2.5 Chemical analysis

The pesticides and their possible metabolites were analysed by Queensland Health, Coopers Plains, Queensland. All collected samples (water and soil) were separated via solid phase extraction (SPE) and examined by liquid chromatography mass spectrometry (LCMS). The analytical methodology (SPE combined with LCMS) is generally utilised by the Great Barrier Reef Catchment Loads Modelling Program (Gallen et al., 2016; Shaw et al., 2010; Vardy et al., 2015; Wallace et al., 2015). One insecticide (imidacloprid) and six herbicides namely imazapic, metolachlor, fluroxypyr, isoxaflutole, glyphosate and haloxyfop, which have been applied in recent years at the monitoring site, were tested in this study (Table 5 and Table A1).

2.5.1 Water Analysis

There were two analytical method groups (QIS 33963 for herbicides and pesticides and QIS 33917 for Glyphosate) for water analysis used in Queensland Health Laboratory. The analysis was performed by direct injection method by filtering 1mL of sample using 0.2 µm filter and analysed on LCMSMS. For water herbicide analysis for imidacloprid, imazapic, metolachlor, fluroxypyr, isoxaflutole and haloxyfop, the method details are provided in Table A2. During analysis, some matrix effects were experienced, and if this increased, the Limit of Reporting (LOR) was increased.

2.5.2 Soil Analysis

There were two analytical method groups (QIS 30814 for glyphosate and QIS 32456 for herbicides and pesticides) in soil / sediment. For QIS 30814: glyphosate and amino methyl phosphonic acid (AMPA) in soil/vegetation by LCMSMS, water was added to soil samples and shaken. The aqueous phase was filtered and analysed via direct injection on the LC-MSMS. On the other hand, QIS 32456: determination of herbicides in soil and sediment by LC-HRAM-Orbitrap, the soil/sediment sample was first shaken with acetone using a tabletop shaker for approximately 12 hours. The herbicides were then extracted using a QuEChERS method. The final extract was analysed by LC-HRAM-Orbitrap. The method details for pesticide and herbicides in soil and sediment are provided in Table A3. Imazapic showed low recovery (<40%) when it was analysed by QIS 33456 method.

Appendix

Table A2. Method details for Pesticides in Water by Direct Injection using LCMSMS and QExactive Orbitrap.

Pesticide	LOR	Units	Accepted Uncertainty (%)	Recovery (%)	Repeatability (r) (%)	Standard Uncertainty (%)
Fluroxypyr	0.05	ug/L	28	111	38	28
Haloxyfop (acid)	0.02	ug/L	26	105	31	26
Hexazinone	0.01	ug/L	25	103	20	12
Imazapic	0.01	ug/L	25	101	14	10
Imidacloprid	0.02	ug/L	25	100	34	21
Imidacloprid (metabolites)	0.02	ug/L	34	108	21	34
Total Imidacloprid	0.04	ug/L	25			
Isoxaflutole metabolite (Diketonitrile)	0.02	ug/L	25	102	20	16
Metolachlor	0.01	ug/L	25	87	16	11

Table A3. Method details for Pesticides in Soil and Sediment by LCMSMS / LC-HRAM-Orbitrap.

Pesticide	Limit of reporting	Units	Recovery %
Fluroxypyr	0.001	mg/kg	55
Haloxyfop (acid)	0.001	mg/kg	69
Imazapic	0.001	mg/kg	22
Imidacloprid	0.001	mg/kg	93
Total Isoxaflutole	0.001	mg/kg	56
Metolachlor	0.001	mg/kg	71
AMPA	0.005	mg/kg	93
Glyphosate	0.005	mg/kg	90