agilent 5975 Gas Chromatograph/Mass Selective Detector (GC/MSD) at ALS Laboratories in Brisbane. The OC pesticides tested for were alpha-BHC, hexachlorobenzene (HCB), beta-BHC, delta-BHC, heptachlor, aldrin, heptachlor epoxide, trans-chlordane, cis-chlordane, alpha-endosulfan, dieldrin, 4.4'-DDE, endrin, beta-endosulfan, 4.4'-DDT, endrin aldehyde, endosulfan sulfate, 4.4' DDT, endrin ketone, and methoxychlor. Limits of reporting (LOR) ranged from 0.05 to 0.2 mg kg^{-1}. Blank (free of contaminant) samples of a similar soil matrix were performed before analysis. Reference material was spiked with 0.5 mg kg^{-1} of each target OC pesticide. Spike recoveries ranged from 77 to 108 % recoveries. During analysis, a selected sample with a representative array of target analytes was split to assess potential matrix interference and homogeneity of samples and spiked with OC pesticides at concentrations between 0.5 and 2 mg kg^{-1}. Spike recoveries ranged from 78.5 to 124 % recovery.

Synthetic pyrethroids were extracted in the same manner as the OC pesticides. Samples were run on an Agilent 59755 GC/MSD in selected ion monitoring (SIM) mode. The list of pyrethroids analysed for were bioresmethrin, phenothrin, lambda-cyhalothrin, permethrin, cyfluthrin, cypermethrin, fenvalerate, esfenvalerate, deltamathrin, tralomethrin, allethrin, transfluthrin, tetramethrin, tau-fluvalinate. The pytrethroid synergist piperonyl butoxide was also tested for. LOR was 0.05 mg kg^{-1} for all pyrethroids. Blanks and reference spikes were performed in the same manner as the OC pesticides. Spike recoveries ranged from 80.5 to 115 % recoveries. Representative samples were split to test for homogeneity and matrix interference and spiked at concentrations of 0.5 mg kg^{-1}. One analyte (bioresmethrin) had recovery of 22.8 % and was therefore discarded from analysis. All other spike recoveries ranged from 81.4 to 115 %.

To determine the organophosphate (OP) and carbamate pesticide, triazine, urea, and chloroacetanilide herbicide, and aminopyrimidine, benzimidazole, and conazole fungicide soil concentrations, 5 g of sample was placed into a 50 mL polypropylene centrifuge tube. 4 mL of acetonitrile (ACN) was added, followed by 6 mL of methanol (MeOH). Centrifuge tubes were vigorously hand shaken and vortexed to mix contents. Tubes were then either sonicated for 15 mins or tumbled for 1 hour. Tubes were centrifuged at 3000 rpm for 5 mins.

25 μL of the supernatant was pipetted into a 10 mL glass tube containing 2 mL of milli-Q water and 25 μL MeOH. Samples were briefly vortexed and filtered into 1.5 mL microcentrifuge tubes. Samples were run on an Applied Biosystems/MDS Sciex API 5000 Liquid Chromatography/mass spectrometry/mass spectrometry (LC/MSMS) with Qjet ion guide at ALS Laboratories in Brisbane. LORs ranged from 0.001 to 1 mg kg^{-1}. Blank samples of a similar soil matrix were run prior to analysis. Reference materials were spiked with standards to concentrations between 0.01 to 4 mg kg^{-1}. Reference material spike recoveries ranged from 63.2 to 103 %. Representative samples were split and spiked with concentrations of contaminants ranging from 0.01 mg kg^{-1} to 4 mg kg^{-1}. Recoveries ranged from 72.8 to 102 %.

2.3.2 Dam sediment cores and sediment dating

Dam sediments were extruded in 1 cm intervals using the provided extruding device from Aquatic Research Instruments. Sediments were frozen, freeze dried, and weighed to obtain dry bulk density (DBD). A separate portion of the sample was kept in the dark at -4° C until pesticide analysis.

For sediment dating, 3 to 6 g of dam sediments were packed into labelled 4 mL plastic vials to a height of 27 mm to establish uniform geometry for gamma detection. Vials were sealed with epoxy resin for 21 or more days to allow ^{222}Rn to establish secular equilibrium between ^{226}Ra and ^{214}Pb. Vials were placed in a high purity germanium (HPGe) well detector (Canberra®). ^{210}Pb activity was measured using the 46.5 keV gamma peak. The mean of the 295.2, 351.9, and 609.3 keV peak areas were used to determine ^{226}Ra activity.

2.3.3 Trace metal contents and enrichment factors (EF)

Trace metals from all samples (terrestrial soil and dam sediment cores) were analysed for trace metals using the methodology outlined in Conrad et al. (2019) and references therein.

We used the Australian and New Zealand Environment Conservation Council (ANZECC) Soil Quality Guidelines (SQG) (Simpson et al. 2013) as threshold values to assess the extent of trace metal contamination (Conrad et al. 2019). Where no ANZECC SQGs existed (for example, selenium (Se) and P), we used SQG values from the literature. SQG for Se was obtained from Van Derveer and Canton (1997). For P, SQG values were obtained from Ontario, Canada sediment quality guidelines (Persaud et al. 1993). We used their value of 600 mg kg^{-1} (the 'lowest effect level' described as 'a level of sediment contamination that can be tolerated by the majority of benthic organisms') as our P SQG default value (Table 2). For our high range P SQG, we used their value of 2000 mg kg^{-1}, described as a 'severe effect level' which indicates 'pronounced disturbance of the sediment dwelling community'. At sediment contents above this value, P is expected to be 'detrimental to the majority of benthic species' (Persaud et al. 1993).

To compare geologic and anthropogenic fractions of trace metals enrichment factors were calculated using aluminium (Al) as the reference material as outlined in Conrad et al. (2019).

3. Results

3.1 Terrestrial soil cores

3.1.1 Pesticides

We detected 52 pesticide residues in the terrestrial soil cores. From the five soil cores from Sites 1 and 2 there were 26 residues (50 %) from six different pesticides detected. The two cores from Site 3 had the other 50 % of residues from seven different pesticides. In total, there was 217 mg of pesticides detected in the 21 core subsamples analysed. By weight, 98 % of the pesticide mass we detected occurred in the Site 3 mix shed, with only small amounts of pesticides in the other cores (Figure 3).

ANZECC guidelines do not exist for the pesticide compounds we detected, therefore no comparison to ANZECC guidelines could be made for our pesticide residues.

No OC pesticide residues were detected above limits of reporting (between 0.05-0.2 mg kg^{-1} depending on specific contaminant) at any of the study sites.

Ethoprophos and dimethoate were the OP pesticides detected. Ethoprophos was detected in Site 1 mix shed 7.5-15 cm depth at a concentration of 0.017 mg kg^{-1} (Table 1). In the Site 2 mix shed ethoprophos contents were of 0.007 and 0.004 mg kg^{-1} at 7.5-15 and 15-30 cm depth, respectively, and in the surface interval (0 – 7.5 cm) of S2 drainage ditch at a concentration of 0.006 mg kg^{-1}. No ethoprophos was detected at Site 3. Dimethoate was found exclusively at Site 3 mix shed in concentrations of 0.195, 0.091, and 0.186 mg kg^{-1} at depths 0 – 7.5, 7.5-15, and 15-30 cm, respectively.

The carbamate insecticide methomyl concentration was greatest at 15-30 cm depth interval of the Site 3 mix shed core (0.074, 0.011, and 0.089 mg kg^{-1} with increasing depth).

The pyrethroid insecticide bifenthrin in the Site 3 mix shed core followed a trend of decreasing concentration with depth (11.4, 1.36, 0.10 mg kg^{-1} at 0-7.5, 7.5-15, and 15-30 cm depth, respectively).

Four fungicides were found. The conzaole fungicide propiconazole was found in Site 2 mix shed (0.10, 0.05, and 0.03 mg kg^{-1} with decreasing core depths), in Site 2 drainage ditch surface interval (0-7.5 cm) at a concentration of 0.020 mg kg^{-1}, and in Site 2 field (0.13 mg kg^{-1} in 0-7.5 and 0.04 mg kg^{-1} in 15-30). Propiconazole in the Site 3 mix shed had the highest concentration of any pesticide we detected. Propiconazole concentrations decreased with depth in the Site 3 mix shed core from 125 to 34.6 to 14.9 mg kg^{-1} as depth increased. Propiconazole also decreased with depth in the Site 3 field core (0.99, 0.28, and 0.21 mg kg^{-1} with increasing depth).

Two aminopyrimidine fungicides were found. Cypronodil had the highest spatial distribution of any contaminant found in our testing, being found in the surface intervals of the mix shed and field cores at all three sites (Table 1). Cypronodil was also found at depths 7.5-15 and 15-30 cm in the Site 3 mix shed and Site 3 field cores. Cypronodil was detected in S2 Field at 15-30 cm depth with a content of 0.068. Pyrimethanil contents were 0.10 mg kg^{-1} in 7.5-15 and 15-30 cm depth in Site 1 field core. The benzimidazole fungicide carbendazim contents decreased with depth in the Site 3 mix shed core (0.021, 0.008, and 0.006 mg kg^{-1} with increasing depths), and was also found in the surface interval (0–7.5 cm) in the Site 3 field,

Site 1 and 2 mix shed cores. Carbendazim contents were highest in the surface of the Site 2 mix shed (0.044 mg kg^{-1}), and relatively low in the bottom interval of Site 2 mix shed (0.006 mg kg^{-1}) site 1 mix shed surface (0.008 mg kg^{-1}).

The aryl urea herbicide diuron was found in all intervals of Site 2 Mix shed (0.010, 0.018, and 0.015 mg kg^{-1} with increasing depth). Site 2 field core had diuron concentrations of 0.010 and 0.014 mg kg^{-1} at depths 7.5-15 and 15-30, respectively. Site 2 drainage ditch cores had diuron contents of 0.02 and 0.012 mg kg^{-1} in 0-7.5 and 7.5-15 cm, respectively.

The triazine herbicide prometryn was detected in the surface interval of the Site 3 mix shed with contents of 0.004 mg kg^{-1}.
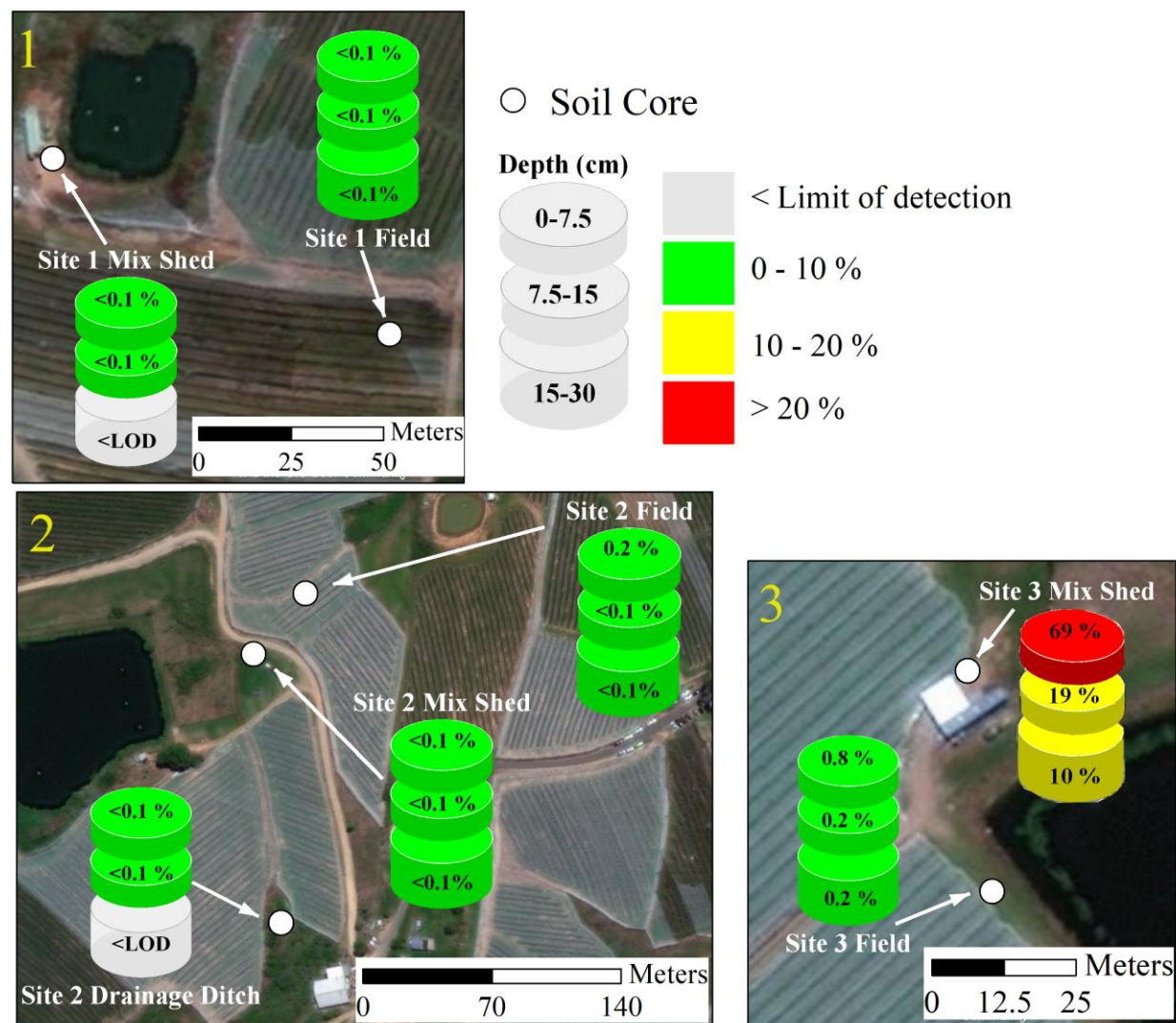
Figure 3. Percentage of total detected pesticide masses (mg) from each terrestrial soil core subsample (coloured cylinders). A total of 217 mg of pesticides were detected from our 21 core subsamples. Soil core intervals classified by colour based on mass percentages of the total detected pesticide mass. Grey: below limit of detection. Green: 0-10 %. Yellow: 10-20 %. Red: > 20 %. Site numbers are displayed in gold in the top right corner of each map. Figure 2 displays a more detailed map of the sampling area and Table 1 displays soil pesticide contents from each subsample.

Table 1. Pesticide soil contents (in mg kg^{-1}) from chemical mixing sheds, agricultural production areas (field), and drainage ditch soil cores from farms in the Coffs Harbour LGA.

Depth (cm)	Pesticide Name	Class/function	Site 1 Mix Shed	Site 1 Field	Site 2 Mix Shed	Site 2 Field	Site 2 Drainage Ditch	Site 3 Mix Shed	Site 3 Field
0-7.5	Bifenthrin	Pyrethroid insecticide	-	-	-	-	-	11.4	-
	Carbendazim	Benzimidazole fungicide	0.008	-	0.044	-	-	0.021	0.008
	Cypronodil	Aminopyrimidine fungicide	0.01	0.058	0.046	0.213	-	13.5	0.751
	Dimethoate	Organophosphate pesticide	-	-	-	-	-	0.195	-
	Diuron	Aryl urea herbicide	-	-	0.01	-	0.02	-	-
	Ethoprophos	Organophosphate pesticide	-	-	-	-	0.006	-	-
	Methomyl	Carbamate insecticide	-	-	-	-	-	0.074	-
	Prometryn	Triazine herbicide	-	-	-	-	-	0.004	-
	Propiconazole	Conazole fungicide	-	-	0.1	0.13	-	125	0.99
	Pyrimethanil	Aminopyrimidine fungicide	-	-	-	-	-	-	-
7.5-15	Bifenthrin	Pyrethroid insecticide	-	-	-	-	-	1.36	-
	Carbendazim	Benzimidazole fungicide	-	-	-	-	-	0.008	-
	Cypronodil	Aminopyrimidine fungicide	-	-	-	-	-	4.69	0.108
	Dimethoate	Organophosphate pesticide	-	-	-	-	-	0.091	-
	Diuron	Aryl urea herbicide	-	-	0.018	0.01	0.012	-	-
	Ethoprophos	Organophosphate pesticide	0.017	-	0.007	-	-	-	-
	Methomyl	Carbamate insecticide	-	-	-	-	-	0.011	-
	Prometryn	Triazine herbicide	-	-	-	-	-	-	-
	Propiconazole	Conazole fungicide	-	-	0.05	-	-	34.6	0.28
	Pyrimethanil	Aminopyrimidine fungicide	-	0.01	-	-	-	-	-
15-30	Bifenthrin	Pyrethroid insecticide	-	-	-	-	-	0.1	-
	Carbendazim	Benzimidazole fungicide	-	-	0.006	-	-	0.006	-
	Cypronodil	Aminopyrimidine fungicide	-	-	-	0.068	-	7.27	0.226
	Dimethoate	Organophosphate pesticide	-	-	-	-	-	0.186	-
	Diuron	Aryl urea herbicide	-	-	0.015	0.014	-	-	-
	Ethoprophos	Organophosphate pesticide	-	-	0.004	-	-	-	-
	Methomyl	Carbamate insecticide	-	-	-	-	-	0.089	-
	Prometryn	Triazine herbicide	-	-	-	-	-	-	-
	Propiconazole	Conazole fungicide	-	-	0.03	0.04	-	14.9	0.21
	Pyrimethanil	Aminopyrimidine fungicide	-	0.01	-	-	-	-	-

3.1.2 Trace metals

Arsenic (As) contents ranged from 3.7 to 99.2 mg kg^{-1}. Eight out of twenty one samples exceeded the ANZECC SQGs for As, all from Site 2 (Table 2). Seven samples from Site 2 cores exceeded the SQG low range value of 20 mg kg^{-1}, while Site 2 drainage ditch core 7.5-15 cm was the highest soil As content (99.2 mg kg^{-1}) and exceeded the SQG high range value (70 mg kg^{-1}). All three sediment intervals and therefore, mean sediment contents in the Site 2 mix shed (mean 23.6 ± 1.3 (standard error) mg kg^{-1}) and drainage ditch (mean 63.8 ± 21.8 mg kg^{-1}) cores exceeded SQG low values.

Lead (Pb) contents ranged from 8.4 to 21.8 mg kg^{-1}. No Pb contents exceeded the ANZECC SQGs.

Cadmium (Cd) contents ranged from 22.2 to 310.8 µg kg^{-1}. No Cd contents exceeded the ANZECC SQGs. Site 1 mix shed had the highest mean Cd contents (201.9 ± 54.5 µg kg^{-1}).

Chromium (Cr) contents ranged from 7.0 to 52.2 mg kg^{-1}. No Cr contents exceeded the ANZECC SQGs. There was relatively high Cr in the Site 1 mix shed core middle interval (7.5-15 cm, 52.2 mg kg^{-1}).

Copper (Cu) contents ranged from 3.4 to 100.3 mg kg^{-1}. Cu contents in the surface interval (0-7.5 cm, 100.3 mg kg^{-1}) of Site 3 mix shed exceeded the ANZECC SQG low range value of 65 mg kg^{-1}. Site 3 mix shed had the highest average Cu contents of any core (48.4 ± 26.4 mg kg^{-1}).

Nickel (Ni) contents ranged from 2.3 to 7.2 mg kg^{-1}. No Ni contents exceeded the ANZECC SQGs.

Selenium (Se) contents ranged from 0.4 to 2.7 mg kg^{-1}. While there is no ANZECC SQG value for Se, one sample (Site 2 drainage ditch, 15-30 cm, 2.7 mg kg^{-1}) exceeded the threshold Se SQG value (2.5 mg kg^{-1}) derived from data in streams of the western United States Van Derveer and Canton (1997).

Zinc (Zn) contents ranged from 10.7 to 638.4 mg kg^{-1}. All three sediment core intervals from the Site 3 mix shed exceeded the ANZECC SQG (mean Zn content: 406 ± 116.9 mg kg^{-1}). From 0-7.5 (638.4 mg kg^{-1}) exceeded the ANZECC SQG high value of 410 mg kg^{-1}. Contents at greater depths (313.2 and 266.7 mg kg^{-1} for 7.5-15 and 15-30 cm) exceeded the SQG low range value (200 mg kg^{-1}). No other samples exceeded the ANZECC SQG for Zn.

Mercury (Hg) contents ranged from 25.0 to 150.2 µg kg^{-1}. Site 3 field 7.5-15 cm (150.2 µg kg^{-1}) was slightly above the SQG low value of 150.0 µg kg^{-1}. Site 2 field had the highest average Hg contents (104.6 ± 4.4 µg kg^{-1}).

Cobalt (Co) contents ranged from 0.7 to 18.2 mg kg^{-1}. There are no ANZECC SQG for Co and no relevant Co SQG could be found in the literature.

Iron (Fe) contents ranged from 1.0 to 5.3 %. Fe content was ~3.5 times greater in the surface of the Site 3 mix shed core than the underlying sediments here. Aluminium (Al) contents ranged from 1.0 to 1.6 %. Al contents varied little amongst sites and depths relative to other elements. Manganese (Mn) contents ranged from 105 to 2634 mg kg^{-1}. Mean Mn contents

were highest in the growing areas (field cores) at Sites 1 and 2. These elements are naturally abundant in the lithosphere therefore, ANZECC SQG do not exist for Al and Mn.

Phosphorus (P) contents ranged from 148.9 to 2272 mg kg^{-1}. No ANZECC SQG exists for P, so instead we used the 'Lowest Effect Level' and 'Severe Effect Level' values (600 and 2000 mg kg^{-1}, respectively) from the Ontario, Canada SQG (Persaud et al. 1993). Site 1 mix shed had the highest mean P contents (1273 ± 507 mg kg^{-1}, > SQG low). The surface interval (0-7.5 cm) of Site 1 mix shed had the highest P contents (2272 mg kg^{-1}, > SQG high). At Site 3 mix shed, 0-7.5 and 7.5-15 cm intervals exceeded the SQG low value (1095 and 745 mg kg^{-1}, respectively).

Table 2. Trace metal and P soil quality guidelines (SQG) and contents from chemical mixing sheds, agricultural production areas (field), and drainage ditch soil cores from farms in the Coffs Harbour LGA. Highlighted cells are above SQG values (> SQG low = highlight only; > SQG high = highlight + bold).

		As	Pb	Cd	Cr	Cu	Ni	Se	Zn	Hg	Co	Mn	Fe	Al	P
Core	Depth	mg kg^{-1}	mg kg^{-1}	µg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	µg kg^{-1}	mg kg^{-1}	mg kg^{-1}	%	%	mg kg^{-1}
Site 1 Mix Shed	0-7.5	13.7	19.4	311	9.9	22.9	4.6	1.4	134.9	55	7.4	670	2.0	1.2	**2272**
	7.5-15	13.1	10.4	145	52.2	8.0	2.5	0.8	57.8	106	5.4	544	1.1	1.1	924
	15-30	9.4	11.9	150	9.5	7.2	2.8	1.5	71.2	65	5.3	2172	2.2	1.2	623
	Mean ± SE	12.1 ± 1.3	13.9 ± 2.8	202 ± 55	23.9 ± 14.2	12.7 ± 5.1	3.3 ± 0.7	1.3 ± 0.2	87.9 ± 23.8	75 ± 16	6.1 ± 0.7	1129 ± 523	1.8 ± 0.4	1.2 ± 0.03	1273 ± 507
Site 1 Field	0-7.5	5.4	14.9	55	7.0	12.2	3.1	1.2	21.4	71	5.7	1014	1.5	1.2	432
	7.5-15	7.6	17.2	54	7.9	11.1	3.8	0.9	21.0	109	10.3	2081	1.9	1.3	284
	15-30	11.4	17.5	199	7.5	9.5	5.6	1.1	33.4	60	12.3	2003	2.2	1.4	259
	Mean ± SE	8.2 ± 1.7	16.5 ± 0.8	103 ± 48	7.5 ± 0.3	11.0 ± 0.8	4.2 ± 0.8	1.1 ± 0.08	25.3 ± 4.1	80 ± 15	9.4 ± 2.0	1699 ± 343	1.9 ± 0.2	1.3 ± 0.08	325 ± 54
Site 2 Mix Shed	0-7.5	25.8	18.7	112	10.5	26.6	6.3	0.4	**638**	67	6.6	457	1.7	1.3	576
	7.5-15	21.3	19.2	116	9.7	25.4	7.0	0.7	313	54	8.0	950	1.7	1.2	529
	15-30	23.8	21.8	135	10.9	29.9	7.1	1.0	267	25	9.0	1033	2.1	1.5	584
	Mean ± SE	23.6 ± 1.3	19.9 ± 1.0	121 ± 7	10.4 ± 0.4	27.3 ± 1.3	6.8 ± 0.2	0.7 ± 0.2	406 ± 117	49 ± 13	7.9 ± 0.7	813 ± 180	1.9 ± 0.1	1.3 ± 0.1	563 ± 17
Site 2 Field	0-7.5	21.8	16.0	82	11.0	24.9	6.4	0.7	89.8	112	7.5	1155	2.1	1.3	521
	7.5-15	20.2	15.6	24	9.7	20.1	7.2	0.6	49.7	105	10.8	1869	2.0	1.4	333
	15-30	15.1	20.4	51	9.9	20.1	7.2	0.8	72.4	97	18.2	2653	2.4	1.6	414
	Mean ± SE	19.0 ± 2.0	17.4 ± 1.5	52.4 ± 16.9	10.2 ± 0.4	21.7 ± 1.6	6.9 ± 0.2	0.7 ± 0.1	70.6 ± 11.6	105 ± 4	12.2 ± 3.2	1893 ± 433	2.1 ± 0.1	1.5 ± 0.1	423 ± 55
Site 2 Drainage Ditch	0-7.5	68.0	17.3	146	8.5	12.4	6.1	1.5	52.3	79	10.1	391	1.3	1.4	545
	7.5-15	**99.2**	20.6	80	13.8	10.0	6.6	1.1	50.3	53	10.6	430	3.8	1.5	467
	15-30	24.2	19.8	29	12.7	10.4	6.7	2.7	51.3	101	8.7	369	4.6	1.5	155
	Mean ± SE	63.8 ± 21.8	19.3 ± 1.0	85 ± 34	11.7 ± 1.6	10.9 ± 0.7	6.4 ± 0.2	1.8 ± 0.5	51.3 ± 0.6	78 ± 14	9.8 ± 0.6	397 ± 18	3.3 ± 1.0	1.5 ± 0.1	389 ± 119
Site 3 Mix Shed	0-7.5	5.1	9.2	62	7.3	100.3	2.3	0.5	73.9	28	1.6	383	1.4	1.0	1095
	7.5-15	3.7	8.4	50	7.0	30.5	2.7	0.8	59.6	87	1.9	261	1.0	1.1	745
	15-30	4.3	10.7	30	9.2	14.4	2.7	0.7	35.5	88	2.9	237	1.6	1.3	510
	Mean ± SE	4.4 ± 0.4	9.4 ± 0.7	47 ± 9	7.8 ± 0.7	48.4 ± 26.4	2.6 ± 0.1	0.7 ± 0.1	56.3 ± 11.2	68 ± 20	2.1 ± 0.4	294 ± 45	1.3 ± 0.2	1.1 ± 0.1	783 ± 170
Site 3 Field	0-7.5	9.7	10.5	30	25.1	4.0	3.3	0.7	14.5	67	0.7	105	5.3	1.3	270
	7.5-15	4.1	9.3	22	8.6	3.4	2.3	0.7	10.7	150	0.8	117	1.6	1.3	149
	15-30	4.7	9.0	30	7.3	8.7	2.3	0.6	14.8	64	0.9	180	1.2	1.2	270
	Mean ± SE	6.2 ± 1.8	9.6 ± 0.5	28 ± 3	13.7 ± 5.7	5.4 ± 1.7	2.6 ± 0.3	0.7 ± 0.1	13.3 ± 1.3	94 ± 28	0.8 ± 0.1	134 ± 23	2.7 ± 1.3	1.3 ± 0.02	230 ± 40
ANZECC SQG	Low	20	50	1500	80	65	21	2.5*	200	150	-	-	-	-	600**
	High	**70**	**220**	**10000**	**370**	**270**	**52**	**4**	**410**	**1000**	-	-	-	-	**2000****
	n > Low	**7**	0	0	0	**1**	0	**1**	**2**	**1**	-	-	-	-	4
Total n = 21	n > High	**1**	0	0	0	0	0	0	**1**	0	-	-	-	-	1

* values from van Derveer and Canton 1997   Highlight = contents > SQG low

** values from Persaud et al. 1993   **Bold + highlight = content > SQG high**

3.2 Dam sediment cores

3.2.1 Sediment density and dating

Sediment dry bulk density (DBD) ranged from 0.37 to 0.85, 0.11 to 0.85, and 0.28 to 0.61 g cm^{-3} in cores from Site 1, 2, and 3, respectively. Mean sediment DBD was 0.64 ± 0.02, 0.39 ± 0.04, and 0.40 ± 0.03 g cm^{-3} in cores from Site 1, 2, and 3, respectively. Sediment DBD in each of the three cores increased with increasing depth (Figure 4). DBD was greatest at the bottom of cores from Sites 2 and 3.

All three cores showed evidence of mixing along the sediment column, as evidenced by the $^{210}Pb_{xs}$ profiles (Figure 4). The lack of $^{210}Pb_{xs}$ decay violates the assumptions of the constant initial concentration (CIC) method (Appleby and Oldfield 1992) used for calculating sediment accumulation rates (SAR) and sediment ages, therefore no SAR, sediment ages, or trace contaminant fluxes could be estimated in our dam cores.
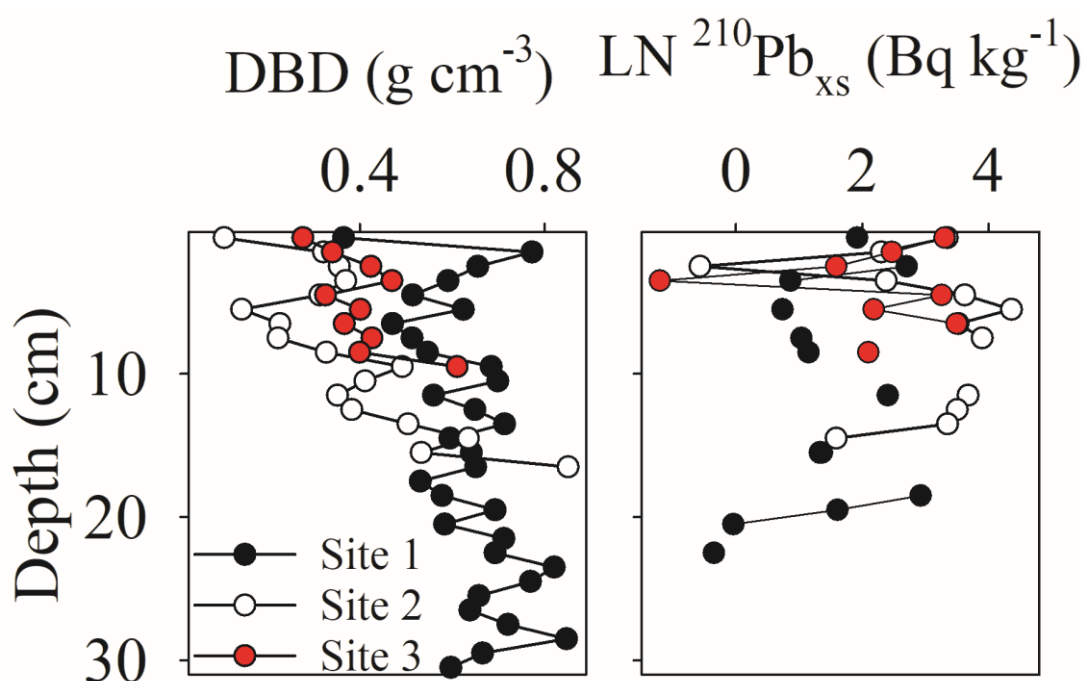
Figure 4. Dry bulk density (DBD, g cm^{-3}) and excess ^{210}Pb ($^{210}Pb_{ex}$) activity (Bq kg^{-1}) plotted against depth from dam sediment cores of Sites 1, 2, and 3. Profiles of $^{210}Pb_{xs}$ indicate mixing, therefore sedimentation rates were not calculated for the dam cores.

3.2.2 Trace metal contents and EF

Mean arsenic (As) contents were 7.7 ± 0.5 (standard error), 19.2 ± 2.2, and 9.5 ± 1.4 mg kg^{-1} for dam cores from Site 1, 2, and 3, respectively (Table 3). In the Site 2 core, As contents increase rapidly from 6.5 cm to 3.5 cm depth, then decrease again rapidly to the surface (Figure 5), however all contents from 0 to 5.5 cm depth exceeded the ANZECC SQG low range value of 20 mg kg^{-1}. In Site 3 core, As contents were elevated between 7.5 and 5.5 cm depths and from 1.5 cm to the surface. The profile of As distribution resembled Fe distribution (Figure 5). EFs at Site 1 reflect natural variation (Zhang and Liu 2002). EF at Site 2 were elevated (EF > 2) between 5.5 and 3.5 cm depths (Figure 6). EF at Site 3 indicated enrichment between 7.5 and 4.5 cm (max EF = 3.6).

Mean cadmium (Cd) contents were 16.4 ± 0.5, 152.9 ± 17.3, and 11.6 ± 5.6 µg kg^{-1} for dam cores from Site 1, 2, and 3, respectively. At Site 2, Cd contents were elevated from 2.5 to 5.5 cm depth. This correlated with severe enrichments of Cd (EF: 6-12 at these depths. At Site 3, Cd increased from 4.5 cm to the surface, corresponding with moderate enrichment at the top (EF = 5 at surface). No Cd contents exceeded the ANZECC SQG.

Mean selenium (Se) contents were 1.3 ± 0.1, 0.8 ± 0.04, and 0.5 ± 0.1 mg kg^{-1} for dam cores from Site 1, 2, and 3, respectively. Due to the low Se contents in the bottom interval at Site 3, there was severe Se enrichment throughout this core. Enrichment factors in the Site 3 core decreased towards the top, however remained severely enriched (EF between 20-80). Despite the severe enrichments at Site 3, no Se contents in the dam cores exceeded the Se SQG from Van Derveer and Canton (1997).

Mean zinc (Zn) contents were 19.2 ± 0.4, 74.1 ± 3.2, and 41.4 ± 1.9 mg kg^{-1} for dam cores from Site 1, 2, and 3, respectively. Zn contents spiked between 6 and 9 cm depths in all three cores. Sites 2 and 3 had slight increases in Zn contents at the surface. There was no Zn enrichment and no Zn contents in the dam cores exceeded the ANZECC SQG.

Mean mercury (Hg) contents were 99.5 ± 5.7, 216.4 ± 45.8, and 141.0 ± 20.9 µg kg^{-1} for dam cores from Site 1, 2, and 3, respectively. Thirteen total samples exceeded the ANZECC SQG low value (150 µg kg^{-1}). Three samples from Site 1 (0.5, 5.5, and 11.5 cm depths), six from Site 2 (6.5 cm and the 12.5 cm to the bottom of the core), and four from Site 3 (1.5-2.5 and 8.5-9.5 cm). The highest Hg contents were found at the bottom intervals of the Site 2 core. Hg contents at the bottom of Site 3 core also exceeded ANZECC SQG low values.

Mean cobalt (Co) contents were 1.5 ± 0.04, 13.5 ± 0.3, and 1.2 ± 0.2 mg kg^{-1} for dam cores from Site 1, 2, and 3, respectively. Co contents were generally very steady at Site 1 and 3. Site 2 Co decreased towards the top of the core. There were no enrichments of Co. No Co SQG could be obtained from the literature.

Mean manganese (Mn) contents were 44.9 ± 2.9, 664.5 ± 38.9, and 54.2 ± 32.2 mg kg^{-1} for dam cores from Site 1, 2, and 3, respectively. At all depths, Mn contents were an order of magnitude greater at Site 2. Mn contents at Site 2 spiked at 10.5 cm depth. Mn contents at Site 3 spiked from 17 mg kg^{-1} 3.5 cm depth to 340 mg kg^{-1} at the top. The rise in contents at the top of the Site 3 core correlated with severe enrichment of Mn (EF ~ 9).

Mean iron (Fe) contents were 3.0 ± 0.2, 2.3 ± 0.1, and 2.0 ± 0.2 % for dam cores from Site 1, 2, and 3, respectively. At 8.5 cm depth in the Site 1 core a spike in Fe contents occurred along with Pb, Zn, and, to a lesser extent, Ni and As. At 15.5 cm depth in the Site 2 core contents of Fe, Pb, Cr, Ni and to a lesser extent Cu spiked together. At 6.5 cm depth in the Site 3 core, contents of Fe, As, Pb, Cu, Ni, Se, and Zn spiked together. As Fe is very abundant in the lithosphere EFs for Fe were not considered.

Mean aluminium (Al) contents were 1.7 ± 0.03, 2.2 ± 0.1, and 0.6 ± 0.1 % for dam cores from Site 1, 2, and 3, respectively. At Site 1, Al contents gradually decreased with depth, whereas, at Site 2, Al contents gradually increased with decreasing depth. At Site 3, Al contents increased from 0.4 % at 3.5 cm to 1.5 % at the surface.

Mean phosphorus (P) contents were 52.9 ± 8.6, 708.4 ± 73.6, and 378.2 ± 199.0 mg kg^{-1} for dam cores from Site 1, 2, and 3, respectively. At Site 1, P contents increased ~ 5 fold from

2.5 cm to the surface (~ 50 to 250 mg kg^{-1}). While no P contents at Site 1 exceeded the SQG from Persaud et al. (1993), EF in the top two intervals of the Site 1 core indicated moderate to severe P enrichment (EF ~ 4-10). At Site 2, P contents spiked to over 1000 mg kg^{-1} (exceeding the SQG low from Persaud et al. 1993) from 6.5 to 3.5 cm depths. EFs at these depths indicated moderate enrichment of P (EF ~ 4). P contents in the surface interval at Site 3 (2161 mg kg^{-1}) exceeded the SQG high value (2000 mg kg^{-1}). Due to the relatively high Al contents in these same sediments (1.54 %), there was only moderate enrichment of P (EF ~ 4).

Mean lead (Pb) contents were 13.7 ± 0.6, 19.0 ± 0.8, and 17.2 ± 1.9 for dam cores from Site 1, 2, and 3, respectively. Mean chromium (Cr) contents were 11.4 ± 0.4, 11.8 ± 0.3, and 4.2 ± 0.7 mg kg^{-1} for dam cores from Site 1, 2, and 3, respectively. Mean copper (Cu) contents were 4.0 ± 0.1, 26.9 ± 1.1, and 15.8 ± 2.6 mg kg^{-1} for dam cores from Site 1, 2, and 3, respectively. Mean nickel (Ni) contents were 2.7 ± 0.1, 9.6 ± 0.3, and 4.4 ± 0.3 mg kg^{-1} for dam cores from Site 1, 2, and 3, respectively. The EFs of Pb, Cr, Cu, and Ni reflect natural variation (Zhang and Liu 2002). No contents of Pb, Cr, Cu, or Ni exceeded the ANZECC SQG.
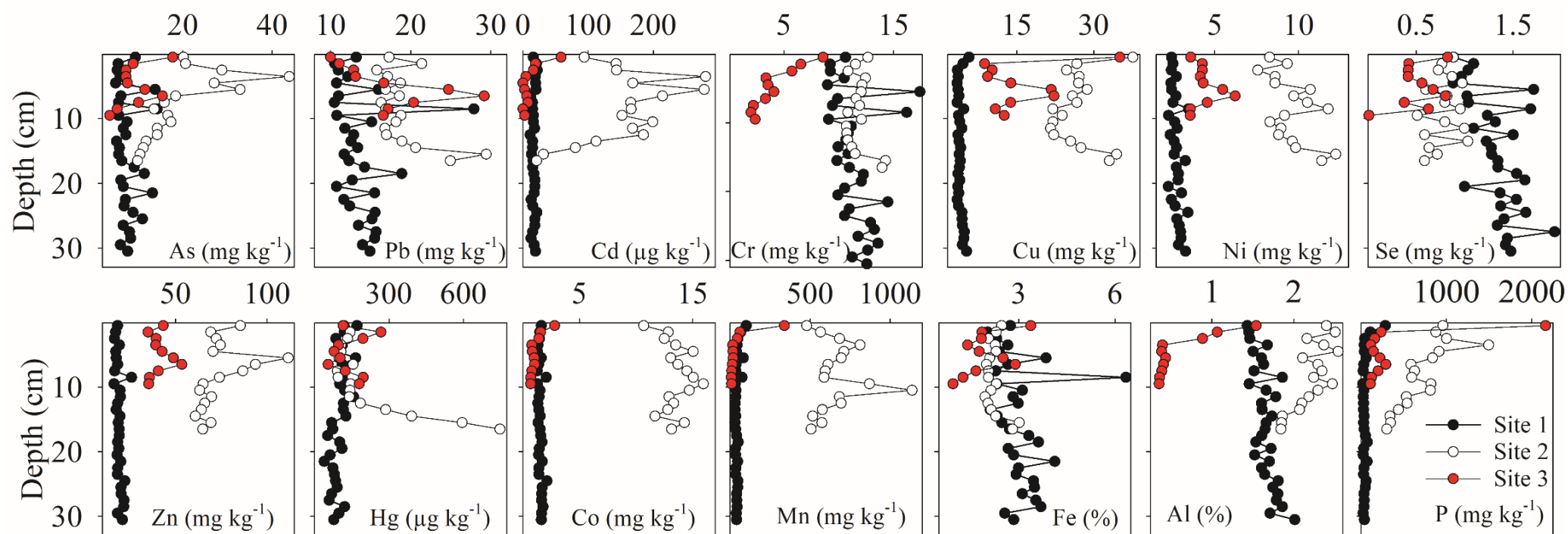
**Figure 5.** Contents of trace metals with depth from dam sediment cores at Site 1 (black), Site 2 (white), and Site 3 (red).
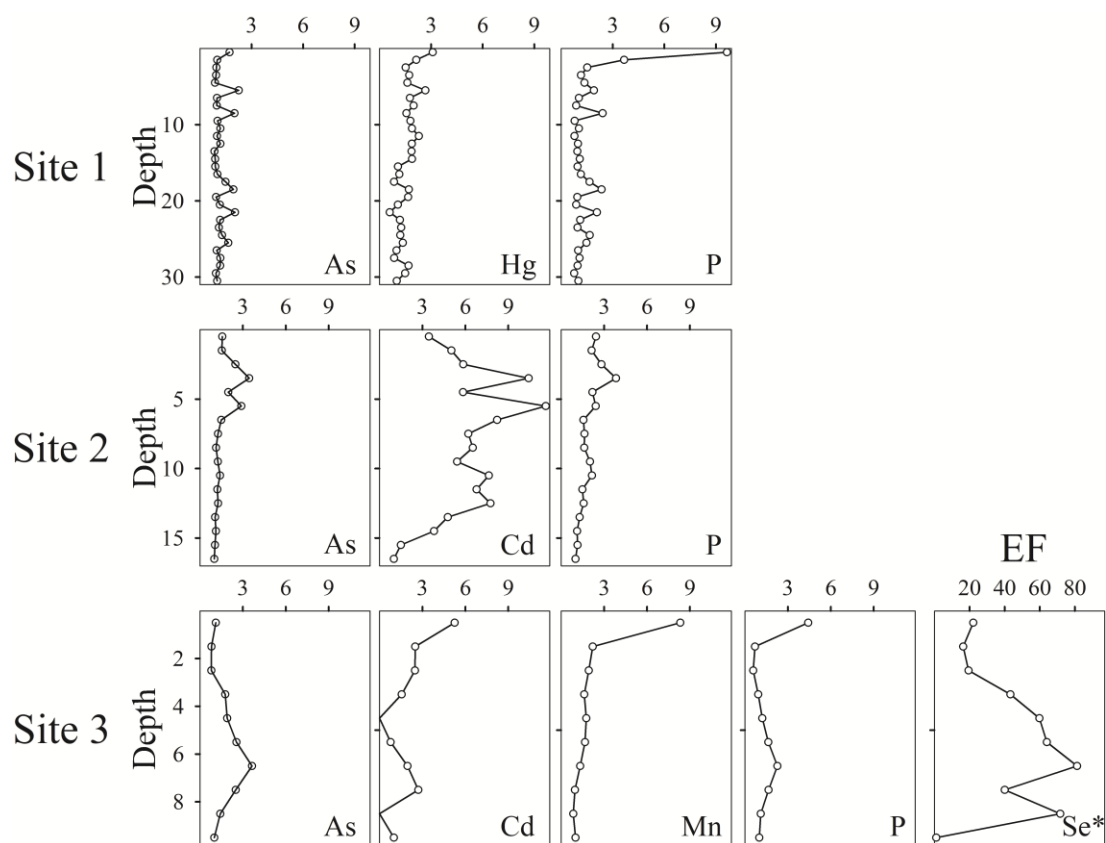
Figure 6. Enrichment factors (EF) depth profiles of trace metals which were moderately to severely enriched in dam cores from each site. EF > 1 signifies anthropogenic portion of that element. Note the different scale of enrichment for each site. *Note large increase in scale for Se at Site 3.

Table 3. Trace metal soil quality guidelines (SQG) and contents from dam sediment cores. Highlighted cells are above SQG values (> SQG low = highlight only; > SQG high = highlight + bold).

Core	Depth	As mg kg^{-1}	Pb mg kg^{-1}	Cd µg kg^{-1}	Cr mg kg^{-1}	Cu mg kg^{-1}	Ni mg kg^{-1}	Se mg kg^{-1}	Zn mg kg^{-1}	Hg µg kg^{-1}	Co mg kg^{-1}	Mn mg kg^{-1}	Fe %	Al %	P mg kg^{-1}
Site 1	0.5	9.4	13.2	16	10.6	5.7	2.4	0.9	18.4	171	1.6	102	2.7	1.4	287
	1.5	5.6	10.5	21	9.2	4.5	2.5	1.1	17.3	120	1.5	67	2.0	1.5	110
	2.5	5.3	11.0	22	9.2	3.4	2.4	1.0	16.7	86	1.5	49	2.3	1.5	46
	3.5	6.0	12.1	19	10.5	3.6	2.7	1.0	19.4	112	1.3	44	2.7	1.7	40
	4.5	5.0	10.7	19	9.0	3.4	2.4	0.9	17.4	94	1.3	40	2.4	1.5	42
	5.5	13.8	16.0	20	17.4	3.6	2.4	1.7	17.6	165	1.6	83	3.8	1.6	63
	6.5	6.2	11.0	12	9.9	3.7	2.7	1.0	18.4	111	1.4	38	2.7	1.6	35
	7.5	5.6	10.5	14	9.4	3.4	2.5	1.0	16.8	116	1.3	36	2.3	1.5	27
	8.5	14.3	27.9	15	16.2	4.6	3.4	1.7	26.0	112	2.1	75	6.3	1.9	93
	9.5	5.7	10.8	16	9.1	3.6	2.2	1.2	16.5	101	1.3	33	2.3	1.5	24
	10.5	7.6	15.1	16	11.1	3.9	2.6	1.3	19.7	121	1.5	37	3.1	1.7	36
	11.5	6.7	11.8	18	10.9	4.3	2.7	1.1	19.9	157	1.4	35	2.8	1.8	28
	12.5	7.3	12.9	11	10.6	3.5	2.3	1.5	18.4	116	1.3	32	3.0	1.6	33
	13.5	5.2	12.5	15	9.9	3.7	2.6	1.2	17.6	116	1.4	31	2.1	1.6	32
	14.5	5.8	13.4	15	10.9	4.1	2.7	1.3	19.7	126	1.5	35	2.3	1.7	39
	15.5	5.7	11.7	13	9.8	3.8	2.6	1.3	18.7	69	1.3	31	2.5	1.7	33
	16.5	6.4	12.3	16	11.0	4.0	3.2	1.3	19.2	73	1.5	34	2.7	1.6	39
	17.5	9.1	14.2	15	12.2	3.8	2.7	1.3	19.3	52	1.6	41	3.3	1.6	55
	18.5	11.4	18.9	17	12.1	3.5	2.8	1.5	18.4	101	1.7	51	3.6	1.5	75
	19.5	6.2	12.7	18	10.5	3.9	2.8	1.6	19.1	111	1.5	34	2.7	1.7	34
	20.5	6.7	10.7	18	9.9	3.5	2.2	1.0	18.1	63	1.4	34.8	2.8	1.5	28
	21.5	13.2	15.5	17	14.5	3.7	3.0	1.4	20.2	39	1.7	47.6	4.1	1.7	74
	22.5	7.2	11.6	13	11.0	3.4	2.4	1.5	18.4	74	1.4	36.5	3.0	1.6	37
	23.5	6.9	12.4	15	10.5	3.6	2.6	1.4	18.3	80	1.4	35.0	2.9	1.6	33
	24.5	8.9	15.5	21	12.9	4.3	3.4	1.6	22.3	84	2.1	48.9	3.5	1.8	62
	25.5	11.0	15.2	18	13.2	4.3	2.7	1.4	20.2	91	1.7	48.5	3.5	1.7	53
	26.5	6.7	13.5	18	11.8	4.4	2.9	1.3	20.3	69	1.7	41.9	3.1	1.8	37
	27.5	8.1	15.7	15	13.6	4.8	3.0	1.9	21.9	59	1.6	42.1	3.5	1.8	40
	28.5	8.3	15.5	12	12.6	4.7	3.0	1.4	21.7	121	1.8	44.7	3.7	1.9	37
	29.5	6.1	14.0	17	11.2	4.4	2.8	1.4	18.3	98	1.6	38.8	2.6	1.7	27
	30.5	7.7	14.9	19	12.6	5.2	3.2	1.5	21.0	78	1.6	40.4	2.8	2.0	42
	Mean ± SE	7.7 ± 0.5	13.7 ± 0.6	16.4 ± 0.5	11.4 ± 0.4	4.0 ± 0.1	2.7 ± 0.1	1.3 ± 0.1	19.2 ± 0.4	99 ± 6	1.5 ± 0.04	44.9 ± 2.9	3.0 ± 0.2	1.7 ± 0.03	53 ± 9
ANZECC SQG	Low	20	50	1500	80	65	21	2.5*	200	150	-	-	-	-	600**
	High	**70**	**220**	**10000**	**370**	**270**	**52**	**4**	**410**	**1000**	-	-	-	-	**2000****
	n > Low	**6**	0	0	0	0	0	0	0	**13**	-	-	-	-	4
Total n = 58	n > High	0	0	0	0	0	0	0	0	0	-	-	-	-	1

* values from van Derveer and Canton 1997
** values from Persaud et al. 1993

Highlight = contents > SQG low
Bold + highlight = content > SQG high

Table 3 (cont). Trace metal soil quality guidelines (SQG) and contents from dam sediment cores. Highlighted cells are above SQG values (> SQG low = highlight only; > SQG high = highlight + bold).

Core	Depth	As	Pb	Cd	Cr	Cu	Ni	Se	Zn	Hg	Co	Mn	Fe	Al	P
		mg kg^{-1}	mg kg^{-1}	µg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	µg kg^{-1}	mg kg^{-1}	mg kg^{-1}	%	%	mg kg^{-1}
Site 2	0.5	20.1	17.3	94	12.7	37.6	8.3	0.9	85.4	119	10.7	478.8	2.5	2.4	960
	1.5	20.6	21.4	143	11.5	26.7	9.3	0.8	69.2	143	12.8	564.8	2.3	2.5	877
	2.5	28.8	15.8	143	10.8	24.7	7.6	0.7	72.2	133	12.5	684.3	2.1	2.2	1002
	3.5	43.8	17.1	280	12.4	27.2	8.6	0.9	74.5	106	13.5	811.6	2.3	2.4	1496
	4.5	27.0	18.7	168	12.1	27.0	8.6	1.0	70.5	107	15.0	711.1	2.3	2.5	915
	5.5	32.8	16.9	278	12.0	28.7	10.7	0.6	111.5	98	13.1	694.3	2.1	2.1	839
	6.5	18.4	18.6	214	11.6	25.9	9.7	0.8	93.6	155	13.7	612.1	2.0	2.3	587
	7.5	15.9	16.3	165	11.9	26.7	10.5	0.8	86.7	92	14.5	594.0	2.1	2.3	629
	8.5	13.6	16.9	166	10.8	22.0	11.8	1.0	74.0	95	15.1	587.4	2.1	2.2	595
	9.5	16.7	18.8	152	12.1	23.8	9.2	0.5	65.1	145	15.9	870.5	2.3	2.5	820
	10.5	17.4	18.2	199	10.7	22.0	8.3	0.8	63.2	143	14.7	1136.7	2.1	2.3	814
	11.5	14.3	16.8	168	10.7	21.6	9.0	1.0	69.7	140	12.9	682.7	1.9	2.2	533
	12.5	14.3	17.0	185	10.8	22.2	8.8	0.6	65.9	185	13.3	693.6	2.0	2.1	542
	13.5	11.8	18.9	112	11.2	25.5	9.6	1.0	64.1	286	12.8	576.9	2.1	2.1	440
	14.5	11.2	20.6	80	11.5	27.5	9.8	0.6	60.8	391	11.7	516.4	2.3	1.9	341
	15.5	10.5	29.4	31	14.3	34.5	12.2	0.7	69.4	595	14.3	574.4	3.0	1.9	348
	16.5	9.9	24.9	21	13.9	33.1	11.4	0.6	64.9	747	13.1	506.9	2.8	1.8	303
	Mean ± SE	19.2 ± 2.2	19.0 ± 0.9	153 ± 17	11.8 ± 0.3	26.9 ± 1.1	9.6 ± 0.3	0.8 ± 0.04	74.1 ± 3.2	216 ± 46	13.5 ± 0.3	665 ± 39	2.3 ± 0.1	2.2 ± 0.1	708 ± 74
Site 3	0.5	17.8	10.0	58	8.6	35.1	3.6	0.8	43.3	115	2.8	339.6	3.4	1.5	**2161**
	1.5	8.9	11.1	19	6.6	8.7	4.2	0.4	35.0	267	1.6	62.2	1.8	1.1	237
	2.5	7.3	12.9	16	5.7	10.2	4.3	0.4	39.4	195	1.4	45.3	1.8	0.9	162
	3.5	7.3	13.1	4	3.4	9.3	4.1	0.4	39.2	96	0.8	16.9	1.4	0.4	116
	4.5	7.6	16.6	0	3.6	13.8	4.3	0.6	42.7	79	0.8	17.9	1.8	0.4	148
	5.5	11.5	24.7	2	4.1	21.7	5.5	0.7	48.8	103	1.0	19.1	2.5	0.4	224
	6.5	15.5	29.2	6	3.3	22.3	6.2	0.8	53.4	54	1.0	14.3	2.9	0.4	293
	7.5	10.1	20.3	8	2.2	13.8	4.6	0.4	40.6	124	0.8	9.8	1.7	0.4	203
	8.5	5.3	17.2	0	2.0	10.8	3.5	0.6	35.8	196	0.7	8.1	1.3	0.4	126
	9.5	3.7	16.6	3	2.4	12.6	3.5	0.0	35.4	180	0.7	9.4	0.9	0.4	112
	Mean ± SE	9.5 ± 1.4	17.2 ± 1.9	11.6 ± 5.6	4.2 ± 0.7	15.8 ± 2.6	4.4 ± 0.3	0.5 ± 0.1	41.4 ± 1.9	141 ± 21	1.2 ± 0.2	54 ± 32	2.0 ± 0.2	0.6 ± 0.1	378 ± 199
ANZECC SQG	Low	20	50	1500	80	65	21	2.5*	200	150	-	-	-	-	600**
	High	**70**	**220**	**10000**	**370**	**270**	**52**	**4**	**410**	**1000**	-	-	-	-	**2000****
	n > Low	**6**	0	0	0	0	0	0	0	**13**	-	-	-	-	4
Total n = 58	n > High	0	0	0	0	0	0	0	0	0	-	-	-	-	1

* values from van Derveer and Canton 1997

** values from Persaud et al. 1993

Highlight = contents > SQG low

Bold + highlight = content > SQG high

4. Discussion

4.1 Pesticide residues in terrestrial cores

Our analyses detected 10 of 97 pesticide molecules tested for. Discussion will be focused around the most abundant pesticides and most contaminated sites.

4.1.1 Spatial distribution of pesticides

Terrestrial cores from Site 3 had the highest degree contamination in our study (Table 1, Figure 3). Fifty percent of pesticide residues (26 out of 52 total detected residues from our 21 core subsamples) were detected in terrestrial soil cores at Site 3 (in the mix shed or field core). The highest contents of all contaminants were found in the Site 3 mix shed core (i.e. propiconazole, cyprodinil, bifenthrin). There may be an increased need for pesticide application at Site 3 relative to the other sites due to site specific pest issues. Site 1 was the least contaminated, with 6 out of 52 detected residues (~ 12 %). Site 2 had 20 pesticide residues detected (~ 38 %), however at this location we sampled an additional core (containing 3 residues, ~ 6 %). The soil cores from other sites had trace amounts of pesticide residues relative to Site 3 (Figure 3). Because pesticides do not occur naturally, their detection signifies that soil composition has been altered by horticultural activities. However, differences in degradation rates, toxicity, and mobility within the environment of each pesticide (discussed further below), means the concerns over environmental impacts of these pesticides is variable.

With respect to pesticides, the identification of chemical mixing sheds as potential hotspots for contaminant accumulation proved feasible. Thirty three out of 52 residues were found in mixing sheds (64 % of all detected residues). Four contaminants (bifenthrin, dimethoate, methomyl, and prometryn) were found exclusively in the mixing sheds and not in growing or drainage areas. The absence of these contaminants from our field cores does not clearly signify their absence from crop production areas. A more widespread sample effort of growing and other use areas may provide a better understanding of the extent of spatial contamination in multiple land use farms in the Coffs Harbour region.

4.1.2 Fungicides

The conazole fungicide, propiconazole found in the soils of the Site 3 mix shed had the highest soil content for any pesticide we detected (mean contents 58.2 ± 38.9 mg kg^{-1}). At contents of 100 mg kg^{-1} propiconazole was found to reduce agricultural soil phosphatase activity by 46 %, which was expected to cause decreased phosphate availability (Kalam et al. 2004). Propiconazole content in the surface interval of the Site 3 mix shed exceeded this threshold (125 mg kg^{-1}), however the contents we observed in the crop production area (field cores, 0.21-0.99 mg kg^{-1}) are below this concentration. If propiconazole contents in the growing areas reach levels similar to in the Site 3 mix shed, exchange of nutrients between the soils and plants may become altered. The propiconazole contents we observed in the Site 3 mix shed were higher than observations from corn and soybean field over 2 growing seasons from the Midwestern United States, while our field cores had orders of magnitude less or similar contents depending on timing of propiconazole application (Edwards et al. 2016).

Another fungicide, cyprodinil, was the most spatially widespread of all pesticides, found in trace amounts in mix shed and field cores at all three sites. It is understandable that we would not find cyprodinil in the Site 2 drainage ditch, as the area up the hill that this drains has been discontinued as the chemical storage/mixing area since 1980 (personal communication with landowner) and cyprodinil is considered a relatively new fungicide (Komárek et al. 2010). Cyprondinil was found at higher contents in Site 1 and 2 field cores than Site 1 and 2 mix shed cores (Table 1), perhaps indicating a separate mixing area for these chemicals at these sites, or alternatively increased accumulation in growing areas due to repeated applications here. The relatively high contents of cyprodinil at the Site 3 mix shed imply increased use of this fungicide at this farm. Bermúdez-Couso et al. (2007) reported surface sediment concentrations of cyprodinil at 0.462 mg kg^{-1} in a Spanish vineyard, orders of magnitude lower than the mean concentration found in the Site 3 mix shed core (8.5 mg kg^{-1}), but elevated compared to the Site 3 field core mean concentration (0.36 mg kg^{-1}) and other surface interval concentrations (see Table 1). Cyprodinil contents may decrease over time, however toxicity of the breakdown products can be greater than the parent product (Nicol et al. 2016). The widespread spatial distribution of cyprodinil across our cores, and potentially more toxic breakdown products make cyprodinil a contaminant to monitor further.

Two other fungicides, pyrimethanil and carbendazim, were found in low contents (0.006 to 0.044 mg kg^{-1}) at all three sites. These fungicides degrade into their by-products within 4 weeks (Baude et al. 1974, Agüera et al. 2000). Carbendazim detection may have resulted from carbendazim applied directly to blueberries or from degradation of benomyl (Baude et al. 1974), a fungicide previously used in banana cultivation, which has been discontinued since 2006 (APVMA 2014). Pyrimethanil degradation products have low toxicity (Sirtori et al. 2012). Sampling for degradation products of pyrimethanil and carbendazim will reveal more information on the environmental fate of these fungicides after application.

Propiconazole, cyprodinil, and carbendazim bind to soil organic and clay particles and are generally immobile in soil (Thorstensen et al. 2001, Komárek et al. 2010, Ahmad 2018), while pyrimethanil may leech into subsurface water under typical field conditions (Komárek et al. 2010). The erosion of soil from areas with high fungicide contents could deliver fungicides into nearby waterways. Erosion of soils from the Site 3 mix shed is of particular concern due to the high concentrations of fungicides here and the lack of connectivity into the dam at Site 3 (Figure 2). Soils eroded from the Site 3 mix shed are probably transported into the natural waterway Bucca Bucca creek.

4.1.3 Herbicides

Diuron is a water soluble aryl urea herbicide commonly applied in Australia, with regulations regarding with specific timing and concentrations of application (APVMA 2012). However, according to the Australian Pesticides and Veterinary Medicines Authority (APVMA) there is no approval for use of diuron on blueberries. In an effort to mitigate aquatic ecosystem harm from diuron runoff use, the APVMA regulated diuron use to a general use concentration of 450 g of active constituent ha^{-1} (APVMA 2012, Holmes 2014). While no official data on diuron application rates for our study area could be obtained, literature comparisons may be useful.

Our soil diuron contents were less than in other studies. Soil diuron contents in grass seed production areas in the northwestern United States were 0.38 mg kg^{-1}, estimated to be 46 %

of the applied diuron (Field et al. 2003). A study of Queensland sugarcane soils found that 267 days after diuron application, diuron surface soil (0-15 cm depth) content was 0.009 mg kg^{-1} (Stork et al. 2008). These diuron contents were slightly lower or within the same range as our surface soil (0-15 cm) contents (0.010-0.020 mg kg^{-1}) from Site 2 mix shed and drainage ditch cores, possibly indicating the application of diuron at Site 2 over the last year. Stork et al. (2008) estimated their observed diuron contents to be equivalent to 22 g of diuron applied ha^{-1} year^{-1} based upon assumptions of time since application, soil density, and depth. This application rate estimate falls well below the 2012 AVPMA diuron general use guideline of 450 g ha^{-1}, possibly signifying diuron application rates at Site 2 could be similar, although this is merely speculation based upon large assumptions. Our relatively low soil diuron concentrations and its water solubility may indicate that diuron is a contaminant that could leach to waterways (Yang et al. 2006, Stork et al. 2008, Liu et al. 2010), however more monitoring during diuron application is needed.

Another herbicide, prometryn, was detected in the surface interval of the Site 3 mix shed core at contents of 0.004 mg kg^{-1}. Prometryn is less soluble in water than diuron, but photodegrades rapidly in the aqueous phase, especially with UV light (Jiang et al. 2017). Prometryn is typically applied wet, therefore prometryn leaching/soil retention may be a low risk due to degradation by sunlight. As we only detected one residue of prometryn just above our limit of detection, prometryn is likely not a widespread contaminant in our blueberry horticultural setting.

4.1.4 Organophosphates

The organophosphate ethoprophos was found in relatively small contents at the mixing sheds of Sites 1 and 2 and the drainage ditch of Site 2 (0.004 to 0.017 mg kg^{-1}). Ethoprophos in the Site 2 drainage ditch core may be from previous land use, as ethoprophos is a common pesticide used in banana cultivation (Collins et al. 1991). Low ethoprophos contents may not simply signify low ethoprophos application rate. Repeated applications of ethoprophos can promote increased rate of biodegradation by soil microbes, albeit with a reduction of the desired pest control effect (Smelt et al. 1987). Populations of some target pest species in this region of NSW are resistant to ethoprophos treatments (Collins et al. 1991). This combination of factors (increased biodegradation after repeated exposure, lowering of pest control effect, and resistant target species) may lead to more frequent, less efficient applications of ethoprophos.

Possibly due to more rapid biodegradation occurring after repeated exposures, our ethoprophos contents are low when compared to the literature. Smelt et al. (1987) found mean contents of 1.22 mg kg^{-1} in the top 25 cm of Dutch potato fields. Our mean contents between Sites 1 and 2 was 0.0085 mg kg^{-1} from our 30 cm sediment cores. Studies report ethoprophos residues disappeared completely below 25 cm depth after 474 days (Boesten and Gottesbüren 2000, Boesten and van der Pas 2000). Assuming similar degradation rates, Sites 1 and 2 may have undergone ethoprophos treatment within this timespan. While ethoprophos contents from our cores were overall low, data on the application and degradation rate of ethoprophos will aid in better understanding the dynamics of optimal ethoprophos use and efficient management practice.

Another organophosphate, dimethoate, was present in the Site 3 mix shed core at all three depths. Dimethoate has low soil persistence and is water soluble, with risk for runoff into

surface and groundwaters (Van Scoy et al. 2016), which may explain the low soil contents we found. Degradation rates of dimethoate in soil vary within the literature, from between 4 days to over two years, depending on soil organic material content (Bohn 1964, El Beit et al. 1981, Martikainen 1996). Sampling of surface and groundwaters, especially shortly after dimethoate application and flood events, could be useful in determining the fate of dimethoate in the environment.

Our soil contents of dimethoate are low compared to toxicity guidelines. Martikainen (1996) reports concentrations above 9 mg kg^{-1} cause mortality in soil invertebrates, while 3 mg kg^{-1} was sufficient to reduce soil invertebrate biomass. Rates safe for human consumption range between 2 to 18 mg kg^{-1} daily (Sanderson and Edson 1964). Soil dimethoate was only found in the mix shed of Site 3, meaning it may not persist for long periods in the growing areas. More data on the transport of dimethoate between soils, surface and groundwaters, and biota will be useful in resolving if dimethoate is a contaminant of concern in blueberry horticulture from this region.

4.1.5 Other pesticides

Site 3 mix shed was the only core where we detected the pyrethroid insecticide bifenthrin. Due to its low water solubility and affinity to bind to organic matter bifenthren is believed to be immobile in the soil and have low groundwater leaching potential, however for these same reasons bifenthrin residues can be very long lasting in the soil (Kamble and Saran 2005). While bifenthrin was highest in the surface sediments of the Site 3 mix shed, we detected residues, albeit decreasing, in the lower sediment intervals of the Site 3 mix shed core. Our detected soil contents of bifenthrin are lower than other studies reporting field soil concentrations. Soils from potato fields of western Canada had mean soil bifenthrin contents of 872.25 + 62.98 mg kg^{-1} 329 days after application, equivalent to 35 % of the field application rate of 349 g active ingredient ha^{-1} (van Herk et al. 2013). While no data pertaining to the application rate of bifenthrin was obtained, our soil bifenthrin contents were 11.4 mg kg^{-1} in surface sediments of the Site 3 mix shed, orders of magnitude lower than reported by van Herk et al. (2013).

Contents of the carbamate insecticide methomyl were greatest in the bottom (15-30 cm) layer of the Site 3 mix shed core. This result may be demonstrative of methomyl's high water solubility and low soil retention affinity (Van Scoy et al. 2013). Evidence of the high methomyl contents in the bottom of our core may indicate risk of transfer to groundwater, however other processes in the soil may be reducing methomyl contents.

Disapperance of methomyl from field soils is typically < 1 month and occurs via microbial degradation (Harvey Jr and Pease 1973, Van Scoy et al. 2013). Reported methomyl soil contents from same day applications were 1.272 ± 0.1 in soils of tomato plants (Malhat et al. 2015) and 0.025-0.035 mg kg^{-1} in sandy loam soils (Bisht et al. 2015). Methomyl disappeared within 15 days after application for both of these studies. Our soil concentrations of methomyl are within this range (mean contents 0.058 mg kg^{-1}). Our results suggest recent environmental exposure to methomyl at the Site 3 mix shed. More sampling is needed to investigate the degradation rates and leaching potential of methomyl in our blueberry horticultural setting.

4.2 Trace metals and P

Phosphorus (P) and arsenic (As) were the elements that most frequently exceeded our SQG in our terrestrial and dam cores (15 subsamples were over the SQG low values, 2 subsamples for P and 1 for As over SQG high values). All of the SQG exceedances for As occurred at Site 2. All cores from Site 2 (mix shed, field, drainage ditch, and dam) had subsamples which exceeded the As SQG. The widespread presence of high As contents at Site 2 is likely due to the use of As pesticides during previous land use. The use of As pesticides in northern NSW is well documented (Smith et al. 1998, Smith et al. 2003). Indeed, the highest As contents were found in the steeply sloping drainage ditch, which served drained the chemical mixing shed used during times of banana cultivation (until 1980). Our results demonstrate the persistence of As in the terrestrial environment from previous land use, even over 15 years after a change in horticultural regime at Site 2.

P contents exceeded the SQG at various locations within each site. The presence of P over the SQG guidelines is probably due to the use of P fertilizers. Mix sheds cores from Site 1 and 3 had mean P contents above the SQG low value, probably due to the increased environmental exposure of fertilizers here. Dam cores at Site 2 and 3 had subsamples which exceeded the SQG. Increased accumulation in these sediments is likely due to deposition of eroded soils rich in P from the surrounding fertilized terrestrial environment. The surface interval of the Site 3 dam core exceeded the SQG high range value, and was the only subsample from this core to exceed any P SQG, and P contents are 9 fold higher than the sediment interval below. While our sediment dating failed to yield an acceptable geochronology in this core, the high P contents in the top sediment layer indicate rapid P accumulation after blueberry cultivation began.

When soils are rich in As and P, dams may prove to be an efficient sink for these contaminants. Dam cores from all three sites displayed various degrees of enrichment with As and P (Figure 6), demonstrating the sediments from retaining ponds proficiency to accumulate these elements. Mean contents and EF for As in the three dam cores were 11.30 mg kg^{-1} and 1.56, respectively, greater than content and enrichment in three sediment cores from the receiving estuary downstream of Sites 1 and 2 (mean content = 6.74 mg kg^{-1}, mean EF = 0.94 , Conrad et al. 2019). The closer proximity of dams to the source of terrestrial As (especially at Site 2) is likely to mean they are receiving more As-rich eroded soils. Despite the lower As contents, the site with no previous banana history (Site 3) had the greatest As enrichment for any of our dam cores (max EF of 2.3, 3.4, and 3.6 for Sites 1, 2, and 3, respectively). The enrichment of As occurred towards the bottom of the Site 3 dam core (Figure 6). Enrichments in the bottom layers of this core could be due to natural processes (i.e. the migration of As along the sediment column under anoxic conditions, Burton et al. 2008).

Mercury (Hg) had 14 subsamples which exceeded the SQG low value. Hg contents just exceeded SQG in the growing area of Site 3 (150.2 µg kg^{-1}), however other literature reports Hg soil contents of 50-350 µg kg^{-1} are within a natural range (Rundgren et al. 1992, Grigal 2003). Investigating baseline contents of Hg in soils from this area would aid in determining if any of the terrestrial soils in our farms are contaminated with Hg. The dam cores had 13 of 14 of the subsamples which exceeded the SQG low range value and overall mean Hg content of the dam cores (141 µg kg^{-1}) was greater than terrestrial cores (78 µg kg^{-1}). The Hg in dam

bottom sediments is likely received during episodic rain events which mobilises organic material bound Hg stored in soils (Shanley and Bishop 2012). Enrichment of sediment with Hg was only observed at Site 1 (Figure 6), however the increased contents of Hg in dam sediments compared to terrestrial soils may signify the role of these retention reservoirs as a sink for Hg from terrestrial runoff. Analysis of sediments downstream of Sites 1 and 2 revealed lower content and no enrichments of Hg (Conrad et al. 2019), suggesting sediments of waterways nearer to the farm can be efficient sinks of terrestrially sourced Hg.

The profile of Hg contents from dam cores of Site 2 and 3 indicate relatively high Hg in bottom sediments (Figure 5), especially at Site 2. Hg is relatively immobile in sediments and profiles of Hg in sediments typically follow patterns of deposition (Lockhart et al. 2000, Rydberg et al. 2008). While sediment dating failed to yield an acceptable geochronology at Site 2, the Hg profile suggests decreasing Hg deposition in the more recent sediments (Outridge and Wang 2015). Despite high Hg contents in the deeper sediments, bioactive methyl-Hg production in the anoxic layer may be low due to loss via diagenetic processes (Rydberg et al. 2008).

Several other localised contaminations were observed. Contamination of zinc (Zn) was localised to the Site 2 mix shed core, however Zn contents here exceeded the SQG high value in surface sediments. Zn over the SQG low was present in all depths along the core (Table 2). High Zn here could be from fertiliser, as Zn is present in trace amounts in certain fertilisers (Nziguheba and Smolders 2008). The surface sediment of the Site 3 mix shed contained copper (Cu) higher than the SQG low value. Elevated Cu in surface sediments may be from Cu-containing fungicides used on blueberry farms (Simpson 2019). Sediments in the surface of the Site 3 mix shed core had high contents of other fungicides (propiconazole and cyprodinil, Table 1). The bottom interval of the Site 2 drainage ditch core contained selenium (Se) greater than the SQG value of Van Derveer and Canton (1997). Elevated Se contents at this location could be caused by the accumulation of salts after evaporation of irrigation waters introduced during times of banana cultivation (Lemly 2004).

5. Conclusions

1. Site 3, especially in the chemical mixing shed, was the site most contaminated with pesticides, in particular the fungicides propiconazole and cyprodinil. Soil contents of these fungicides should decrease as they degrade via natural processes, however breakdown products may have increased toxicity in the soil environment.

2. Arsenic contents over the ANZECC SQG low values were observed in the mix shed, field, drainage ditch, and dam cores at Site 2. Arsenic contamination at this location is suspected to be from pesticide application during previous land use for banana cultivation.

3. Contents of mercury (Hg) from dam sediment cores at all three sites exceeded ANZECC SQG low values. Dam sediments contained high amounts of Hg relative to terrestrial soils. We attribute this result to the mobility of Hg in the agricultural soils and the retention of Hg in aquatic sediments with low oxygen.

4. Localised contamination with zinc (Zn), phosphorus (P), and copper (Cu) occurred in mix sheds from different sites. These contaminants are likely sourced from agricultural treatment products which are frequently exposed to the environment at mix shed locations.

These results build upon our previous work from areas downstream of Sites 1 and 2 and demonstrate that waterways on the farm may be useful in retaining certain nutrients and trace metals from intensive horticulture. This work also proved to be a useful preliminary assessment in identifying pesticides contamination from blueberry horticultural practices in the Coffs Harbour LGA.

In order to identify contaminants of particular concern, a multiple lines of evidence approach was used. Our evaluation of pesticide and trace metal contamination concern was based on their environmental and aquatic toxicity, magnitude of soil/sediment contents, spatial distribution, and persistence and mobility within the environment to generate a rating of overall concern (Table 4). We qualified toxicity based on environmental effects, as soil and sediments were the environmental mediums considered in this report, not exposure directly or through food. Pesticide environmental toxicities were rated referencing the Globally Harmonized System (GHS) of classification and labelling of chemicals. The GHS is an international chemical hazard classification system developed by the United Nations to identify environmental human and health risks associated with commercially available chemicals (SWA 2019b).

We identified the herbicide diuron, trace metals cadmium and mercury, and the nutrient phosphorus (P) as contaminants of high concern based upon their relatively high contents, extensive distributions amongst our study sites, potential for negative effects on biota, long environmental residence times, and mobility in the terrestrial/aquatic environment.

Uncertainties and conflicts in the literature did not allow us to confidently qualify overall concern for all contaminants. The literature reports variable degradation rates and solubility/desorption behaviours for cyprodinil, dimethoate, and propiconazole (see appendix for literature). Due to their inherent toxicity, we believe that the detection of any pesticide makes it a potential risk. More data pertaining to the breakdown and transport of the pesticides we detected is necessary in order to confidently qualify these contaminants in our risk assessment framework. Therefore the overall concern for all of the pesticides we detected has been qualified as potential (Table 4).

The classes of pesticides we did not detect have been classified as uncertain, as their absence from our samples does not signify their absence from other horticultural landscapes in the Coffs Harbour LGA.

Contamination of arsenic (As) was localised to Site 2. We qualified the overall concern for As as potential. We recommend other locations with banana cultivation history should be assessed for As contamination.

Contamination of zinc (Zn) was localised. Zn accumulation is common in horticultural landscapes, and contamination of Zn has occurred in sediments downstream of Sites 1and 2. It is possible our spatially restricted sampling may not have identified full extent of Zn contamination. The trace metal manganese (Mn) may be an important carrier for other trace metals and harmful to biota above certain amounts, although no ANZECC SQG exists for this element (see appendix for cited literature). These uncertainties did not allow for us to qualify overall concern for Zn and Mn with confidence.

Although here we have made a preliminary qualification of contaminants of concern, we would like to acknowledge that our sampling regime was restricted spatially. In order to have

more confidence in broadly identifying horticultural contaminants of concern from Coffs Harbour horticultural industries, we recommend further studies should more intensely sample soils on farms, especially in growing areas.

Table 4. Summary of environmental and aquatic toxicity, detections, magnitude of concentration (either ANZECC SQG or enrichment factors), spatial distribution amongst our study sites, and persistence and mobility within the environment for pesticides and trace metals investigated in this study. Contaminants evaluated with literature, online databases, data from this report, and our judgement to generate a rating of overall concern. Red, yellow, and green text indicate high, moderate, and low risk, respectively. Overall risk of some contaminants remains **uncertain** due to conflicting reports from the literature and lack of more specific geochemical data. Literature cited in appendix.

Pesticides	Toxicity	Detection	Spatial distribution	Persistence	Mobility	Overall concern
Bifenthrin	High	Detected	Confined	High	Low	**Potential**
Carbendazim	High	Detected	Extensive	Variable	Low	**Potential**
Cypronodil	High	Detected	Extensive	Low	Moderate	**Potential**
Dimethoate	High	Detected	Confined	Variable	High	**Potential**
Diuron	High	Detected	Moderate	High	High	**High**
Ethoprophos	High	Detected	Moderate	High	Moderate	**Potential**
Methomyl	High	Detected	Confined	Low	Moderate	**Potential**
Prometryn	High	Detected	Confined	Low	Moderate	**Potential**
Propiconazole	High	Detected	Moderate	Variable	Low	**Potential**
Pyrimethanil	Moderate	Detected	Confined	Low	High	**Potential**
Organochlorines	High	Undetected	N/A	High	Low	**Uncertain**
Traiazine Herbicides	High	Undetected	N/A	Moderate	Low	**Uncertain**
Triazinone Herbicides	High	Undetected	N/A	Moderate	Low	**Uncertain**

Trace Metals	Toxicity	Exceeded SQG or displayed enrichment	Spatial distribution	Persistence	Mobility	Overall concern
Arsenic	High	Yes	Moderate	High	Moderate	**Potential**
Lead	High	No	Confined	High	Moderate	**Low**
Cadmium	High	Yes	Moderate	High	High	**High**
Chromium	Moderate	No	Confined	High	Moderate	**Low**
Copper	Moderate	Yes	Confined	High	Moderate	**Low**
Nickel	Moderate	No	Confined	High	Moderate	**Low**
Selenium	Moderate	Yes	Confined	High	Moderate	**Low**
Zinc	Moderate	Yes	Confined	High	Moderate	**Uncertain**
Mercury	High	Yes	Extensive	High	High	**High**
Cobalt	Moderate	No	Confined	High	Moderate	**Low**
Manganese	Moderate	No	Confined	High	High	**Uncertain**
Iron	Low	No	Confined	High	High	**Low**
Aluminium	Low	No	Confined	High	Moderate	**Low**
Phosphorus	Moderate	Yes	Extensive	High	Moderate	**High**

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Appendix

Literature cited for Table 4. All references here appear in reference list above.

Pesticides	Literature cited
Bifenthrin	Kamble and Saran 2005, SWA 2019a, van Herk et al. 2013
Benomyl	Ahmad 2018, Austin and Briggs 1976, Baude et al. 1974, Rhodes and Long 1974, SWA 2019a
Cypronodil	Bermúdez-Couso et al. 2007, Cayman Chemical Company 2018, Komarek et al. 2010
Dimethoate	Bohn 1964, El Beit et al. 1981, Martikainen 1996, Sanderson and Edson 1964, SWA 2019a, Van Scoy et al. 2016
Diuron	Field et al. 2003, Stork et al. 2008, SWA 2019a, Tixier et al. 2000
Ethoprophos	Boesten and Gottesbüren 2000, Boesten and van der Pas 2000, Smelt et al. 1987, SWA 2019a
Methomyl	Cox et al. 1992, Harvey Jr and Pease 1973, Malhat et al. 2015, SWA 2019a, Van Scoy et al. 2016
Prometryn	Jiang et al. 2017, Khan 1982, National Center for Biotechnology Information 2018
Propiconazole	Edwards et al. 2016, Kim et al. 2002, Riise et al. 2004, SWA 2019a, Thorstensen et al. 2001, Wu et al. 2003
Pyrimethanil	Aguera et al. 2000, Garau et al. 2002, Rose et al. 2009, Sirtori et al. 2012, SWA 2019a
Organochlorines	SWA 2019a
Triazine Herbicides	SWA 2019a
Triazinone Herbicides	SWA 2019a

Trace Metals	Literature cited
Arsenic	Burton et al. 2008, Simpson et al. 2013
Lead	Roussiez et al. 2013, Simpson et al. 2013
Cadmium	Conrad et al. 2019, Mortvedt and Osborn 1982, Roussiez et al. 2013, Simpson et al. 2013, Xue et al. 2000
Chromium	Roussiez et al. 2013, Simpson et al. 2013, Xue et al. 2000
Copper	Roussiez et al. 2013, Simpson et al. 2013, Xue et al. 2000
Nickel	Roussiez et al. 2013, Simpson et al. 2013, Xue et al. 2000
Selenium	Lemly 2004, van Derveer and Canton 1997
Zinc	Conrad et al. 2019, Nziguheba and Smolders 2008, Simpson et al. 2013, Xue et al. 2000
Mercury	Shanley and Bishop 2012, Simpson et al. 2013
Cobalt	Li et al. 2009
Manganese	Li et al. 2014, Simpson et al. 2013
Iron	Simpson et al. 2013
Aluminium	Roussiez et al. 2013, Simpson et al. 2013
Phosphorous	Carpenter 2005, Conrad et al. 2019, Persaud et al. 1993