EMRC

Protecting Perth's Eastern Region

Helping the Helena establishing a baseline of water quality pollutants for linkages in fish and mussel decline

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Government of Western Australia
Department of Water

SWAN RIVER TRUST

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The following people were integral to the successful completion of this project and report:

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Executive Summary

Industrial, agricultural and residential activities within water catchments are known to contribute contaminants to their receiving environments. Within the context of this study, the receiving environment is the Helena River, with this tributary eventually flowing into the Swan River.

Previous studies (Nice *et al*., 2009), (Klunzinger *et al*., 2012) have identified the Helena River as a priority area for sampling and analysis of non-nutrient pollutants including heavy metals and pesticides.

More specifically, this project follows on from the recommendations of fish and macro-invertebrate surveys conducted by EMRC and Wetland Research and Management in 2010 and 2011. It was recommended that sites be sampled for non-nutrient pollutants to determine if links exist between fish paucity and pollution in summer time pools.

The current study involved sampling sediment and water at various sites along the Helena River over a period of twelve months. Selection of sites focused on those areas which potentially have high levels of non-nutrient contamination due to current and historic pesticide use and other potentially contaminating industrial activities within the region and their position in the catchment.

Key pollutants identified during this study were: polycyclic aromatic hydrocarbons (PAHs), total petroleum hydrocarbons (TPHs), anionic surfactants, metals and herbicides. Key areas of the river were identified for further investigation including: the middle Helena sites between the Lower Helena Reservoir and Mundaring Weir, and sites in the lower Helena bordered by agricultural areas. In addition, all sites were flagged for further investigation for the distribution of cationic and non-ionic surfactants in water.

Recommendations of this study include: long term monitoring to pick up spikes and changes in water quality and analysis specifically for non-ionic and cationic surfactants in water. Fish tissue analysis for contaminants is also recommended to determine the level of persistence of metals and other contaminants that have a tendency to bio-accumulate. In the case that follow up sampling confirms contamination in middle Helena sites: sediment toxicology investigations should be undertaken.

Results of this study act as a baseline for further sampling, analysis and investigation to occur in key areas highlighted in this report.

Table of Contents

1 Background

The Helena River is mostly ephemeral, flowing June to January with an average flow of 3.1 GL per year. The headwaters are located in the Shire of York on the Darling Plateau. The river flows through the Darling Scarp and Coastal Plain before its confluence with the upper reaches of the Swan River in Guildford (Swan River Trust, 2010).

For the purpose of this study, the area of focus is restricted to the Eastern Hills Catchment Management Program locale where the Helena River traverses three local governments, these being the Shire of Kalamunda, Shire of Mundaring and the City of Swan.

Within the Catchment soils range from shallow earths, sandy and lateritic gravels on the Darling Scarp, to sandy, gravelly soils on the foothills to the west and alluvial red earths close to the confluence with the Swan River (Swan River Trust, 2010). Groundwater is considered to have a minor influence on water level and the flow of the Helena River.

It is believed that, in most instances, chemicals entering the environment break down into non-volatile organic constituents and degrade naturally. However, sampling regimes to date have failed to provide an understanding of the location and persistence of non-nutrient contaminants throughout waterways in Western Australia (WA). Further, there is a deficiency of data for environmental fate and synergistic affects for these chemicals in freshwater ecosystems world-wide, with no such data existing for south-west WA.

In 2009, the Department of Water conducted an assessment of contaminants in the Swan and Canning Catchment Drainage System as part of the Swan River Trust's Non-Nutrient Contaminants Program (NNCP). This study identified issues with Polycyclic Aromatic Hydrocarbons (PAHs), Organo-chlorine (OC) pesticides and metals, and a potential issue with herbicides, subsequently prioritising the Helena River for further investigation (Nice *et al*., 2009).

In 2010 and 2011 fish and macro-invertebrates were surveyed in the Helena River. The subsequent report recommended seasonal water quality data be collected and analysed to determine if pollutants (e.g. insecticides, herbicides, heavy metals, hydrocarbons) might be responsible for the paucity of fish and crayfish in the lower and middle reaches. A sub-set taken from each sub-catchment was recommended, with a minimum of at least three sites from each sub-catchment to be included. It was recommended that preference be given to sites known to be in the receiving environment for point and/or diffuse source pollutants (EMRC & WRM, 2011). This study follows on from recommendations made in these studies.

The results of this study therefore act as a baseline for non-nutrient contaminants in the Helena River Catchment. This information can be used as a base for future research to build upon to determine if linkages exist between water quality pollutants and fish and mussel decline in the Helena River.

2 Introduction

The Helena River is one of the main tributaries to the Perth Swan River and runs through the Helena Catchment area which is comprised of residential, industrial and agricultural areas as well as state forest and parks. Summertime pools along the river are important ecological refuge areas in times of summer drying when the river disconnects. The river also flows through the drinking water catchment area that supplies 25-40% of the water to the Goldfields and Agricultural Water Supply Scheme (WAPC, 2010).

Input of chemicals to the Helena River from overland flow and drainage is not recorded and the types, quantities and timing of inputs is unknown. Various studies have collected data which shows declining numbers of native fish, invertebrates and mussels within the river. The cause of this is believed to be a combination of factors including infrastructure barriers to gene flow, habitat degradation, high nutrient inputs, rising salinities and low dissolved oxygen (Klunzinger *et al*., 2012), (EMRC & WRM, 2011), (Smith *et al*., 2011).

There is a lack of data for non-nutrient pollutants in the Helena River and thus research is required to determine if there are links between low native fish numbers and non-nutrient pollutants (Nice *et al*., 2009), (EMRC & WRM, 2011).

Studies on freshwater species such as the mussel Westralunio carteri have suggested links between chemical pollution and species decline. It is thought that mussels found with deformed shells within the middle Helena River may be demonstrating chronic effects of pesticide exposure (Klunzinger *et al*, 2011). Other studies found low fish and crayfish numbers in the middle and lower reaches of the river and recommendations suggested pollutant testing to be carried out (EMRC & WRM, 2011).

This study will form a baseline for further research to be conducted to determine if links exist between fish and macro-invertebrate decline, and the presence of pollutants in the Helena River.

2.1 Guideline values applied

Table 1 guideline values referred to in this study

Non-nutrient contaminants in sediment	Australian and New Zealand Environment and Conservation Council (ANZECC) and the Agriculture and Resource Management Council of Australia and New Zealand guidelines (ARMCANZ) (2000) Interim Sediment Quality Guideline Trigger Values (ISQG) low and high (see Appendix 1) Canadian Council of Ministers of the Environment (1995). Protocol for the derivation of Canadian sediment quality guidelines for the protection of aquatic life. (see Appendix 1)
Non-nutrient contaminants in surface water	Australian and New Zealand Environment and Conservation Council guidelines for Fresh and Marine Water Quality- guidelines for 95% Ecosystem Protection in fresh waters (ANZECC and ARMCANZ 2000) (see Appendix 1)
Physical measurements in surface water	ANZECC guidelines for South West Australia for Lowland Rivers. (see Appendix 1)

3 Methods

3.1 Site selection

Sites were selected based on their location relative to land-use and on the location of sites used in macro-invertebrate studies which focused on diversity and abundance of freshwater fish and crayfish in summer pools within the river. Seven of the eight sites selected in this study were pools that were also assessed as part of the fish and macro-invertebrate surveys in 2010 and 2011. (EMRC & WRM, 2011).

Five sites were selected from the lower Helena, two from the middle and one from the upper catchment. These sites are mapped in Figures 1 to 4 below.

Site selection was strongly influenced by the presence of permanent water. Other sites which may have been more appropriate could not be sampled due to the requirement for them to have water at every sampling event.

Table 2: Site details of those sites sampled in this study, far left column denotes sites also sampled in WRM 2010, 2011 fish surveys.

Fish survey site	Site name	Location	Easting	Northing
Not surveyed	**Helena 1**	Helena Valley floodplain. 5.7 km upstream of Swan River confluence	406672	6469864
Site 4	**Helena 2**	Helena Valley floodplain. 6.7 km upstream of Swan River confluence	407030	6469612
Site 7	**Helena 3**	Helena Valley floodplain. 8.1 km upstream of Swan River confluence	407950	6469590
Site 20	**Helena 4**	State Forest, Helena river below PHD at Craignish Gauging Station. 12.1 km upstream of Swan River confluence.	411964	6466323
Site 18	**Helena 5**	State Forest, Helena river below PHD wall. 12.7 km upstream of Swan River confluence.	412554	6466029
Site 14	**Helena 6**	Helena River above PHD. 22.9 km upstream of Swan River confluence.	418387	6465445
Not surveyed	**Helena 6a**	Bourkes Gully , Helena River north of site 6 on the Mundaring Loop Trail	420113	6465359
Site 13	**Helena 7**	Helena River above PHD 24.9 km upstream of Swan River confluence.	419951	6464551
Site 11	**Helena 8**	State Forest, Helena River headwaters above Mundaring Weir. 54.4 km upstream of Swan River confluence.	441603	6466283

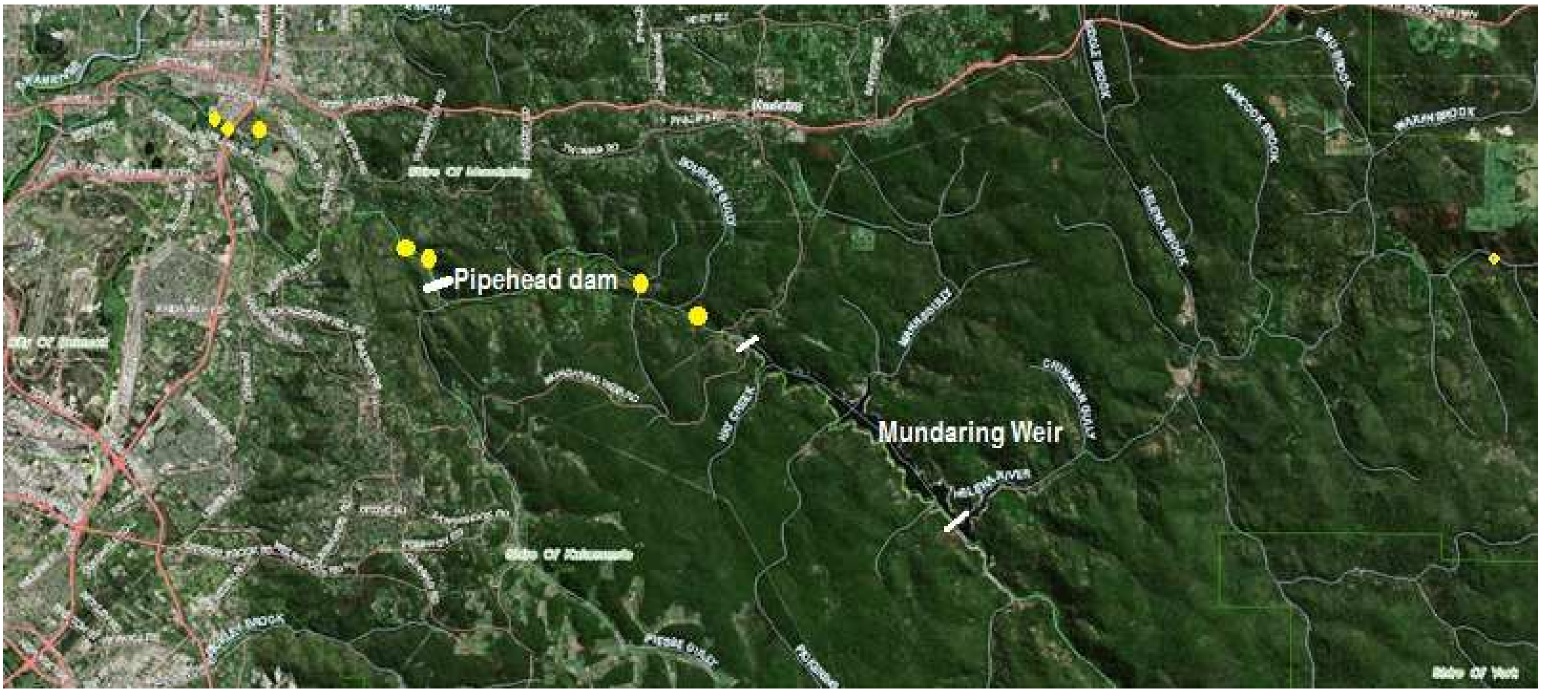

Figure 1: Sites sampled during this study (yellow markers)

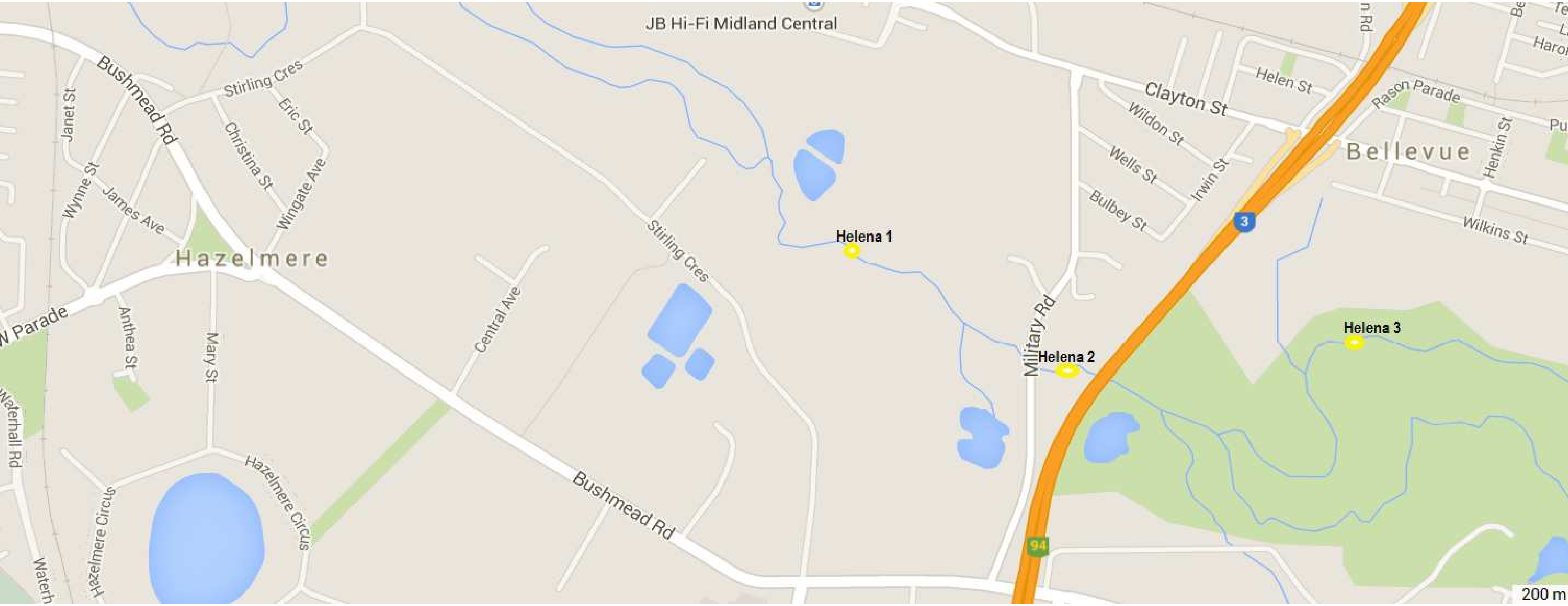

Figure 2: Sites sampled within the Lower Helena River

Figure 3: Sites sampled within the Middle Helena River. Note that Helena 6a was sampled on only one occasion within April 2014

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Figure 4: One site sampled within the Upper Helena River

3.2 Sampling methods and frequency

Water sampling methods on all occasions were conducted in line with the Sampling and Analysis Plan (SAP) and the documents - Surface water sampling methods and analysis - technical appendices; and Field sampling guidelines: A guideline for field sampling for surface water quality monitoring programs (DoW, 2009).

Sediment was sampled using a 90mm polycarbonate corer with the first 3 cm of each core being removed and placed in stainless steel bowl. Once sufficient material was collected to fill a sterilised 250 mL jar the composite of the cores was homogenised and decanted into the sediment jar until the jar was completely full.

Sampling occurred on a quarterly basis with water samples taken in April, July, October 2013, and January 2014. Sediment sampling took place in April and October 2013. Helena 6a was sampled on only one occasion, April 2014.

3.3 Quality control

Samples were subject to the following laboratory quality control measures: at least one procedural blank and duplicate analysis per process batch and; one matrix and surrogate spike for each soil and water type. The following field sampling quality control measures were also taken: Water - field replicate and field blank samples; and sediment - field replicate sample on the first sampling event.

3.4 Water and sediment quality parameters

Parameters were selected based on land use activities within the Helena River Catchment and those contaminants which have not previously been sampled for but could cause harm to the environment.

The surface water parameters were separated into the following groups:

Group 1: Physical parameters
Group 2: Surfactants and Glyphosate
Group 3: Chlorinated Acidic Pesticides
Group 4: Organochlorine/Organophosphate herbicides/ pesticides
Group 5: Heavy metals
Group 6: Polycyclic Aromatic Hydrocarbons (PAHs)/Total Petroleum Hydrocarbons (TPHs)

Surfactants were not analysed in sediment, all other parameters were the same. Sediment was also analysed for Total Organic Carbon and a particle size analysis performed for each site.

Samples were collected by an NRM Officer from the Eastern Metropolitan Regional Council (EMRC) and an officer from the Department of Water (DoW). They were analysed by National Association of Testing Authorities (NATA) accredited laboratories: Analytical Reference Laboratory (water analyses) and National Measurement Institute (sediment analyses).

Laboratory analysis and limits of reporting

The LOR used in this study were the lowest available using the accredited methods from commercial laboratories. The ANZECC guidelines used for reference are derived from toxicity data and in many cases are lower than the levels of reporting able to be achieved by current analytical methods. A summary of parameters and methods for lab analysis can be found in Appendix 2, Table 13.

3.5 Data analysis

Raw data was compared to guidelines and plotted against sites to identify spatial trends. Ecosystem health and recreational health guidelines referred to as pools have high ecosystem value and are also used by the public for various recreational purposes. PAH data was normalised to Total Organic Carbon (TOC) for each sample and then compared to guidelines. The amount of organic material in sediment strongly influences the persistence and bioavailability of PAHs in aquatic ecosystems and therefore the toxicological effects of those contaminants. Therefore it is necessary to normalise PAH data to assessments of TOC in sediment (ANZECC/ARMCANZ, 2000).

4 Results

4.1 In-situ data measurements

- Temperature of pools was highest in January and lowest in July. There was less variation in temperature between pools within the July sampling compared with January. Largest variation in temperatures between seasons occurred in the middle Helena sites (5, 6 & 7). No guidelines exist for water temperature. (Figure 5)

- pH at Helena 1 was very low (acidic) in April 2013. pH at Helena 1,2,3 and 6 failed to meet the ANZECC guidelines for ecosystem health in July 2013 (Helena 2 in both April and July 2013). All other sites were within recommended guidelines. (Figure 6)

- Conductivity was highest in January and April and lowest in July and October, values exceeded the guideline levels on every occasion. Conductivity was considerably higher at Helena 8 and unlike the other sites sampled; conductivity was not reduced in the winter months. Conductivity at Helena 1 varied substantially between seasons (Figure 7).

- Dissolved oxygen was at its lowest at the end of summer and highest at the end of winter. Most sites failed to meet the ANZECC guidelines for ecosystem health. Measurements taken in April 2014 were lower when compared with dissolved oxygen in April 2013. (Figure 8).

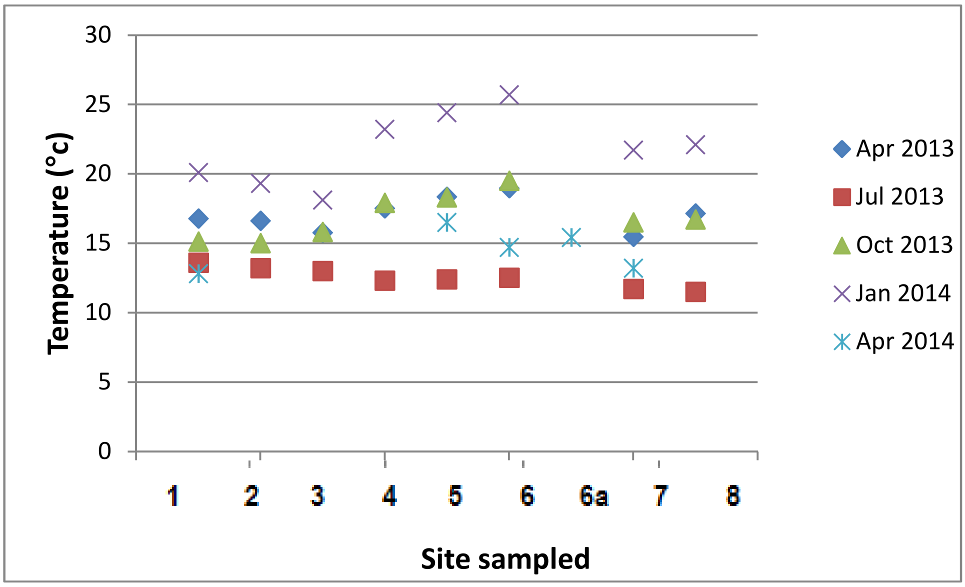


Figure 5: Water temperature recorded at each site at each sampling event.
Note: April 2014 sampling was completed at Helena 1,5,6,7 and 6a only.
Helena 6a was sampled on one occasion only

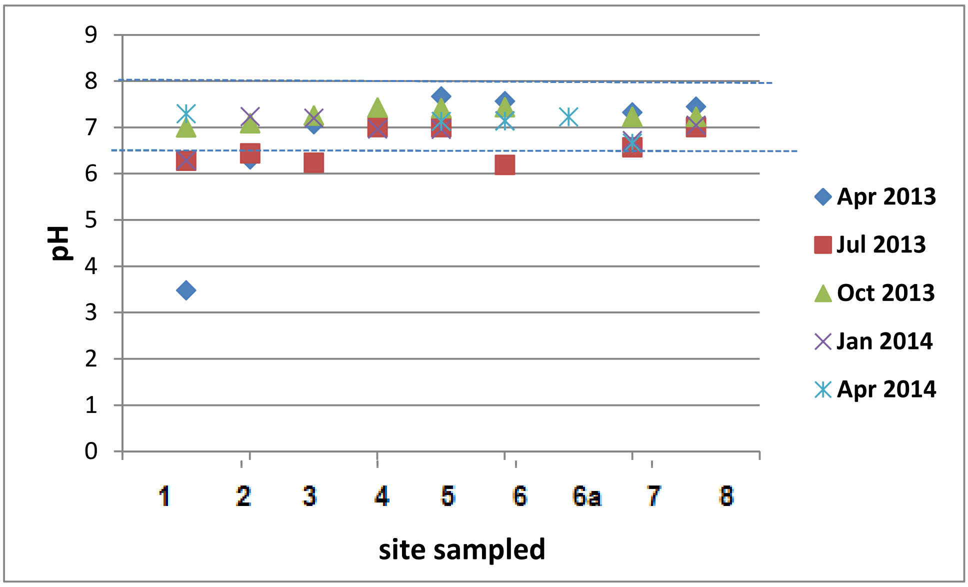


Figure 6: pH recorded at each site at each sampling event.
Note: April 2014 sampling was completed at Helena 1,5,6,7 and 6a only.
Helena 6a was sampled on one occasion only

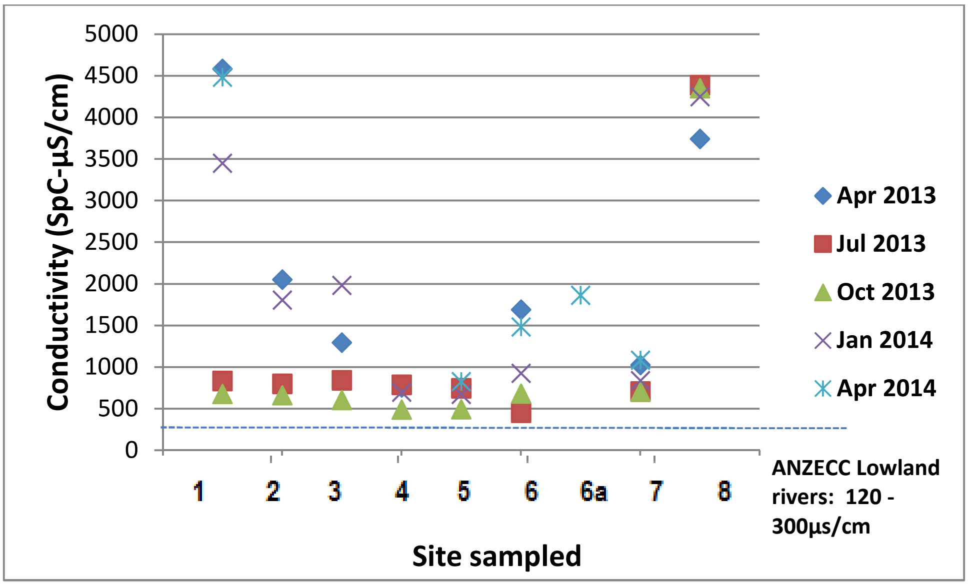


Figure 7: Conductivity measurements from each site at each sampling event. Note: April 2014 sampling was completed at Helena 1,5,6,7 and 6a only. Helena 6a was sampled on one occasion only

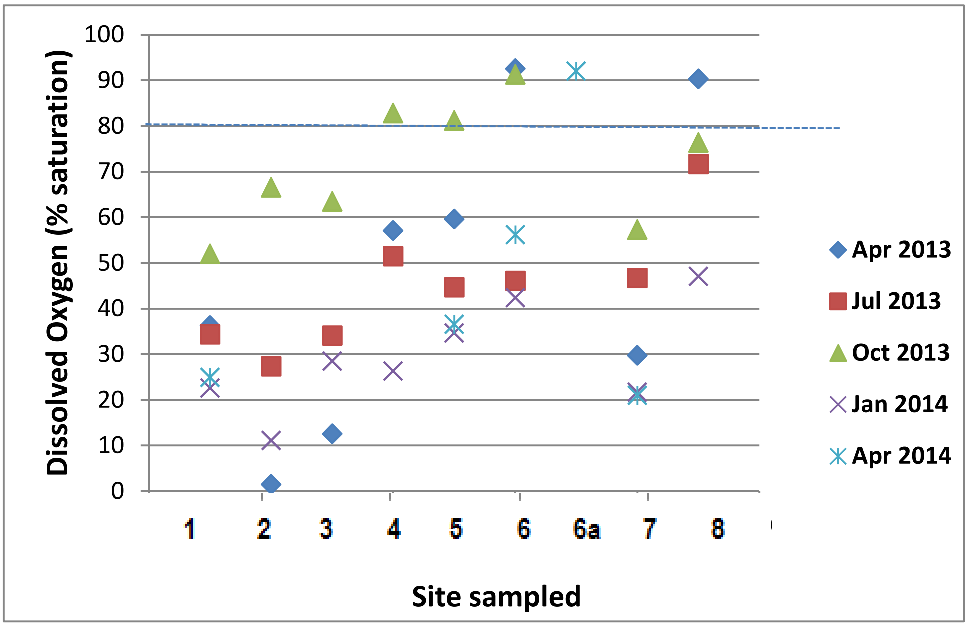


Figure 8: Dissolved oxygen recorded at each site at each sampling event. Note: April 2014 sampling was completed at Helena 1,5,6,7 and 6a only. Helena 6a was sampled on one occasion only

4.2 Particle Size Analysis

Particle distribution was not analysed for the April 2013 sampling event.

Particle distribution in sediments changed significantly between sampling. During the October 2013 sampling the dominant fraction at most sites was coarse sand with the silt fraction more dominant at Helena 5. At the April 2014 sampling event more sediments were dominated by the silt fraction (Table 3), however, Helena 2,3,4 and 8 were not sampled at this time.

Table 3: Results of the Particle Size Analysis conducted for sites in October 2013 and April 2014

Site (October 2013)	Clay % (<4µm)	Silt % (4-62µm)	Fine sand % (62-250µm)	Medium sand % (250-500µm)	Coarse sand % (500-2000µm)	Gravel (>2000µm)
Helena 1	7.63	22.07	14.00	17.90	**36.30**	2.10
Helena 2	11.67	**25.33**	16.79	22.51	21.40	2.30
Helena 3	14.57	30.64	11.99	2.79	**35.20**	4.80
Helena 4	5.76	16.28	7.61	9.35	**43.30**	17.70
Helena 5	9.89	**40.58**	17.21	3.91	21.30	7.10
Helena 6	5.96	14.39	14.85	16.30	**41.70**	6.80
Helena 7	8.54	18.89	22.16	23.21	**23.50**	3.70
Helena 8	5.89	22.62	9.79	11.80	**40.80**	9.10

Site (April 2014)	Clay % (<4µm)	Silt % (4-62µm)	Fine sand % (62-250µm)	Medium sand % (250-500µm)	Coarse sand % (500-2000µm)	Gravel (>2000µm)
Helena 1	4.30	9.90	2.72	17.68	**35.30**	30.10
Helena 5	7.15	**47.13**	22.24	4.08	7.50	11.90
Helena 6	11.36	**45.87**	11.71	1.46	14.20	15.40
Helena 7	3.32	13.84	3.73	2.10	**63.40**	13.60
Helena 6a	18.16	**69.56**	7.14	0.44	2.20	2.50

4.3 Organic Carbon Analysis

Total Organic Carbon (TOC) was analysed in April 2013, October 2013 and April 2014. Samples analysed in April 2014 were for sites Helena 1, 5, 6, 6a and 7 only. Organic matter was generally higher in the middle sites and lower in the lower and upper site(s), with Helena 5 showing the highest organic matter on each sampling occasion (Figure 9).

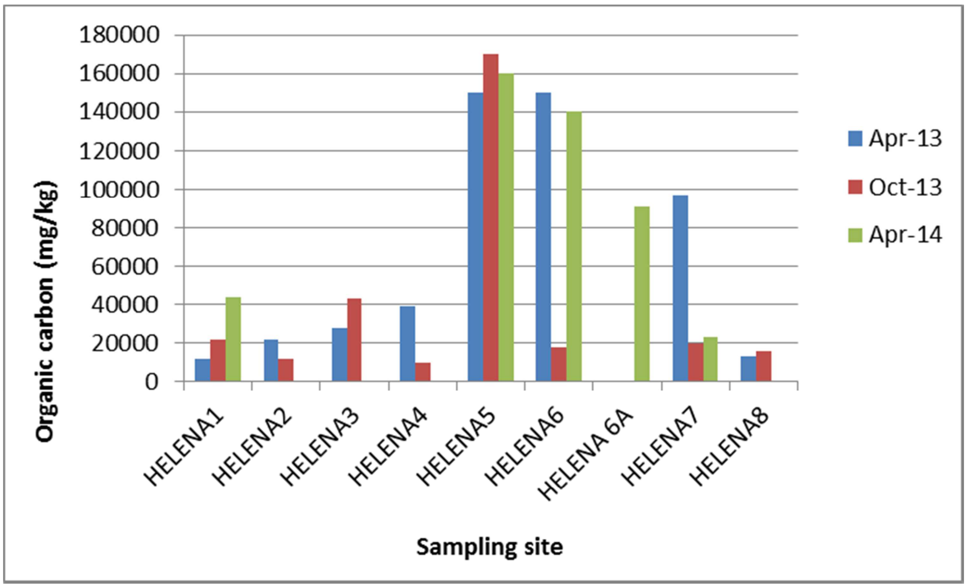


Figure 9: Total Organic Carbon (TOC) for sediment samples from April and October 2013 and April 2014.

Note: only 5 sites were sampled in April 2014, including Helena 6a which was sampled only on this occasion.

4.4 Organics

Of the suite of organics tested for in this study, surfactants, tested as Methylene Blue Active Substances (MBAS) were found consistently at all sites in every sampling event. Glyphosate and Dimethyl tetrachloroterephthalate (DCPA) were detected on one occasion each at two separate sites. No other organic contaminants were detected. This does not necessarily suggest that these contaminants are not present; however, they do not exist at concentrations relevant to the levels of reporting (LOR) used in this study.

- Anionic surfactants were tested for in water and were found consistently in every sample analysed (Figure 10). Anionic surfactant was also detected in the blank sample which was likely due to contamination. However, taking into account this level of contamination all detect data would still be above the level of reporting for MBAS and often exceeded the ANZECC guideline for recreational water quality.

- All sites exceeded the guideline level for MBAS in water for recreational purposes on at least one occasion, even with the consideration of contamination in each sample. No guideline exists for MBAS in water for ecosystem health.

- Glyphosate was detected in sediment at site 1 on one occasion. No guideline exists for glyphosate in sediment.

- DCPA (Dimethyl tetrachloroterephthalate) was detected in water on one occasion at Site 3.

- 2-4-D (2,4-dichlorophenoxyacetic acid) was also detected at Site 3 on a separate occasion.

4.4.1 Adjuvant- surfactants

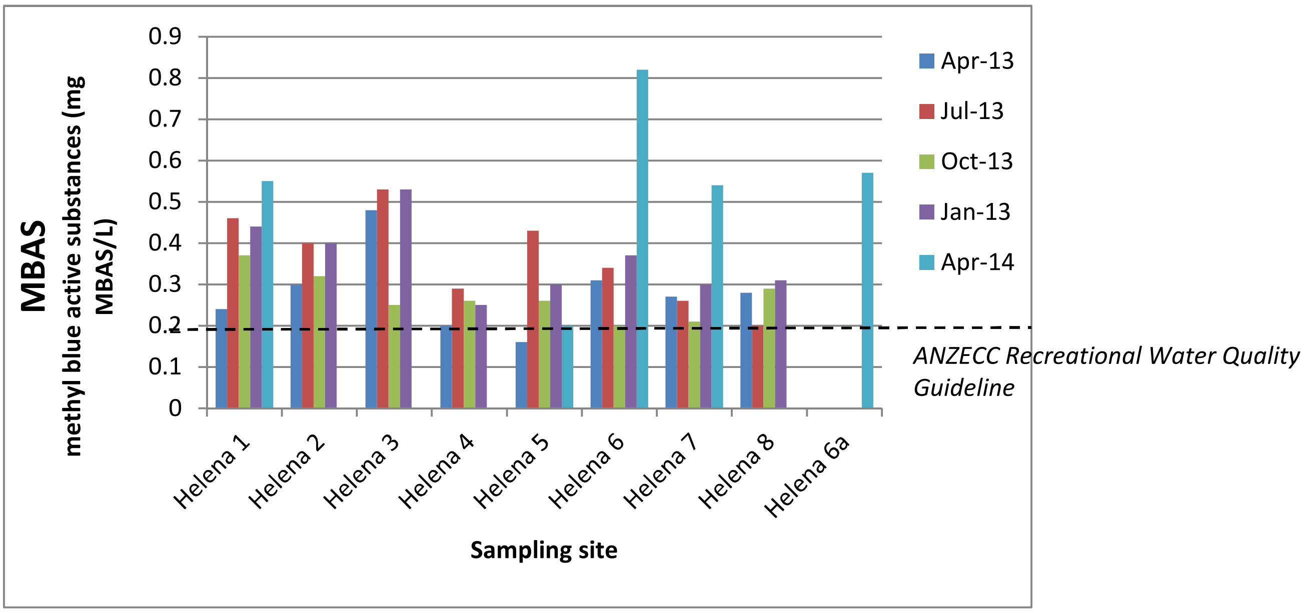


Figure 10: Detections of Methylene Blue Active Substances (MBAS) at each site at each sampling event.

4.4.2 Glyphosate

Glyphosate was detected in sediment at a rate of 1.2 mg/Kg at Site 1 in October 2013. No guideline exists at this time. No other sites were above the LOR 0.5 mg/Kg.

4.4.3 Other organics

DCPA (Dimethyl tetrachloroterephthalate) was detected in water at a rate of 0.018 µg/L at site 3 in April 2013. The acidic herbicide 2-4-D (2,4-dichlorophenoxyacetic acid) was also detected at a rate of 0.3 µg/L at Site 3 on one occasion in January 2014.

4.5 Metals

- Aluminium and iron were the most commonly detected metals in both sediment and water. The highest detection of aluminium in sediment was site 6 and iron at site 5. Aluminium exceeded guideline levels for water at least once in each site with the exception of Helena 8 and Helena 6a (Figure 13).

- With the exception of arsenic and mercury, all metals were detected within sites of the middle Helena at every sampling event. Arsenic was detected in the middle and in the lower Helena sites as well as in water in the upper Helena (Figure 15; Figure 22).

- Copper exceeded the guideline for 95% ecosystem protection in water at every site on every sampling occasion and was detected at 100 times the guideline level in October 2013 at Helena 3 (Figure 17). Zinc exceeded guidelines often in the lower sites, Helena 1-3 (Figure 14).

- Chromium exceeded the guideline level for ecosystem protection in water on 5 occasions (Figure 11).

- Lead and mercury were only detected in sediment in this study. Lead was detected frequently and exceeded the Canadian ISQG value at Helena 3 (concentration: 40 mg/kg; CCME ISQG= 35 mg/kg, CCME, 1995). Mercury exceeded the ISQG low trigger value at site 6 (concentration: 0.2 mg/L; ISQG low: 0.15 mg/L. Detections at sites 5 and 7 were close to the low trigger value (Figure 24) No other metals exceeded the low ISQG in sediment.

Figure 11 to Figure 26 below show metals detected in sediment and water during this study.

4.5.1 Metals in water

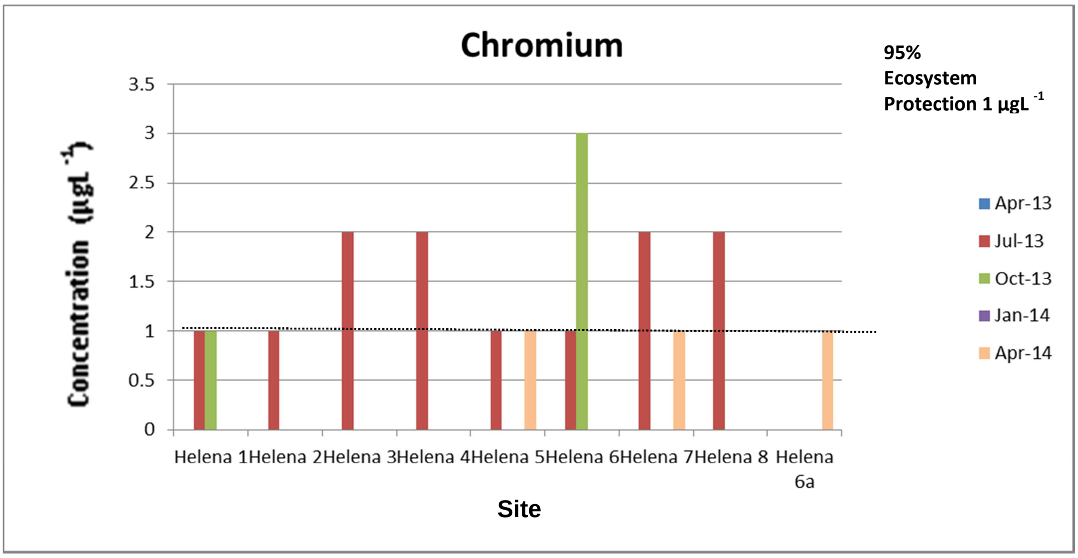


Figure 11: Chromium detected in water at sampling events; April, July & October 2013, January & April 2014.

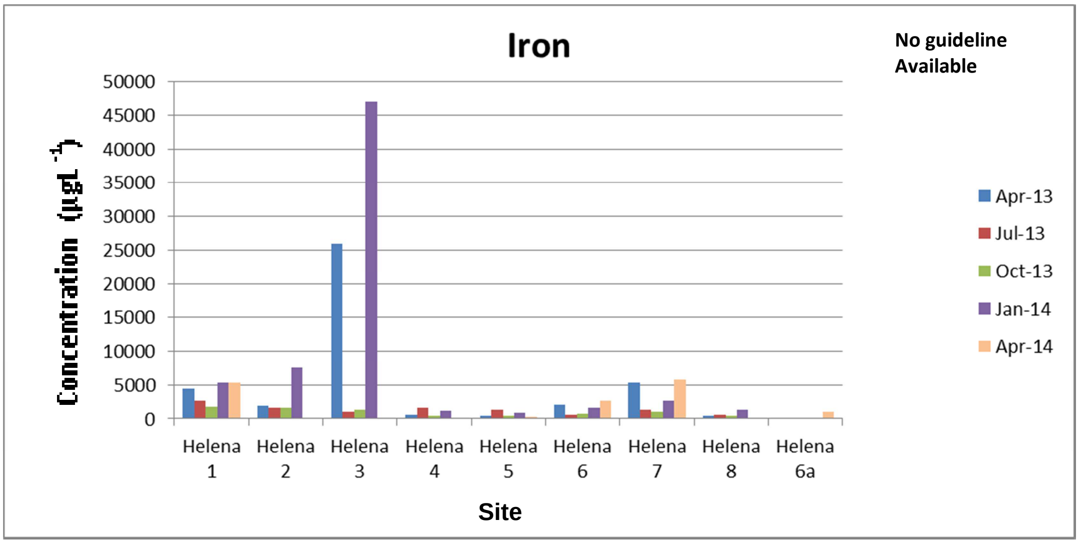


Figure 12: Iron detected in water at sampling events; April, July & October 2013, January & April 2014.

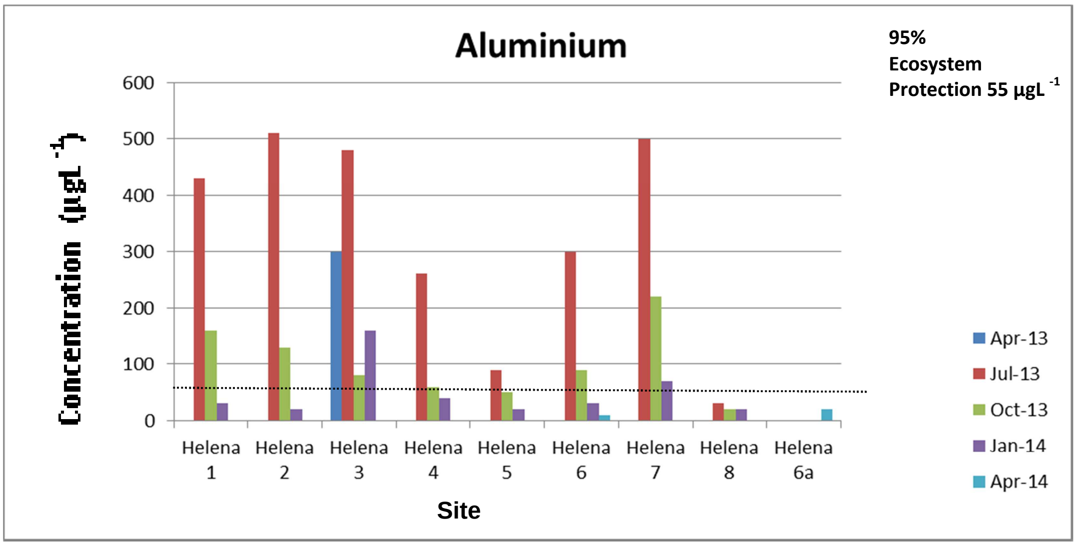


Figure 13: Aluminium detected in water at sampling events; April, July & October 2013, January & April 2014.

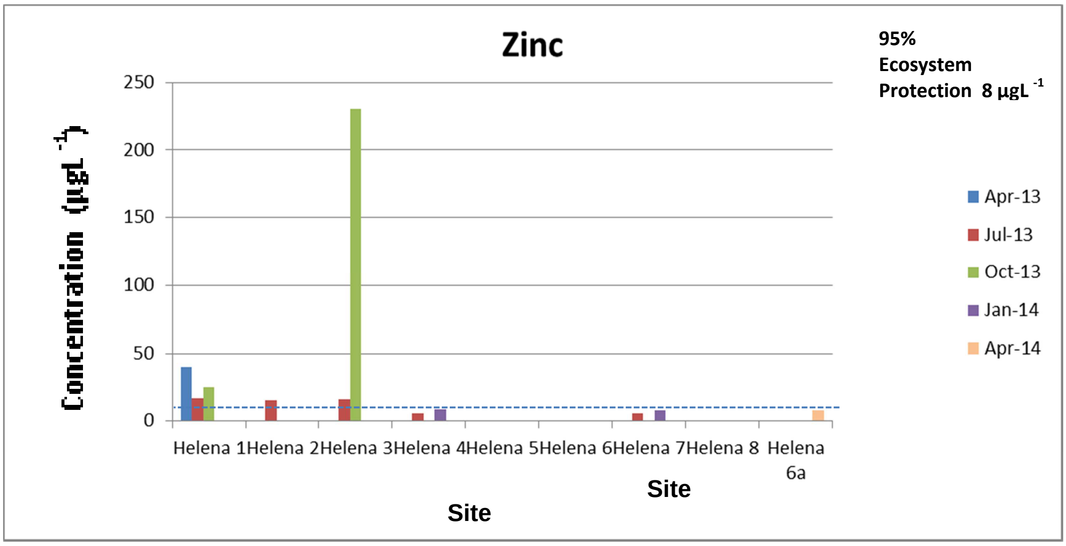


Figure 14: Zinc detected in water at sampling events; April, July & October 2013, January & April 2014.

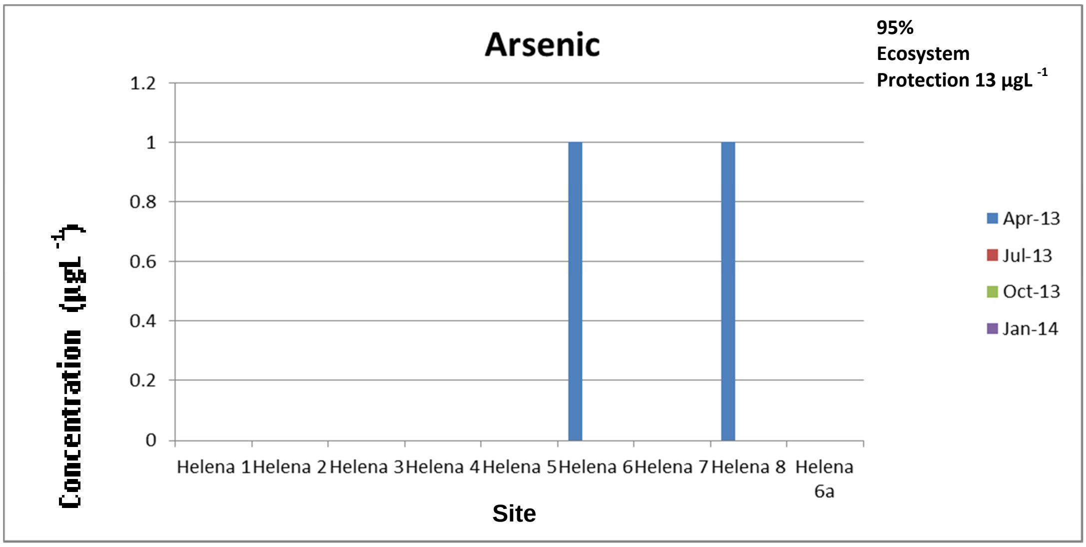


Figure 15: Arsenic detected in water at sampling events; April, July & October 2013, January & April 2014.

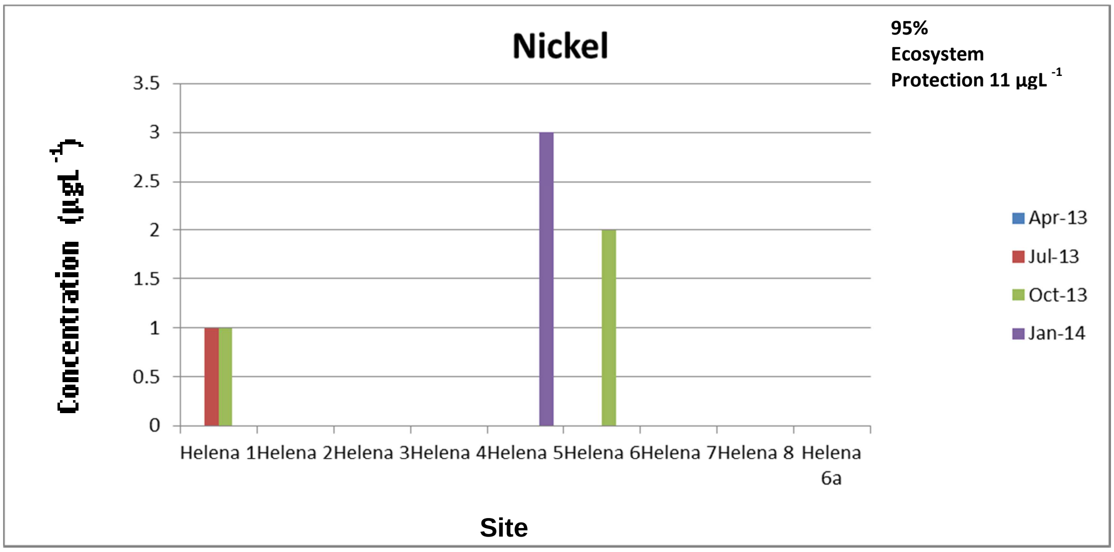


Figure 16: Nickel detected in water at sampling events; April, July & October 2013, January & April 2014.

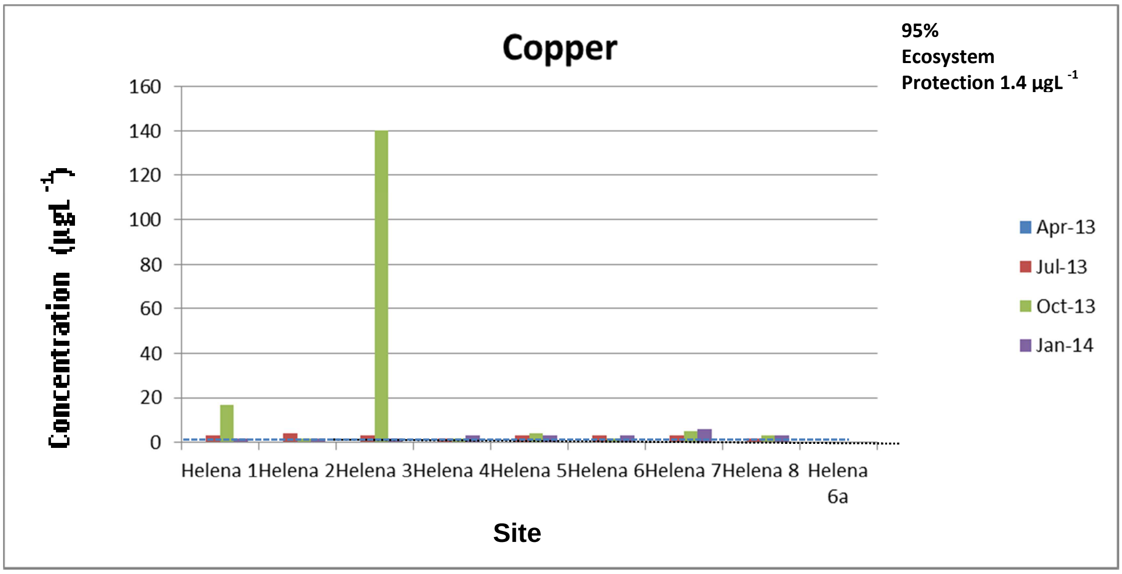
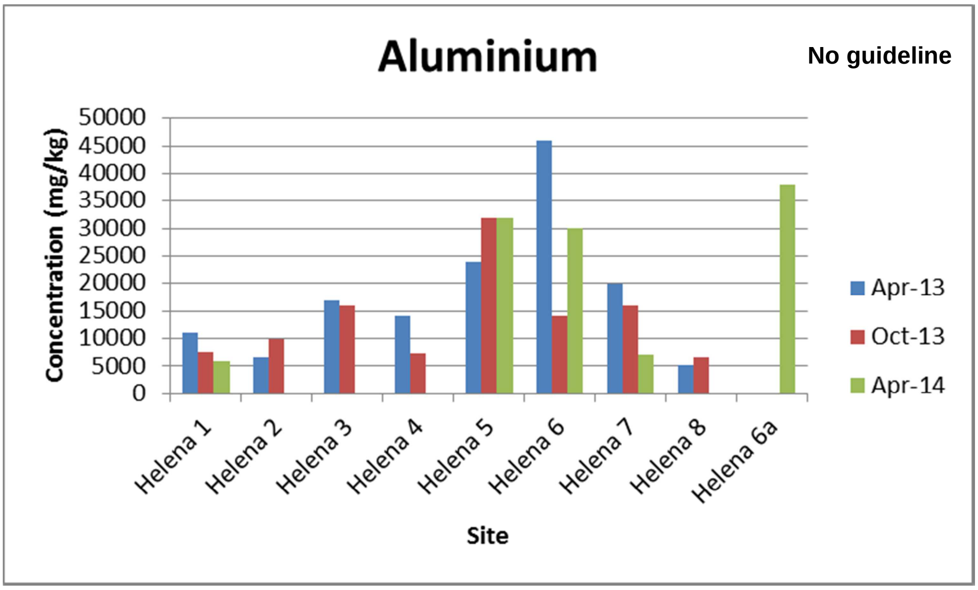


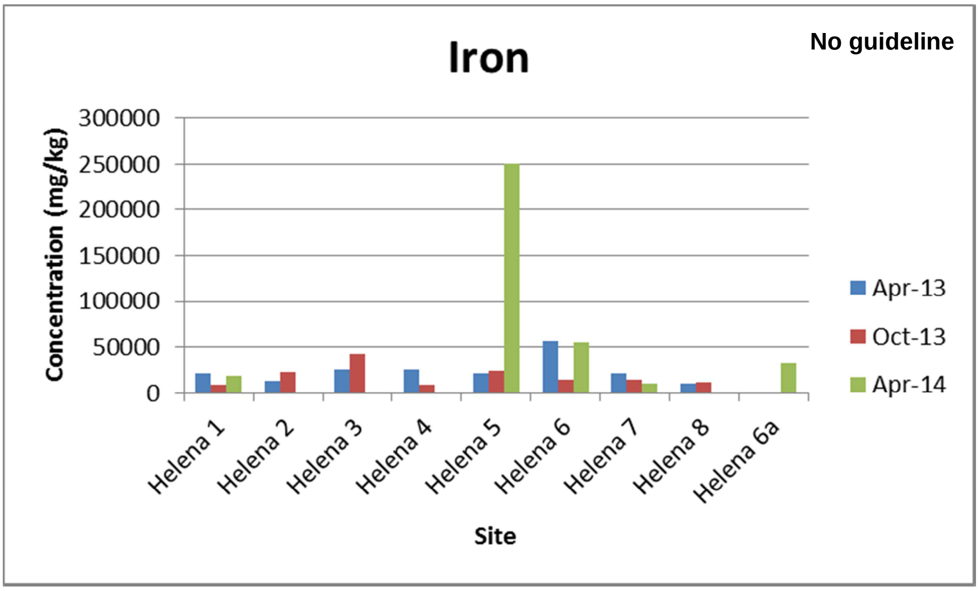
Figure 17: Copper detected in water at sampling events; April, July & October 2013, January & April 2014.

4.5.2 Metals in sediment



No guideline

Figure 18: Aluminium detected in sediment at sampling events; April & October 2013, & April 2014.



No guideline

Figure 19: Iron detected in sediment at sampling events; April & October 2013, & April 2014.

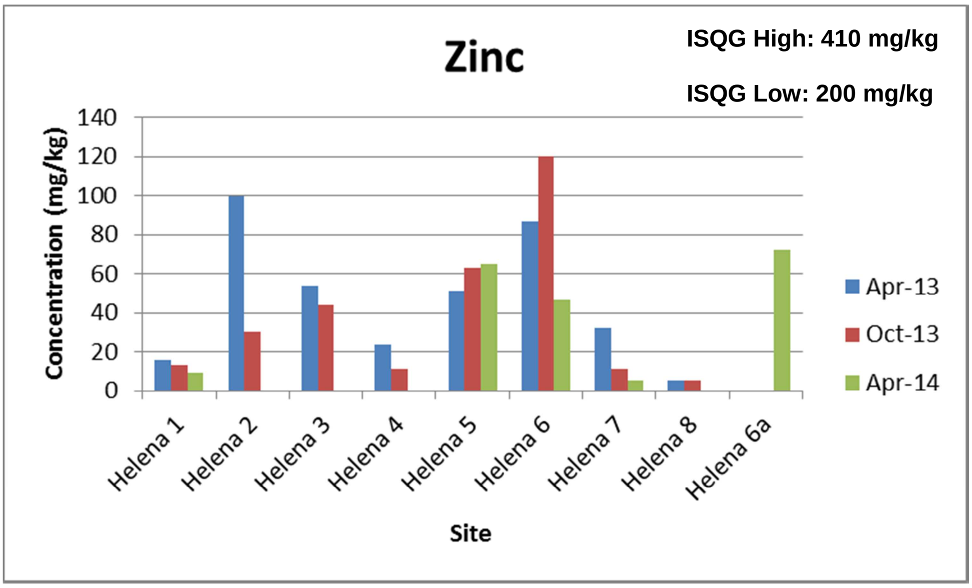


Figure 20: Zinc detected in sediment at sampling events; April & October 2013, & April 2014.

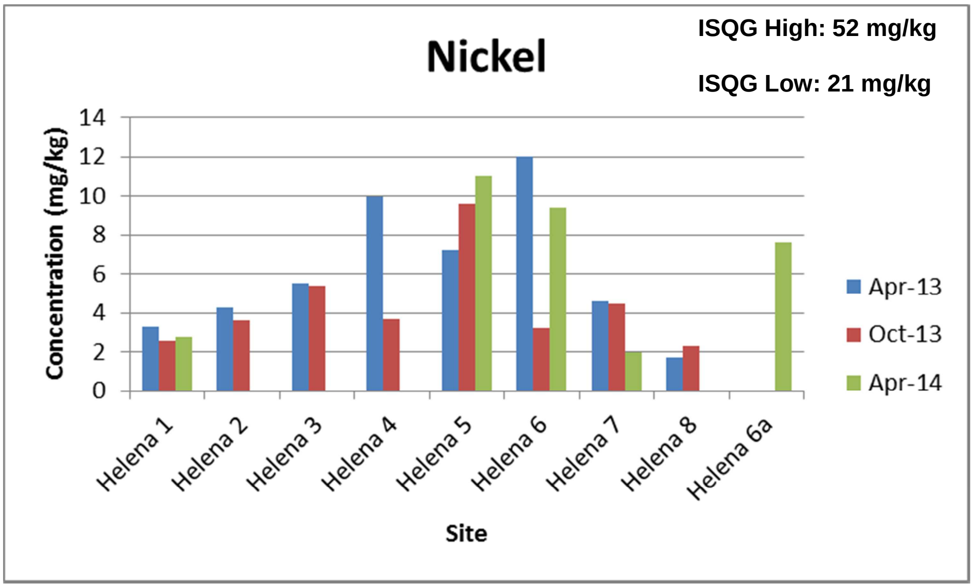


Figure 21: Nickel detected in sediment at sampling events; April & October 2013, & April 2014.

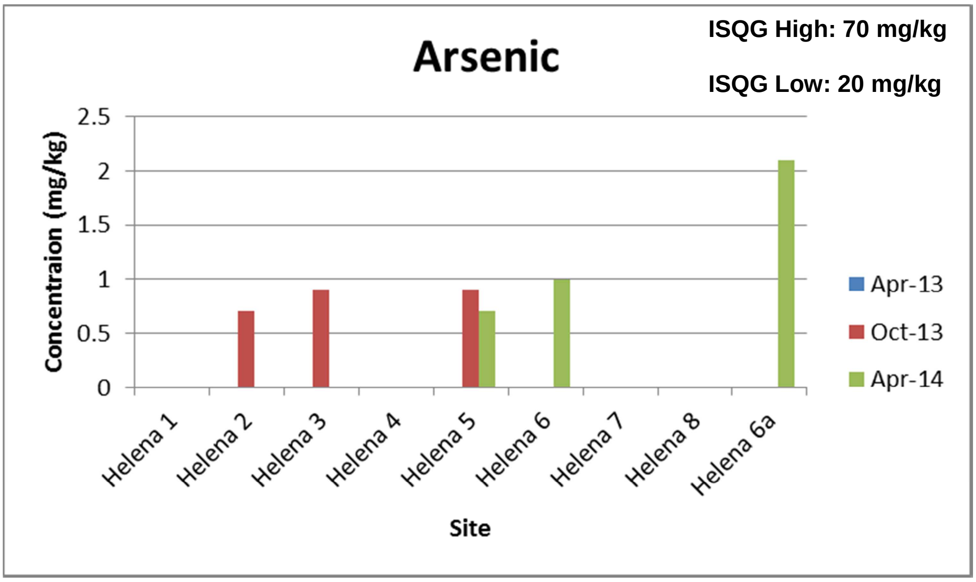


Figure 22: Arsenic detected in sediment at sampling events; April & October 2013, & April 2014.

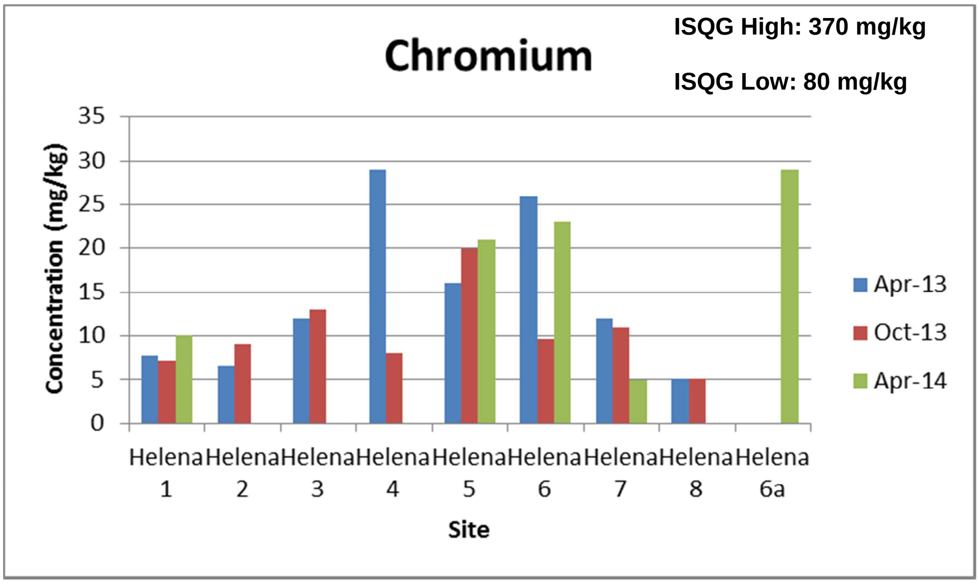


Figure 23: Chromium detected in sediment at sampling events; April & October 2013, & April 2014.

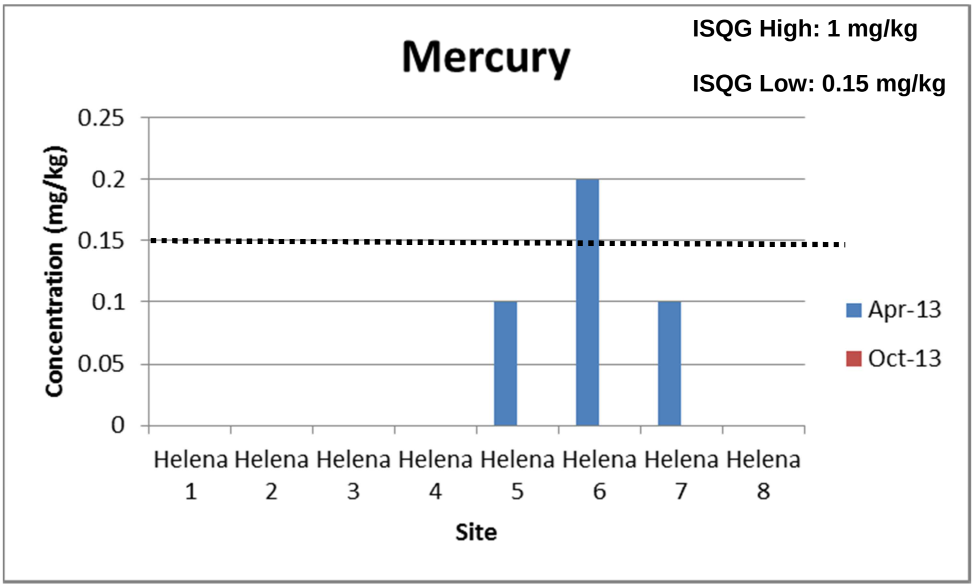


Figure 24 : Mercury detected in sediment at sampling events; April & October 2013, & April 2014.

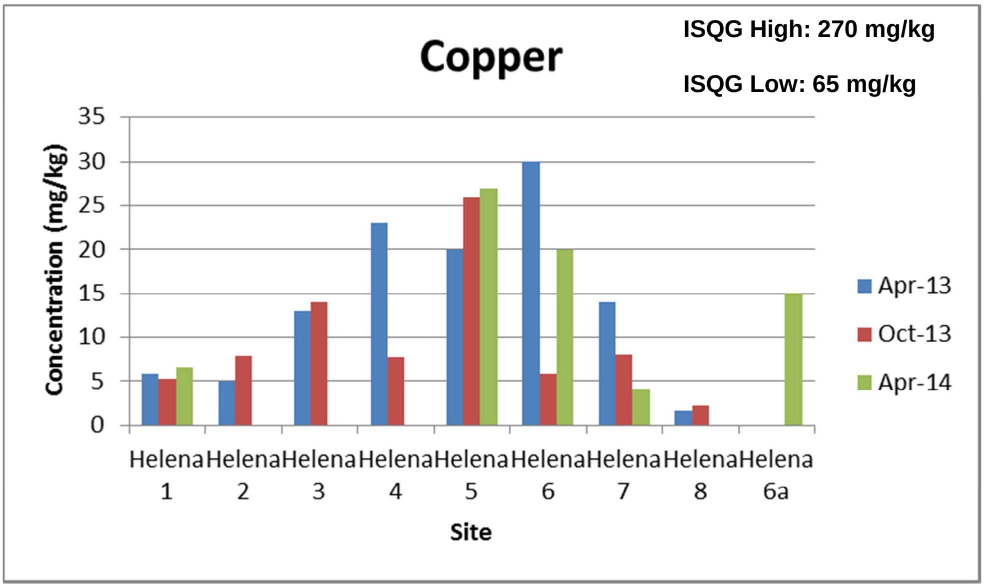


Figure 25: Copper detected in sediment at sampling events; April & October 2013, & April 2014.

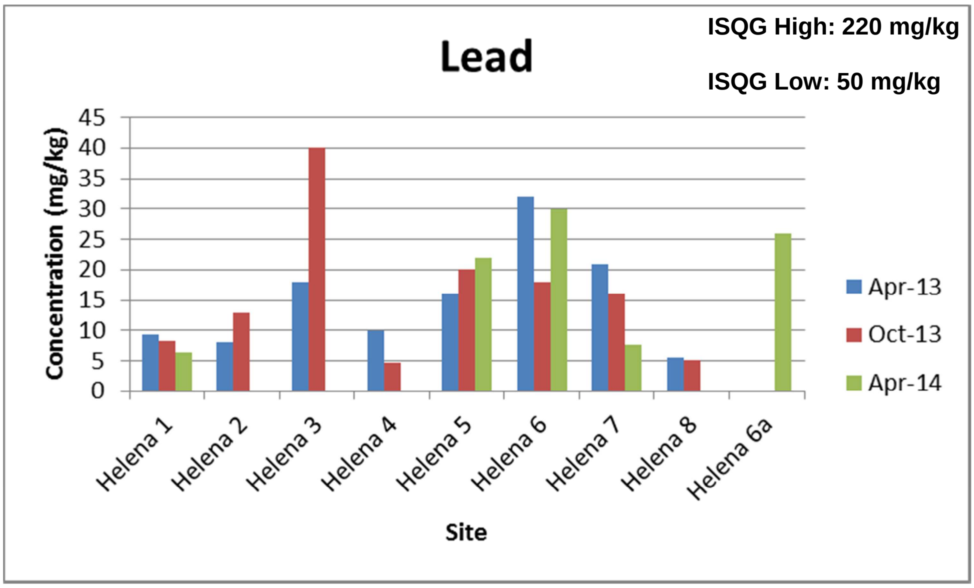


Figure 26: Lead detected in sediment at sampling events; April & October 2013, & April 2014.

4.6 PAHs and TPHs in sediment and water

Polycyclic Aromatic Hydrocarbons (PAHs)

- PAHs detected in this study were; acenaphthylene, 2-Methylnaphthalene, Naphthalene, Phenanthrene, Anthracene, Fluoranthene, Benz(a)anthracene, Pyrene, Benzo (b+ k) fluoranthene, Benzo (a) pyrene, Indeno (1,2,3,c,d) pyrene, Benzo (g,h,i) perylene and Chrysene (Table 4).

- PAHs were consistently detected in sediment with four PAHs (Fluoranthene, Pyrene, Benzo (a) pyrene, and Chrysene) detected in every sediment sampling event (Table 4) and in every sample from Helena 6. PAHs were only detected on one occasion in water samples (October 2013) and only at Helena 4 and 5. These were; 2-Methylnaphthalene and Naphthalene.

- The highest abundance of PAHs was detected at Helena 6, with levels and diversity of PAHs decreasing in Helena 5 and 7. There was one exceedance of the ANZECC ISQGs with levels of phenanthrene at Helena 6 (Figure 27). Although no other PAH data exceeded the low trigger value ISQGs, anthracene (concentration: 0.073 mg/kg; ISQG low: 0.085 mg/kg) and fluoranthene (concentration: 0.58 mg/kg; ISQG low: 0.6 mg/kg) came very close to exceeding the low trigger value.

Total Petroleum Hydrocarbons (TPHs)

- Petroleum hydrocarbons were only detected in sediment and only at the April sampling events. Most abundantly in April 2013. A decreasing gradient of Total TPHs was detected between Helena 5, 6 and 7.

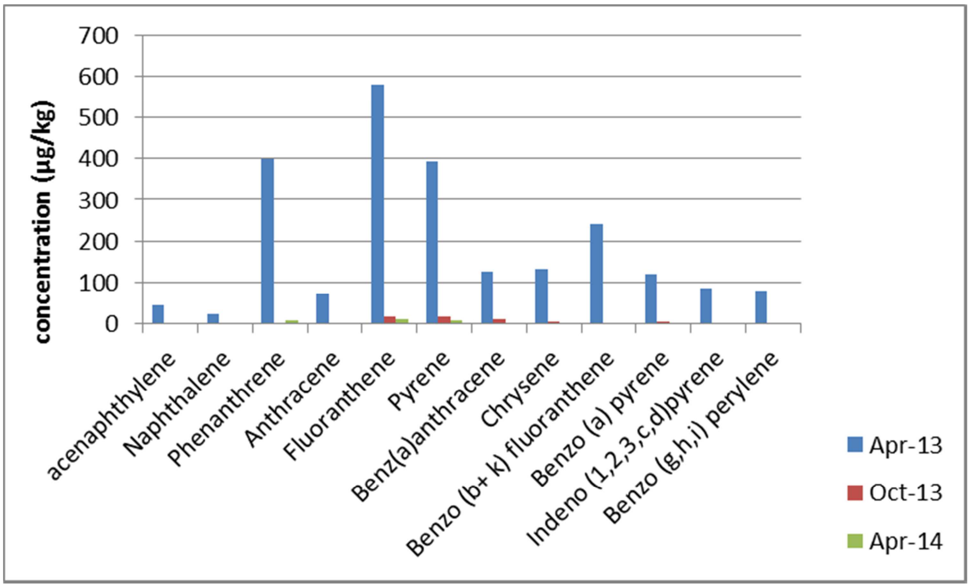


Figure 27: Total PAH concentrations (µg/kg dry weight normalised to 1% organic carbon) detected in sediment at Helena 6 at sampling events; April and October 2013, and April 2014

Table 4: PAH concentrations detected at all sites (expressed in µg/kg dry weight). Note: data not normalised to organic carbon percentage.

	Helena 1			***Helena 2***			***Helena 3***		
PAH µg/kg	Apr 13	Oct 13	Apr 14	Apr 13	Oct 13	Apr 14	Apr 13	Oct 13	Apr 14
Acenaphthylene	▨	▨	▨	**20**	▨	▨	▨	▨	▨
Naphthalene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Phenanthrene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Anthracene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Fluoranthene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Pyrene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Benz(a)anthracene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Chrysene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Benzo (b+ k) fluoranthene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Benzo (a) pyrene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Indeno (1,2,3,c,d)pyrene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Benzo (g,h,i) perylene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Total PAHs	▨	▨	▨	▨	▨	▨	▨	▨	▨

	Helena 4			***Helena 5***			***Helena 6***		
PAH	Apr 13	Oct 13	Apr 14	Apr 13	Oct 13	Apr 14	Apr 13	Oct 13	Apr 14
Acenaphthylene	30	▨	▨	180	▨	▨	690	▨	▨
Naphthalene	▨	▨	▨		▨	▨	380	▨	▨
Phenanthrene	▨	▨	▨	50	▨	▨	6000	▨	110
Anthracene	▨	▨	▨		▨	▨	1100	▨	▨
Fluoranthene	▨	▨	▨	90	▨	50	8700	30	170
Pyrene	▨	▨	▨	60	▨	30	5900	30	130
Benz(a)anthracene	▨	▨	▨	30	▨	20	1900	20	20
Chrysene	▨	▨	▨	30	▨	▨	2000	10	30
Benzo (b+ k) fluoranthene	▨	▨	▨		▨	▨	3600	▨	30
Benzo (a) pyrene	▨	▨	▨	40	▨	▨	1800	10	30
Indeno (1,2,3,c,d)pyrene	▨	▨	▨		▨	▨	1300	▨	▨
Benzo (g,h,i) perylene	▨	▨	▨		▨	▨	1200	▨	20
Total PAHs	▨	▨	▨	500	▨	▨	34000	▨	550

▨ < LOR

	Helena 7			***Helena 8***			***Helena 6a***		
PAH	Apr 13	Oct 13	Apr 14	Apr 13	Oct 13	Apr 14	Apr 13	Oct 13	Apr 14
Acenaphthylene	80	▨	▨	▨	▨	▨	▨	▨	▨
Naphthalene		▨	▨	▨	▨	▨	▨	▨	▨
Phenanthrene	20	▨	▨	▨	▨	▨	▨	▨	▨
Anthracene		▨	▨	▨	▨	▨	▨	▨	▨
Fluoranthene	40	▨	▨	▨	▨	▨	▨	▨	▨
Pyrene	40	▨	▨	▨	▨	▨	▨	▨	▨
Benz(a)anthracene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Chrysene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Benzo (b+ k) fluoranthene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Benzo (a) pyrene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Indeno (1,2,3,c,d)pyrene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Benzo (g,h,i) perylene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Total PAHs	▨	▨	▨	▨	▨	▨	▨	▨	▨

▨ < LOR

Table 5: Polycyclic Aromatic Hydrocarbons in water

	October 2013							
Site >	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Analyte (µg/L)								
Naphthalene				0.1	0.1			
2-Methylnaphthalene				0.1				

Table 6: Total Petroleum Hydrocarbons in sediment

	April 2013										April 2014		
Site >	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**1**	**5**	**6**	**7**	**6a**
Analyte (mg/Kg)													
TPH C6 - C9		26		26	180	180	180						
TPH C10- C14		81	150	170	720	420	310						
TPH C15- C28		410	220	1000	4900	4100	2700			450			120
TPH C29 - C36		640	360	1200	4500	4400	3000						
Total TPH		1200	730	2400	10,000	9000	6200			450			

▨ < LOR

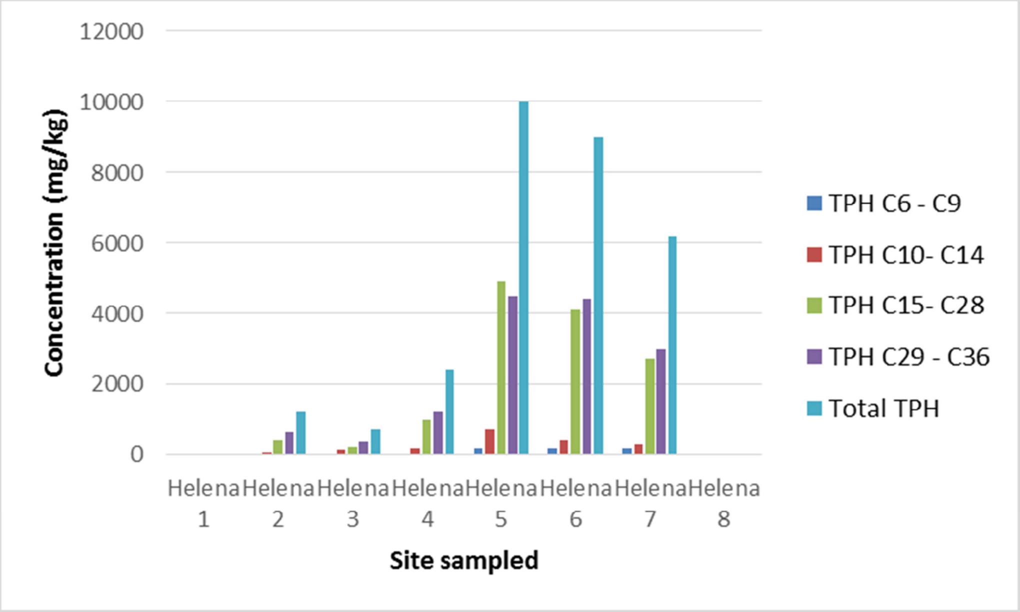


Figure 28: Total Petroleum Hydrocarbons detected in sediment in April 2013.

5 Discussion

Trends for in-situ water quality data were generally as expected, such as seasonal changes in water temperature due to increased rainfall, connection of the river and subsequent filling of pools.

Low pH at Helena 1 in April 2013 may be attributable to iron reducing bacteria as iron flocculates were noted on the day of sampling. Conductivity values fluctuated with seasonal rainfall and river flow however, Helena 1 showed high variations which are likely due to saline mixing caused by intrusion of estuarine water during the drier months. Helena 8 did not vary and was consistently high due to its position in the landscape and being fed by a saline spring.

Low dissolved oxygen was unlikely to be a function of the presence of organic matter as sites with low dissolved oxygen (Helena 1,2 and 3) did not correspond with sites that showed high organic matter (Helena 5 and 6). Helena 6a, although sampled only once, was well oxygenated but also showed relatively high organic matter.

In general, a large spike in contaminants occurred in both sediment and water from the middle Helena sites; Helena 5, Helena 6 and Helena 7 for all contaminant groups. Most contaminants were detected more frequently and at higher concentrations in sediments. The heterogeneous nature of sediments means that their size distribution can vary considerably over very short periods of time, influencing sediment contaminants, and may explain the highly variable sediment contaminant data obtained between sampling events. Some contaminants in water demonstrated seasonal influences, with lower sites showing peaks in some contaminants after winter rains.

5.1 Organics

5.1.1 Adjuvant- surfactants

Surfactants were measured in this study using the MBAS assay which specifically measures anionic (negatively charged) surfactants. Cationic (positively charged) and non-ionic surfactants were not measured in this study.

Surfactants are used in household and industry to increase the effectiveness of active ingredients within herbicides and other products. They enter water ways through waste water and overland flow. Surfactants are known to have varying degrees of toxicological effects in aquatic ecosystems (ANZECC/ARMCANZ, 2000) but the presence of surfactants in water also increases the mobility of other pollutants increasing their bioavailability.

Higher levels of anionic surfactants were detected in the lower sites (Helena 1, 2, 3) and this was probably due to the surrounding land-use such as agriculture and industry. Another influence may be the flow of pollutants downstream, with higher levels in July after winter rains than at any other sampling. A gradient of increasing concentration was also seen between Helena 6 and 7 which may suggest a source entering the river at Helena 6.

Possible sources of surfactants within the Helena River are herbicide application or household and industrial waste water. The application of Class A fire suppressant foams is also a known cause of surfactant contamination in the environment (Adams and Simmons, 1999).

Howe *et al*. (2001) found that surfactants and surfactant blends contained within popular glyphosate formulations were likely to be the most toxic component of these products. The polyethoxylated tallowamine surfactant (POEA) was shown to cause growth abnormalities in tadpoles, inhibited metamorphosis and a skewed sex ratio towards female tadpoles. These types of effects suggest endocrine disruption caused by surfactants. The above mentioned is the same surfactant which is contained within the most commonly used glyphosate product within the Helena River catchment.

It is important to note that high salinity levels within the Helena River (Smith *et al*., 2007) and particularly in the upper Helena, which is spring fed by a salt water aquifer; may have also influenced results obtained during this study. It has been noted that results obtained from the MBAS assay can be strongly influenced by the presence of salts, namely chloride ions. With elevated chloride levels, this interference can be significant (Çetintürk and Güven, 2009), (George and White, 1999).

None the less, due to the widespread use of surfactants in the Perth metropolitan region it is certain that surfactants are present in water ways and therefore further clarification is required to determine the source of MBAS in this study, and to eliminate other possibilities such as the transport of pollutants within groundwater.

It is worth noting that previous studies (Nice *et al*., 2009) did not detect surfactants in surface water in the drainage of the Helena River sub-catchment. This may suggest overland flow to be the main contributor of anionic surfactants to the Helena River or alternatively a diluting effect on surfactants in drainage systems and a concentration effect in pools.

5.1.2 Glyphosate

Glyphosate based formulations are of the most widely and intensively used pesticides worldwide, being sold primarily as the isopropylamine salt and used as a foliar spray or applied as a concentration and wiped over foliage (US EPA, 2013).

Glyphosate enters the environment when it is used for non-selective control of woody and herbaceous weeds in food production, forestry and for the management of native vegetation. It is also used around water ways and can enter wetlands, streams and rivers in this way. Glyphosate can also enter the environment during manufacture, transport, storage, disposal and spills.

When entering the environment it has a strong tendency to adsorb to the upper layers of sediment. Especially those sediments high in aluminium and iron oxides (US EPA, 2013), which is a prominent characteristic of sediments of the Darling Scarp laterite. This may be a reason this study detected glyphosate in sediment and not water.

Furthermore, glyphosate has been shown to have a half-life of between 35 and 60 days but within water bodies high in organic material and suspended particles half-lives of as little as 1.5 to 11 days have been observed (Schuette,1998). The latter may suggest that this detection is due to a local input of glyphosate, especially considering the property bordering the river is a maintained grass area that may have been subject to weed control treatment. It is possible that a more regular sampling regime may result in more frequent detections of glyphosate.

Exposure studies have been undertaken to determine acute toxicity effects of glyphosate to aquatic organisms but there is a large gap in knowledge of chronic effects over long periods of time and effects to different species and their differing life stages.

Concentration effects of glyphosate in shallow pools should also be considered. Rzymski *et al*., (2014) studied invertebrates in a lake that had received an acute load of glyphosate and found significant reductions (between 38% and 77%) in numbers of benthic organisms including worms, snails and insects at the sites that had been treated with glyphosate. It is likely that exposure rates in shallow pools would be significantly higher when glyphosate is being sprayed in these areas due to summer drying, substantially reducing water volume of pools, and creating a concentration effect for organisms living in pools.

With consideration of the above discussion, the limited number of sediment sampling events undertaken in this study and the lag time between events has acted as a hindrance to obtaining accurate estimates of the presence of pesticides such as glyphosate in sites sampled. Further studies are required to determine presence and persistence of glyphosate in summertime pools.

5.1.3 Other organics

DCPA

DCPA (Dimethyl tetrachloroterephthalate) also known as Dacthal is a pre-emergent herbicide that is used to control annual grasses and broadleaf weeds in both agricultural and ornamental landscaping settings. It is classed as a possible human carcinogen.

This study detected DCPA in surface water in April 2013 and no detections occurred thereafter. There are no guidelines for the presence of DCPA in surface waters. The half-life of this compound in surface water in the presence of sunlight is 3 days so this is likely to be the reason it was not detected in sediment and may suggest a recent input to the system. It is worth noting that the single detection does not suggest this chemical was not present on other occasions. Its rapid degradation means that a more frequent sampling regime is required to determine the full extent of the presence of DCPA in pools.

In surface water, DCPA rapidly degrades into the metabolite Tetrachloroterephthalic acid (TPA). TPA is particularly mobile and persistent in the field. Data suggests that TPA will leach to groundwater wherever DCPA is used regardless of the soil type (US EPA, 1998). In addition, volatilisation from soil is a major source for DCPA residue on surface areas such as other plants, where it has not been applied. Future analyses sampling programs should include analysis for TPA in sediment, surface water and groundwater at this site.

2,4-D

2,4-dichlorophenoxyacetic acid is an acidic herbicide used to control various broadleaf weeds.
Studies have found Toxicity of 2,4-D to vary considerably depending on the particular formulation it is contained within, and large variations in toxicity between test species. As found with other herbicides, toxicity effects of herbicide formulations were found to be far more severe than the 2,4-D alone (US EPA, 2004).

Due to the breakdown of this herbicide in the aqueous environment, 2,4-D is most commonly found as the free anion which makes it near impossible to test for and identify separate formulations. The low level detected in this study should be used as an indicator for further sampling to occur. No effects on ecosystem health can be assumed at this stage.

5.2 Metals

Metals can be contributed to surface waters and sediments from road runoff due to brake and tyre deterioration, fuel combustion, roof runoff, municipal waste sites, and various industrial activities such as metal refining and chemical manufacturing.

Metals were found in sediment and water and often exceeded the water quality guidelines for 95% ecosystem protection (ANZECC/ARMCANZ, 2000), however did not often exceed ISQGs. It is important to note that metals detected in surface water are for ‘total metals’ only, they were not filtered to remove suspended sediments and therefore these results do not necessarily reflect metal bioavailability. Future studies should use dissolved metal concentrations as a suggestion of metal bioavailability.

With the exception of iron and aluminium, metals in water were detected more sporadically. This is likely due to the fact that this study sampled summertime pools which disconnected from one another for a large portion of the year when the river was not flowing, therefore disallowing the complete transport of metal contaminants downstream. Aluminium and iron concentrations may have been more consistent throughout sites due to the inherent nature of these in the lateritic soils of this catchment. Metals may be released from the sediment in each pool. Aluminium was highest in the lower sites at the end of July, which may suggest the transfer of metals down the river in winter rainfall.

Iron detected in water at Helena 1,2 and 3 was higher in January and April when dissolved oxygen was also very low which might suggest a connection between low dissolved oxygen and metal release from sediment.

In contrast to water, with the exception of mercury and arsenic, sediment metal concentrations were more consistent across sites and tended to be highest in sediments from the middle Helena. This was likely due to the high levels of organic carbon this study found in sediments of the middle Helena.

The fate of heavy metals in aquatic environments is determined largely by the presence of biofilms on sediment. Metals will readily adsorb to sediment that is high in organic material especially those coated in metal oxides such as oxides of iron and manganese. These interactions make metals more stable bound to sediment and more likely to move out of the water column.

Chromium in water exceeded the ecosystem protection guideline on 5 occasions. Sources of chromium contamination in waterways can come from various activities such as textile, chemical and steel manufacturing as well as vehicle brakes and catalytic converters. Toxicity of chromium is dependent on its ionic state as this will determine is biological activity in the environment. Hexavalent chromium is most commonly produced by industrial processes and is much more toxic than its other forms. pH has also been shown to have dramatic consequences for ecosystem health, such as chromium toxicity in the early life stages of fresh water carp (Stouthart *et al*, 1995). Thus further investigation is required to determine the form of chromium present and its capacity for toxicity.

The detection of lead above Canadian ISQG GL and unusually high levels of copper, zinc and iron in water at Helena 3 may suggest an historic source of contamination. A contaminated site exists approximately 800 m north east of this site where a clay mine was in operation prior to 1950. Clay pits were subsequently filled with industrial wastes comprising of bituminous sludge, oily residues and acidic wastewater. Remediation to contain contaminated soil and groundwater was not undertaken until 1998. This may have caused contamination of the Helena River in this location.

It is still important to note that measures of lead do not necessarily indicate bioavailability as the presence of iron oxides in sediment under oxidising conditions has been shown to strongly immobilize and tightly bind lead to sediment. Previous studies on bottom dwelling organisms suggest that iron rich sediment can inhibit lead bioavailability (John and Leventhal, 1996).

Nonetheless, lead has a tendency to bio-accumulate in macrophytes and benthic organisms (US EPA, 2011) and with a lack of bioavailability data, further sampling and analysis is required to determine the level of risk this poses to aquatic organisms at sites where lead was detected.

It is evident from this study that a build-up of heavy metals exists in the middle reaches of the Helena River, with mercury exceeding GL levels at Helena 6. This may be due to historical influences, such as the train line built in the late 1800's which crossed over this part of the Helena River.

It is important to understand physiochemical influences on the bioavailability of metals in aquatic environments. Such as with decreasing pH, metals desorb from surfaces, become mobile and prone to speciation. Adsorption capacity of metals varies considerably at varying pH values. Other influences such as temperature affect the speed of chemical and metabolic processes, further influencing bioavailability and uptake of these contaminants (John and Leventhal, 1996).

Further studies should be conducted to assess bioavailability of metals and the possible sources for these metals.

5.3 PAHs

Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are a class of organic compounds that contain two or more fused aromatic rings and only hydrogen and carbon atoms. They enter the environment from incomplete combustion of organic matter such as wood burning, asphalt roads, car bodies and motor vehicle exhaust (Berko, 1999). Many are used in industry for making dye, plastics and pesticides.

Several PAHs are known to have carcinogenic effects and some have been shown to be endocrine disruptors and to cause birth defects in laboratory animals (US EPA, 2008).

PAHs enter aquatic environments in road runoff and waste water. When in these environments, their solubility is determined by factors such as pH, temperature, and dissolved oxygen, the bioavailability of other contaminants and the presence of organic matter and colloidal fractions. The rate of PAH breakdown is also determined by the number of aromatic rings, which determines the density of different PAHs (Berko, 1999).

It is also important to consider the bioavailability of PAHs to organisms in the receiving environment. The presence of organic matter in sediment will allow adsorption of PAHs to organic material, making it less available for uptake by organisms and controlling the leaching of PAHs down the soil profile (Petruzzelli *et al*, 2002).

This study detected low molecular weighted PAHs; naphthalene, phenanthrene and anthracene in sediment at Helena 6 which would suggest a recent and fresh input to the system. The same detections were not made when sampling was repeated the same time the following year. This might suggest that an acute input occurred at this time. Alternatively, rainfall patterns may have caused higher runoff from surrounding tributaries, with high rainfall events occurring in March 2013 (BOM, 2014).

Phenanthrene normalised to 1% TOC, exceeded the ISQG low trigger value at Helena 6. Further site specific studies are required to determine the toxicological relevance of this detection.

Frequent detections of Fluoranthene, Pyrene, Benzo (a) pyrene and Chrysene in sediment may be due to their 4 and 5 ring structure, having a lower solubility and higher persistence than lower molecular weighted PAHs. Possible sources for these compounds are numerous, with all being linked with vehicle exhaust, coal tar operations, combustion of organic matter and various industrial practices (Berko, 1999).

High levels detected at Helena 6 with decreasing levels at 5 and 7 might suggest Helena 6 to be receiving high levels of PAHs, and a dilution of contaminants with flows into Helena 5 and 7.

5.4 TPHs

Total Petroleum Hydrocarbons (TPHs)

TPHs refers to a family of several hundred compounds that are derived from crude oil. Due to the large number of chemicals found in crude oil, it is not practical to measure each one separately and so they are measured together as the TPH concentration.

Petroleum hydrocarbons enter the environment through the mining, processing, use and disposal of petroleum and petroleum products.

TPHs in the C29–C36 and C15-C28 range were found in considerably higher concentrations than those within C6-C9 and C10-C22 ranges. These lower detections may be due to the fact that those in the latter ranges (lower molecular weight) are considered to be more degradable due to their compound structure, thus are less likely to persist in the environment (Battelle, 2007).

A gradient of decreasing concentration of TPHs from Helena 5 to Helena 7 was observed. This may suggest a fresh input of hydrocarbons at Helena 5 at this time and may be due to surface runoff caused by the high rainfall event prior to sampling in April 2013, with just 7mm of rainfall recorded in March 2014 compared with 71mm in March 2013. However, this study did not gain sufficient data to determine any conclusive patterns in relation to season.

This study did not detect TPHs in water; this is likely due to the nature of hydrocarbons, having low solubility in water and a high affinity for adsorption to organic matter (Battelle, 2007), and may also explain the considerably lower concentration detected in downstream sites. *Nice et al., 2009* also did not detect TPHs in surface water samples when analysing a drain site on the Helena River.

5.5 Particle Size

Sediment Quality guidelines may be used to predict when toxic effects of a contaminant are unlikely to occur, however, they do not account for change in toxicity due to sediment type, species specific effects and other environmental variables (Canadian Council of Ministers of the Environment, 1995).

Sediment fraction type and proportion, influences the oxidation and reduction potential of sediments and surrounding water. Consideration of sediment composition is essential in interpretation of the toxicological capacity of pollutants. For example, silt and clay fractions have been found to aid in the breakdown of PAHS by increasing their bioavailability (Cui *et al*, 2010), making them available for breakdown by micro-organisms in sediment.

Further, coarse sand fractions compared with silt and clay will have greater pore water and the potential to store compounds within these micro niches. The physio chemical characteristics of pore water can differ strikingly from those of surrounding water and sediments. Microorganisms living within burrows in sediment are more exposed to compounds in pore water compared with those adsorbed to sediment particles. Therefore, pollutant exposure from pore waters is generally more evident than exposure from sediments (Winger and Lasier, 1997).

Due to the influence of season and flow on sediments, particle size distribution should be determined at every sampling event. Therefore no strong inferences can be made between contaminant data and sediment particle distribution from this study.

6 Reference to previous studies

The EMRC and Wetland Research and Management (WRM) conducted fish and macro-invertebrate surveys in 2010 and 2011 to determine species composition in permanent pools along the Helena River. Findings concluded that species richness was highest at a site in the lower Helena but this was due to the presence of estuarine and marine vagrants. However, native species abundance was lower at these sites. Sites in the upper reaches of the river showed higher abundance but medium species richness.

They concluded that physical alterations to the river flow (i.e. obstructions to gene flow caused by the Lower Helena Reservoir and the Mundaring Weir) were in large part causal to these low numbers and diversity of native fish and crayfish. However, it was advised that water quality analyses be undertaken to determine if other pressures existed.

Further sampling and analysis is required to determine any conclusive links between fish paucity and pollutants in the river. However, the current study can conclude the following:

- Helena 6 was found to contain the highest concentrations and most frequent detections of pollutants; heavy metals and PAHs and TPHs. Data suggested this site to be receiving a recent or fresh source of PAHs (Figure 29). WRM also found this site to have the **highest abundance of exotic species** of all sites studied, with a **very low abundance of native** species. Mostly composed of the exotic freshwater fish *Gambusia*.

- A decreasing gradient in concentration and diversity of pollutants was detected from Helena 6 to Helena 5 and Helena 7. Fish studies showed species richness of native fish to increase between Helena 6 and 5 with pools 6 and 7 to show similar species richness but a greater abundance of native species in pool 7. Exotic species abundance also followed the same trend with a decrease in abundance from Helena 6 to Helena 5.

This comparison might suggest that sites with better water quality are supporting species to persist and reproduce in these pools and supporting a greater diversity of species as conditions become more favourable for more species.

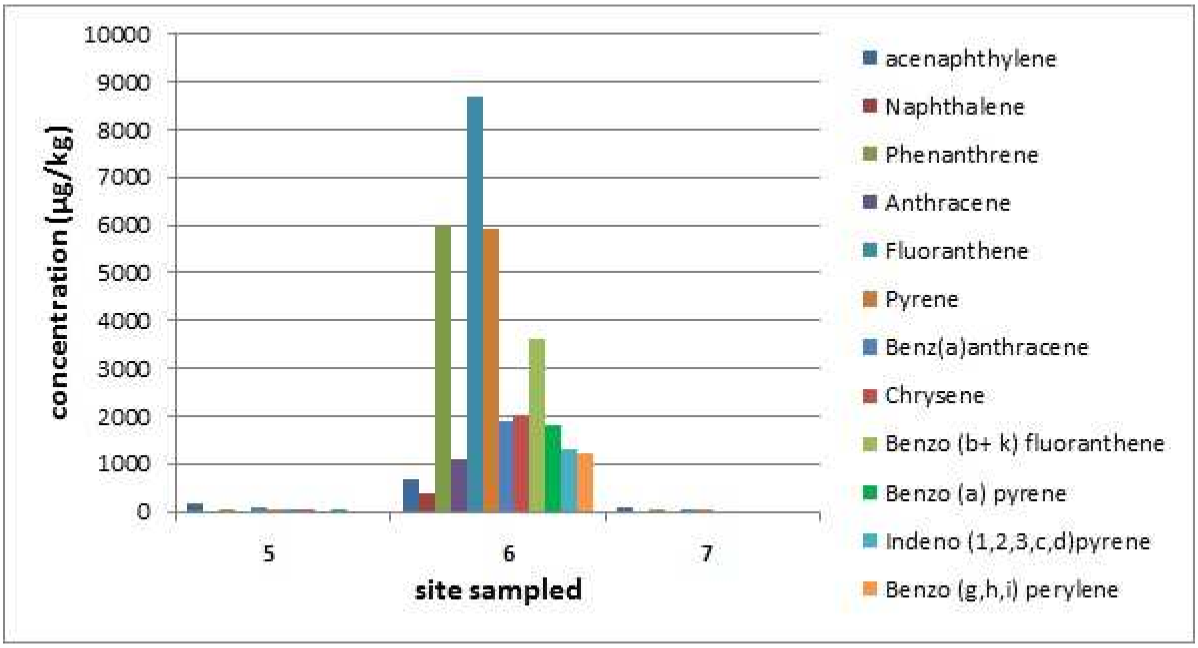


Figure 29: Raw data for PAH concentrations (µg/kg dry weight) detected in sediment at Helena 5, 6 and 7 in April 2013.

The middle Helena River has been earmarked previously, where Klunzinger *et al*., 2012 found deformed mussel shells in the Lower Helena Reservoir. It is suggested that shell deformities often occur due to long term exposure to heavy metals and agricultural and industrial chemicals (Klunzinger *et al*., 2012).

This study could not make clear connections between mussel shell deformities and heavy metal contaminants; however we have identified the middle Helena as a hot spot for pollutants. Further, considering this water flows into the Lower Helena Reservoir and may accumulate for an extended period before being pumped back up stream, it is possible that contaminant exposure to mussels within the dam would be magnified.

Piesse Brook, a main tributary to the Helena River which also flows directly into the Lower Helena Reservoir, transverses land uses such as orchards and hobby farms where chemicals may be used to aid production. Therefore this may be an important area for focus of future investigations.

Although toxicity effects of common herbicides have been demonstrated for some aquatic species, toxicity effects for surfactants within herbicide formulations are not well understood and those studies that have taken place have found detrimental chronic effects to be caused by common herbicide emulsions and especially from their component surfactants alone: e.g. Howe *et al*. (2001).

Bundock *et al.*, (2013) analysed germination rates for Western Australian native seeds treated with commonly used surfactants and herbicides. Germination rates were compared to those of seeds from the controls and it was found that adjuvants often had a greater effect on germination than the active ingredients (herbicides) they were combined with. Of the test species studied, 7 out of 10 were negatively affected by two of the adjuvants studied, the third adjuvant negatively affected germination and development in all 10 species studied. Adjuvants reduced germination by as much as 65%. It is therefore important that surfactant analysis be a focus for future research.

It is also very important to note that there is a severe lack of focus on pesticide formulations, the toxicology of their individual constituents, degradates of these constituents and how these constituents interact with one-another at a molecular level as they break down. When bioaccumulation of glyphosate was measured in the benthic invertebrate *Lumbriculus variegatus*, it was shown that the accompanying constituents of the particular glyphosate formulation in question had more eco-toxicological relevance than the glyphosate itself (Contardo-Jara *et al*., 2008). Pesticide formulations and the inter toxicity effects during their breakdown in solution requires greater focus.

7 Conclusion

This study found issues with contaminants within the middle reaches of the Helena River and select sites in the Lower Helena River. Key contaminants identified were; PAHs, heavy metals, anionic surfactants and herbicides.

The results of this study have found issues with heavy metals, surfactants and hyrdrocarbons, particularly PAHs. Hydrocarbon data suggests a possible connection between native fish paucity, the abundance of exotic fish; and pollutants in the river. Further investigation is required to obtain enough data to complete a statistical analysis of this relationship.

This study determined relative abundance and diversity of total metals only in sediment and water. Our results did not account for the environmental interface of microorganisms in sediment such as metals contained in pore waters or metals attached to particulate matter. Our study also did not analyse sediment physiochemical parameters and therefore does not account for speciation of metals under different physiological conditions and how this might determine metal bioavailability, bioaccumulation or toxicological effects in the environment.

The current study only allowed for snapshots of pollutants at time of sampling and does not take into consideration the environmental fate and breakdown of pollutants in wetland environments. This was a baseline study only and further investigations must encompass regimes of long term sampling together with collection of sediment toxicology data for sites identified as a priority.

Further extensive assessment and evaluation of aquatic toxicity of pesticide formulations is still required to be undertaken by government bodies and associated research organisations to determine the true risks that are involved with pesticide use.

8 RECOMMENDATIONS FOR MANAGEMENT

Major Issues

The main pollutants identified through this study were; heavy metals, PAHs and TPHs, and surfactants. It is important to note that these results do not suggest that other contaminants such as pesticides are not present in the system or causing ecosystem toxicity effects. The sparse nature of data obtained through a grab sampling program such as this does not give a true and embodied representation of water quality in the Helena River sampling area. This study is intended as a baseline on which further investigations should be based.

Although many of the contaminants tested for in this study were not detected, it should be noted that unsuitable limits of reporting exist for many of the contaminants and therefore these results do not suggest that contaminants are not present. If more suitable levels of reporting become available, a similar study should be repeated.

Recommendations:

- Revegetation and rehabilitation of riparian vegetation along channels to sites that were found to have contaminants and of areas directly fringing industrial and agricultural activities, such as Helena 1 and Helena 3. This can prevent runoff of contaminated sediment into the river and act as a barrier for flow of windblown particles into the waterway.

- Conduct a whole sediment toxicity investigation and bioaccumulation study at Helena 6, including a gradient study to determine source of hydrocarbon pollution between Helena 5, 6 and 7. Pore water should be tested for presence and concentration of hydrocarbons. If toxicity exists then benthic community structure should be analysed to determine extent of influence.

- Further analyses for non-ionic and cationic surfactants in summertime pools. Any further analyses for surfactants should aim to use methods alternative to the MBAS assay to eliminate this as a possible source of inaccuracy.
    - If subsequent studies show surfactants to be present in the pool Helena 8 then groundwater should become a focus for future analyses of surfactants.

- Develop a long term monitoring plan to identify spikes or changes in water quality that would normally be missed in a grab sampling program. This program should include metal analysis for total dissolved metals and acid soluble metals to determine actual bioavailability of metals in associated samples.

- Engage landholders and business owners to develop a pesticide tracking program to record usage, including amounts, locations and timing of pesticide applications so that a reference database can be created that enables hot spots and target areas for management to be established.

- Future studies should focus on the existence of pollutants within fish and mussel tissue as this will allow the detection of pollutants such as OC pesticides and heavy metals which are known to resist breakdown in ecosystems through persistence and bioaccumulation within animal tissues.

Table 7: Key issues identified and recommendations for their management

<table>
<tr><th>Identified issue</th><th colspan="2">Research</th><th>Management</th></tr>
<tr><td rowspan="2">Pesticides and heavy metals</td><td rowspan="2">Fish and mussel tissue analysis for heavy metals and pesticides especially those known to bio-accumulate.</td><td rowspan="4">Long term monitoring program to pick up spikes and changes in water quality that would be missed in a grab sampling program.</td><td>Rehabilitation of existing riparian vegetation and revegetation of areas bordering pools especially those identified- Helena 1 and Helena 3.</td></tr>
<tr><td rowspan="3">Development of pesticide tracking programs to record usage of pesticides in industrial and agricultural settings in the Helena River Catchment. Particularly the Piesse Brook.
Continue to work with research organisations and relevant government agencies (Department of Water, Swan River Trust) to improve water quality of the Helena River Catchment.
Develop a community engagement and education program relating to the impacts of non-nutrient contaminants on water quality in the Helena River.</td></tr>
<tr><td>PAH and TPH contamination in the Middle Helena River</td><td>Sediment toxicology investigation and gradient study at Helena 5, 6 and 7.</td></tr>
<tr><td>Anionic surfactants</td><td>Further analyses for non-ionic and cat-ionic surfactants in water at all sites.</td></tr>
</table>

9 ACRONYMS

DCPA:	Dimethyl tetrachloroterephthalate
DO:	Dissolved oxygen
DoW:	Department of Water
EHCMP	Eastern Hills Catchment Management Program
ISQG:	Interim Sediment Quality Guidelines
LOR:	Level of Reporting
MBAS:	Methylene Blue Active Substances
NATA:	National Association of Testing Authorities
ND:	Non detect
OC pesticide:	Organochlorine pesticide
OP pesticide:	Organophosphorus pesticide
PAH:	Polycyclic Aromatic Hydrocarbon
TOC:	Total Organic Carbon
TPH:	Total Petroleum Hydrocarbon
WRM:	Wetland Research and Management

10 Glossary of terms

Bioaccumulation: The increasing concentration of a compound in the bodies of living organisms at a higher concentration than that of surrounding mediums and a resulting successive increase in concentration through the food chain.

Bioavailable: The proportion of total chemical in the environment that is available to be taken up by organisms.

Detection limit: The lowest concentration of a substance that can be reported as present with a specified degree of certainty by definite complete analytical procedures.

Endocrine disruptor: A chemical that can interfere with an organism's hormone system and produce adverse developmental, reproductive, neurological, and immune effects for that organism or its progeny.

Heavy metals: Those metals of relatively high atomic weight. These types of metals cause toxic effects especially to nervous systems.

Oxidation: The combination of oxygen with a substance or the removal of hydrogen from it, or any reaction in which an atom loses electrons.

Pesticides: "A pesticide is any substance or mixture of substances used to destroy, suppress or alter the life cycle of a pest… Pesticides include herbicides, fungicides, insecticides, fumigants, bactericides, rodenticides, baits, lures, repellents and pesticides used on animals to control external parasites" (New South Wales Environment Protection Authority, http://www.epa.nsw.gov.au/pesticides/Pesticides.htm).

Legally, a pesticide has the same 'definition as an agricultural chemical product' i.e. "a substance or mixture of substances that is represented, imported, manufactured, supplied or used as a means of directly or indirectly destroying, stupefying, repelling, inhibiting of, or preventing infestation by or attacks of, any pest in relation to a plant, a place or thing; or destroying a plat; or modifying the physiology of a plant or pest so as to alter it natural development, productivity, quality or productive capacity" (DoH 2010).

Polycyclic Aromatic Hydrocarbons (PAHs): A group of organic compound composed of carbon and hydrogen atoms that are formed during the incomplete combustion of coal, oil and gas, garbage, or other organic substances.

Surfactant: Compounds that lower the surface tension of a liquid, allowing for more efficient spreading of products such as herbicides, detergents, and foaming agents such as firefighting foams and retardants.

Total Petroleum Hydrocarbons (TPH): A large family of several hundred chemical compounds that are derived from crude oil and the production of petroleum products.

Pore water: The water contained in the spaces between sediment particles, in which sediment biota may be in direct association with.

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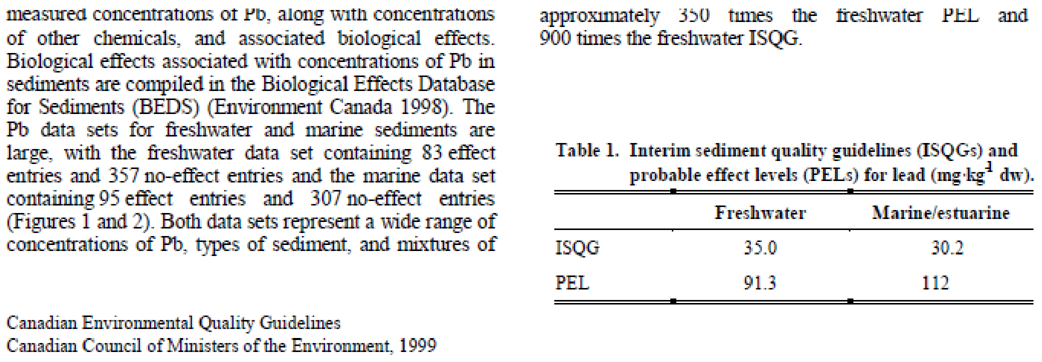
Appendix 1

Table 8: Canadian Interim Sediment Quality Guideline (ISQG) value and Probable Effect Level (PEL) for iron in water.



measured concentrations of Pb, along with concentrations of other chemicals, and associated biological effects. Biological effects associated with concentrations of Pb in sediments are compiled in the Biological Effects Database for Sediments (BEDS) (Environment Canada 1998). The Pb data sets for freshwater and marine sediments are large, with the freshwater data set containing 83 effect entries and 357 no-effect entries and the marine data set containing 95 effect entries and 307 no-effect entries (Figures 1 and 2). Both data sets represent a wide range of concentrations of Pb, types of sediment, and mixtures of

Canadian Environmental Quality Guidelines
Canadian Council of Ministers of the Environment, 1999

approximately 350 times the freshwater PEL and 900 times the freshwater ISQG.

Table 1. Interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for lead (mg·kg^{-1} dw).

	Freshwater	Marine/estuarine
ISQG	35.0	30.2
PEL	91.3	112

LEAD

Canadian Sediment Quality Guidelines
for the Protection of Aquatic Life

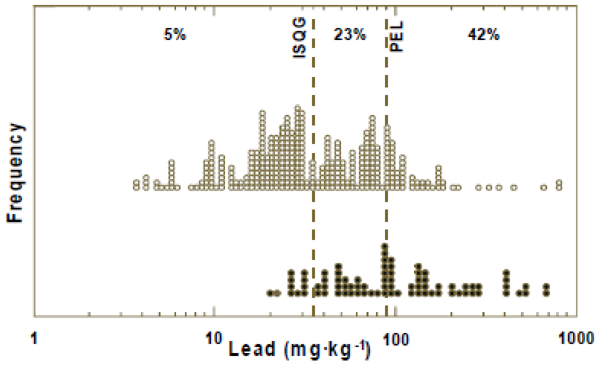


Figure 1. Distribution of concentrations of lead in freshwater sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.

Table 9: ANZECC Interim Sediment Quality Guidelines (ISQGs)

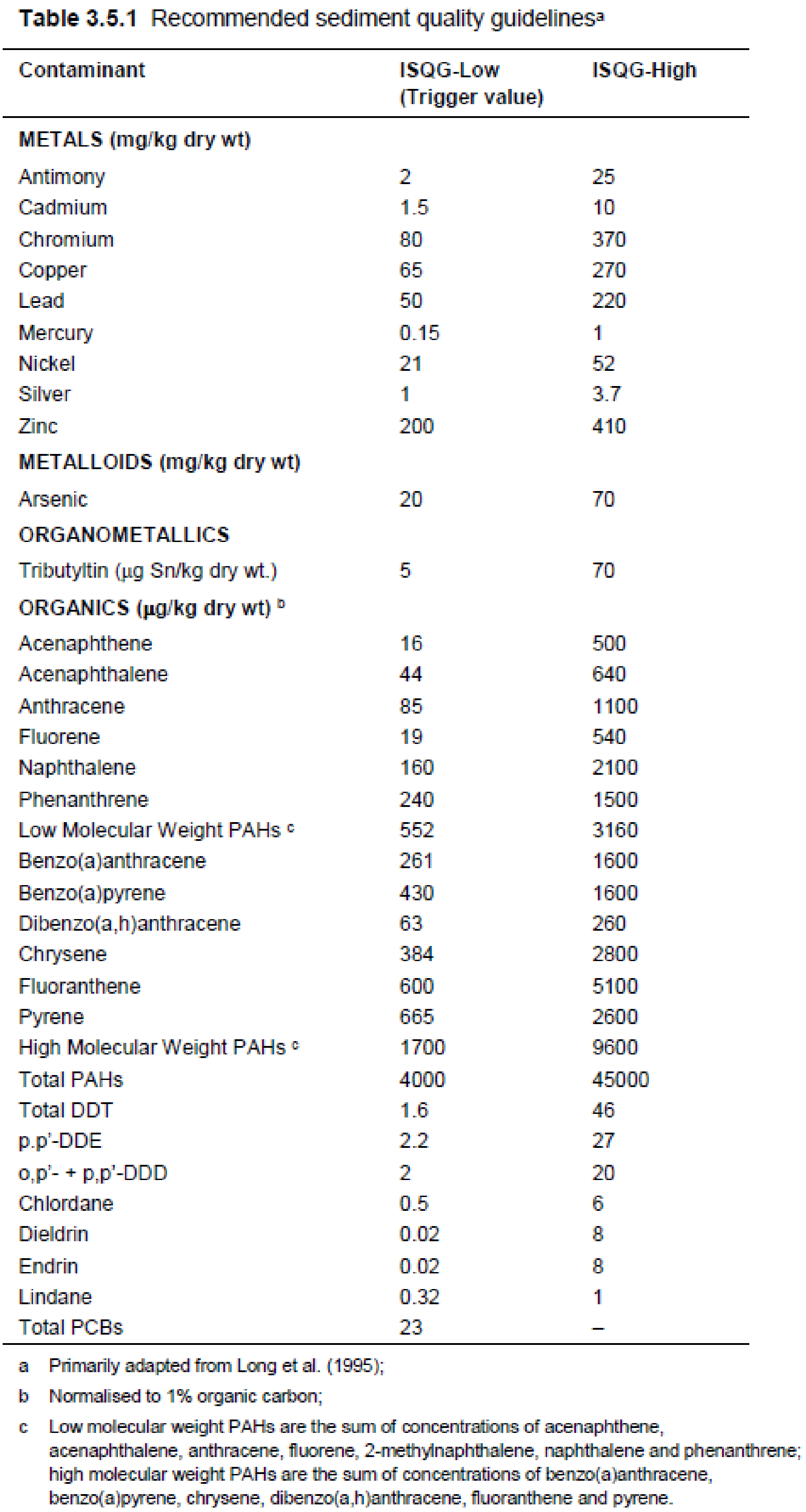


Table 3.5.1 Recommended sediment quality guidelines[a]

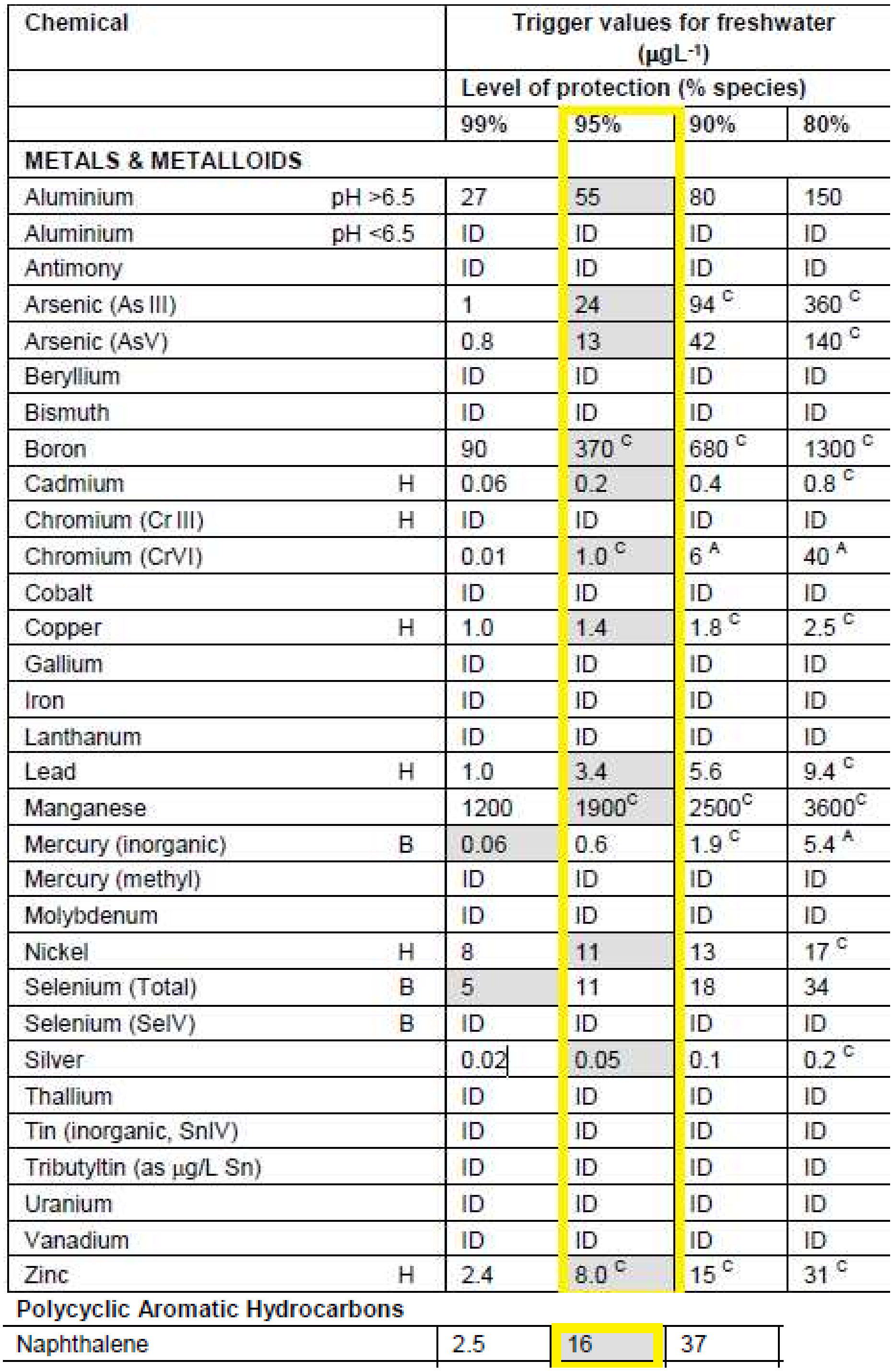
Contaminant	ISQG-Low (Trigger value)	ISQG-High
METALS (mg/kg dry wt)		
Antimony	2	25
Cadmium	1.5	10
Chromium	80	370
Copper	65	270
Lead	50	220
Mercury	0.15	1
Nickel	21	52
Silver	1	3.7
Zinc	200	410
METALLOIDS (mg/kg dry wt)		
Arsenic	20	70
ORGANOMETALLICS		
Tributyltin (µg Sn/kg dry wt.)	5	70
ORGANICS (µg/kg dry wt) [b]		
Acenaphthene	16	500
Acenaphthalene	44	640
Anthracene	85	1100
Fluorene	19	540
Naphthalene	160	2100
Phenanthrene	240	1500
Low Molecular Weight PAHs [c]	552	3160
Benzo(a)anthracene	261	1600
Benzo(a)pyrene	430	1600
Dibenzo(a,h)anthracene	63	260
Chrysene	384	2800
Fluoranthene	600	5100
Pyrene	665	2600
High Molecular Weight PAHs [c]	1700	9600
Total PAHs	4000	45000
Total DDT	1.6	46
p.p'-DDE	2.2	27
o,p'- + p,p'-DDD	2	20
Chlordane	0.5	6
Dieldrin	0.02	8
Endrin	0.02	8
Lindane	0.32	1
Total PCBs	23	–

[a] Primarily adapted from Long et al. (1995);

[b] Normalised to 1% organic carbon;

[c] Low molecular weight PAHs are the sum of concentrations of acenaphthene, acenaphthalene, anthracene, fluorene, 2-methylnaphthalene, naphthalene and phenanthrene; high molecular weight PAHs are the sum of concentrations of benzo(a)anthracene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene and pyrene.

Table 10: ANZECC Water Quality Guidelines for the protection of Ecosystem Health- 95% level of protection



Chemical		Trigger values for freshwater (µgL^{-1})			
		Level of protection (% species)			
		99%	95%	90%	80%
METALS & METALLOIDS					
Aluminium	pH >6.5	27	55	80	150
Aluminium	pH <6.5	ID	ID	ID	ID
Antimony		ID	ID	ID	ID
Arsenic (As III)		1	24	94 ^{C}	360 ^{C}
Arsenic (AsV)		0.8	13	42	140 ^{C}
Beryllium		ID	ID	ID	ID
Bismuth		ID	ID	ID	ID
Boron		90	370 ^{C}	680 ^{C}	1300 ^{C}
Cadmium	H	0.06	0.2	0.4	0.8 ^{C}
Chromium (Cr III)	H	ID	ID	ID	ID
Chromium (CrVI)		0.01	1.0 ^{C}	6 ^{A}	40 ^{A}
Cobalt		ID	ID	ID	ID
Copper	H	1.0	1.4	1.8 ^{C}	2.5 ^{C}
Gallium		ID	ID	ID	ID
Iron		ID	ID	ID	ID
Lanthanum		ID	ID	ID	ID
Lead	H	1.0	3.4	5.6	9.4 ^{C}
Manganese		1200	1900^{C}	2500^{C}	3600^{C}
Mercury (inorganic)	B	0.06	0.6	1.9 ^{C}	5.4 ^{A}
Mercury (methyl)		ID	ID	ID	ID
Molybdenum		ID	ID	ID	ID
Nickel	H	8	11	13	17 ^{C}
Selenium (Total)	B	5	11	18	34
Selenium (SeIV)	B	ID	ID	ID	ID
Silver		0.02	0.05	0.1	0.2 ^{C}
Thallium		ID	ID	ID	ID
Tin (inorganic, SnIV)		ID	ID	ID	ID
Tributyltin (as µg/L Sn)		ID	ID	ID	ID
Uranium		ID	ID	ID	ID
Vanadium		ID	ID	ID	ID
Zinc	H	2.4	8.0 ^{C}	15 ^{C}	31 ^{C}
Polycyclic Aromatic Hydrocarbons					
Naphthalene		2.5	16	37	

Table 11: ANZECC guidelines for recreational purposes- MBAS

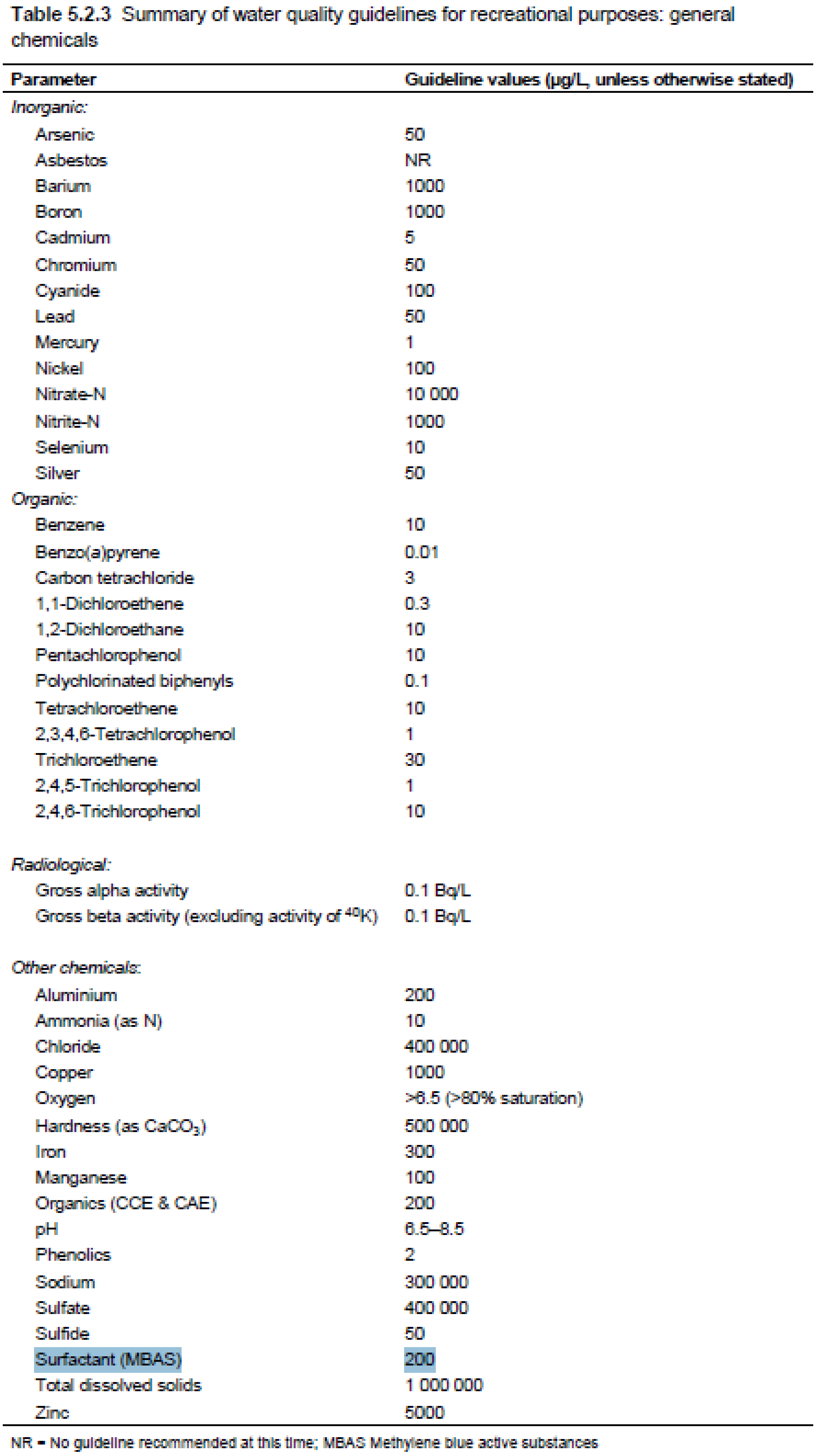
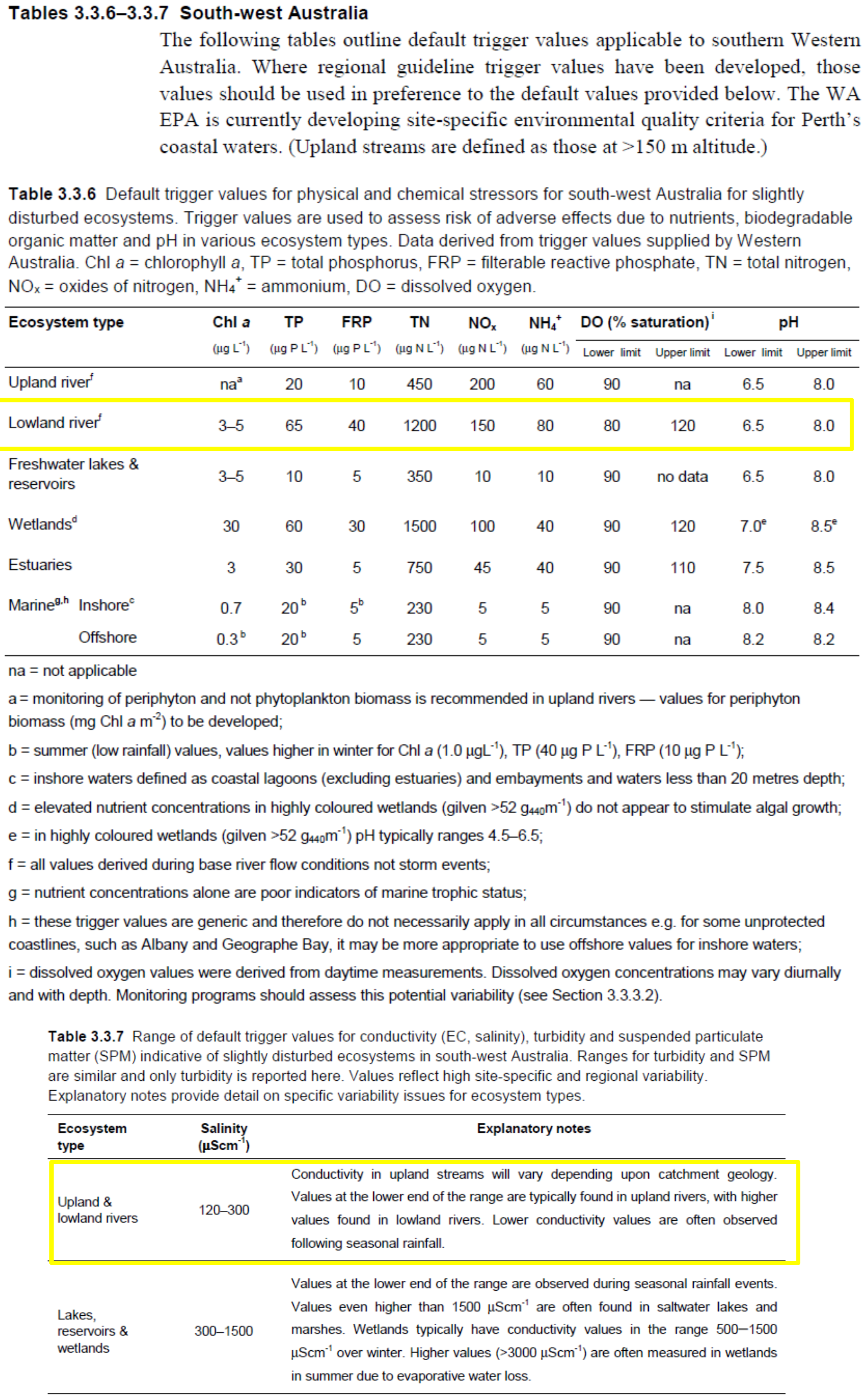


Table 5.2.3 Summary of water quality guidelines for recreational purposes: general chemicals

Parameter	Guideline values (µg/L, unless otherwise stated)
Inorganic:	
Arsenic	50
Asbestos	NR
Barium	1000
Boron	1000
Cadmium	5
Chromium	50
Cyanide	100
Lead	50
Mercury	1
Nickel	100
Nitrate-N	10 000
Nitrite-N	1000
Selenium	10
Silver	50
Organic:	
Benzene	10
Benzo(*a*)pyrene	0.01
Carbon tetrachloride	3
1,1-Dichloroethene	0.3
1,2-Dichloroethane	10
Pentachlorophenol	10
Polychlorinated biphenyls	0.1
Tetrachloroethene	10
2,3,4,6-Tetrachlorophenol	1
Trichloroethene	30
2,4,5-Trichlorophenol	1
2,4,6-Trichlorophenol	10
Radiological:	
Gross alpha activity	0.1 Bq/L
Gross beta activity (excluding activity of ^{40}K)	0.1 Bq/L
Other chemicals:	
Aluminium	200
Ammonia (as N)	10
Chloride	400 000
Copper	1000
Oxygen	>6.5 (>80% saturation)
Hardness (as $CaCO_3$)	500 000
Iron	300
Manganese	100
Organics (CCE & CAE)	200
pH	6.5–8.5
Phenolics	2
Sodium	300 000
Sulfate	400 000
Sulfide	50
Surfactant (MBAS)	200
Total dissolved solids	1 000 000
Zinc	5000

NR = No guideline recommended at this time; MBAS Methylene blue active substances

Table 12: ANZECC Water Quality Guidelines for physical variables in Lowland Rivers.



Tables 3.3.6–3.3.7 South-west Australia

The following tables outline default trigger values applicable to southern Western Australia. Where regional guideline trigger values have been developed, those values should be used in preference to the default values provided below. The WA EPA is currently developing site-specific environmental quality criteria for Perth's coastal waters. (Upland streams are defined as those at >150 m altitude.)

Table 3.3.6 Default trigger values for physical and chemical stressors for south-west Australia for slightly disturbed ecosystems. Trigger values are used to assess risk of adverse effects due to nutrients, biodegradable organic matter and pH in various ecosystem types. Data derived from trigger values supplied by Western Australia. Chl *a* = chlorophyll *a*, TP = total phosphorus, FRP = filterable reactive phosphate, TN = total nitrogen, NO_x = oxides of nitrogen, NH_4^+ = ammonium, DO = dissolved oxygen.

Ecosystem type	**Chl *a***	**TP**	**FRP**	**TN**	**NO_x**	**NH_4^+**	**DO (% saturation)**[i]		**pH**	
	($\mu g\ L^{-1}$)	($\mu g\ P\ L^{-1}$)	($\mu g\ P\ L^{-1}$)	($\mu g\ N\ L^{-1}$)	($\mu g\ N\ L^{-1}$)	($\mu g\ N\ L^{-1}$)	Lower limit	Upper limit	Lower limit	Upper limit
Upland river[f]	na[a]	20	10	450	200	60	90	na	6.5	8.0
Lowland river[f]	3–5	65	40	1200	150	80	80	120	6.5	8.0
Freshwater lakes & reservoirs	3–5	10	5	350	10	10	90	no data	6.5	8.0
Wetlands[d]	30	60	30	1500	100	40	90	120	7.0[e]	8.5[e]
Estuaries	3	30	5	750	45	40	90	110	7.5	8.5
Marine[g,h] Inshore[c]	0.7	20[b]	5[b]	230	5	5	90	na	8.0	8.4
Offshore	0.3[b]	20[b]	5	230	5	5	90	na	8.2	8.2

na = not applicable

a = monitoring of periphyton and not phytoplankton biomass is recommended in upland rivers — values for periphyton biomass (mg Chl *a* m^{-2}) to be developed;

b = summer (low rainfall) values, values higher in winter for Chl *a* (1.0 μgL^{-1}), TP (40 $\mu g\ P\ L^{-1}$), FRP (10 $\mu g\ P\ L^{-1}$);

c = inshore waters defined as coastal lagoons (excluding estuaries) and embayments and waters less than 20 metres depth;

d = elevated nutrient concentrations in highly coloured wetlands (gilven >52 $g_{440}m^{-1}$) do not appear to stimulate algal growth;

e = in highly coloured wetlands (gilven >52 $g_{440}m^{-1}$) pH typically ranges 4.5–6.5;

f = all values derived during base river flow conditions not storm events;

g = nutrient concentrations alone are poor indicators of marine trophic status;

h = these trigger values are generic and therefore do not necessarily apply in all circumstances e.g. for some unprotected coastlines, such as Albany and Geographe Bay, it may be more appropriate to use offshore values for inshore waters;

i = dissolved oxygen values were derived from daytime measurements. Dissolved oxygen concentrations may vary diurnally and with depth. Monitoring programs should assess this potential variability (see Section 3.3.3.2).

Table 3.3.7 Range of default trigger values for conductivity (EC, salinity), turbidity and suspended particulate matter (SPM) indicative of slightly disturbed ecosystems in south-west Australia. Ranges for turbidity and SPM are similar and only turbidity is reported here. Values reflect high site-specific and regional variability. Explanatory notes provide detail on specific variability issues for ecosystem types.

Ecosystem type	**Salinity (μScm^{-1})**	**Explanatory notes**
Upland & lowland rivers	120–300	Conductivity in upland streams will vary depending upon catchment geology. Values at the lower end of the range are typically found in upland rivers, with higher values found in lowland rivers. Lower conductivity values are often observed following seasonal rainfall.
Lakes, reservoirs & wetlands	300–1500	Values at the lower end of the range are observed during seasonal rainfall events. Values even higher than 1500 μScm^{-1} are often found in saltwater lakes and marshes. Wetlands typically have conductivity values in the range 500–1500 μScm^{-1} over winter. Higher values (>3000 μScm^{-1}) are often measured in wetlands in summer due to evaporative water loss.

Appendix 2

Table 13 Limits of reporting and methods of laboratory analysis for analytes in freshwater and sediment

	Method of analysis		water	sediment
Parameter	**water**	**sediment**	**Limit of Reporting (ug/L)**	**Limit of reporting (mg/kg)**
Surfactant (MBAS)	GC-ITDS analysis	-	1	1
Glyphosate		Total Acid Extractable and Dissolved Elements in Water (APHA (21st Edition), 3010 and 3030 USEPA 6010, 6020, 200.7, 200.8 and 200.2	50	-
Chlorinated Acidic Pesticides	GC-ITDS analysis			
2,4-D			0.1	0.1
2,4 – DB			-	0.1
2,4,5-T			0.1	0.1
2,4,6-T			0.1	-
2,4,5 - TP			-	0.1
MCPA			0.1	0.1
MCPP			-	0.1
Dicamba			0.1	0.1
Dichloroprop			-	0.1
Triclopyr			0.1	0.1
Picloram			0.2	0.1
Fluazifop			0.4	0.1
Fluroxypyr			-	0.1
Clopyralid			0.4	0.1
Metsulfuron methyl			0.5	1
Organochlorine Pesticides	GC-ECD analysis (EPA 3510C, 3620B, 3660B, APHA 6630, NATA Tech Note 10)			
Aldrin			0.001	0.01
BHC's			0.001	-
alpha - BHC			-	0.01
beta - BHC			-	0.01
delta - BHC			-	0.01
gamma - BHC (Lindane)			-	0.01
Bifenthrin			0.05	-
Chlordane			0.001	-
cis - Chlordane			-	0.01
trans - Chlordane			-	0.01
Oxychlordane			0.001	0.01
Chlorothalonil			0.01	-
Dieldrin			0.001	0.01

	Method of analysis		water	sediment
Parameter	water	sediment	Limit of Reporting (ug/L)	Limit of reporting (mg/kg)
DDE			0.001	0.01
DDD			0.001	0.01
DDT			0.001	0.01
Fipronil			0.02	-
HCB			0.001	0.01
Heptachlor			0.001	0.01
Heptachlor epoxide			0.001	0.01
Endrin			0.01	0.01
Endrin aldehyde			-	0.01
Endrin ketone			-	0.01
Endosulphan I			0.001	0.01
Endosulphan II			0.001	0.01
Endosulphan Sulphate			0.001	0.01
Methoxychlor			0.02	0.01
Vinclozolin			0.02	-
Organophosphate Pesticides	GC-ECD analysis (EPA 3510C, 3620B, 3660B, APHA 6630, NATA Tech Note 10)			
Azinphos ethyl			-	0.1
Azinphos methyl			-	0.1
Bromophos ethyl			0.005	-
Chlorfenvinphos (E)			-	0.1
Chlorfenvinphos (Z)			-	0.1
Chlorpyrifos			0.005	0.1
Chlorpyrifos methyl			-	0.1
Demeton - S - methyl			-	0.1
Diazinon			0.01	0.1
Dichlorvos			-	0.1
Dimethoate			-	0.1
Ethion			0.01	0.1
Fenitrothion			0.01	0.1
Fenthion			-	0.1
Malathion			0.01	0.1
Parathion (ethyl)			0.02	0.1
Parathion methyl			0.02	0.1
Pirimiphos ethyl			-	0.1
Pirimiphos methyl			-	0.1
Heavy Metals	ICP-OES, ICP-MS, AAS (APHA, 3030, 3110, EPA 3120; APHA 3125, EPA 200.2, 200.8; APHA, 3030, 3110, Varian analytical methods for flame spectroscopy, EPA 7000B)			
Al			10	1

	Method of analysis		water	sediment
Parameter	**water**	**sediment**	**Limit of Reporting (ug/L)**	**Limit of reporting (mg/kg)**
As			1	0.5
Cd			0.1	0.5
Cr			1	0.5
Cu			1	0.5
Fe			10	1
Zn			5	0.5
Ni			1	0.5
Pb			1	0.5
Se			1	0.5
Hg	AAS-VGA analysis (ASTM D 3223-95, APHA 3112 B, EPA SW-846 Method 7471A, Varian VGA-77, Publication No 85 101047 00)		0.1	0.2
PAH	GC-ITDS analysis (ASTM Standards Method No D 4657-92, EPA 3510C, 8270C, British Columbia Ministry of Water, Land and Air Protection, Analytical Method 7)			
Acenaphthene				0.5
Acenaphthylene				0.5
Anthracene				0.5
Benz[a]anthracene				0.5
Benzo[a]pyrene				0.5
Benzo[b,k]fluoranthene				1
Benzo[g,h,i]perylene				0.5
Chrysene				0.5
Dibenz[a,h]anthracene				0.5
Fluoranthene				0.5
Fluorene				0.5
Indeno[1,2,3-cd]pyrene				0.5
Naphthalene				0.5
2-Methyl-naphthalene				
Phenanthrene				0.5
Pyrene				0.5
TPH	GC-FID analysis (EPA 3510C, Contaminated soils: diesel fuel contamination / Paul T. Kostecki, Edward J.Calabrese, 1992, California Department of			

	Method of analysis		**water**	**sediment**
Parameter	**water**	**sediment**	**Limit of Reporting (ug/L)**	**Limit of reporting (mg/kg)**
	Health Services USA method , 1985. Recommended Methods of Analysis for Organic Components, required by AB 1893)			
C6 - C9			20	25
C10 - C14			20	50
C15 - C28			40	100
C29 - C36			40	100