Dissolved metal concentrations in the Port of Lyttelton

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This short report presents the results of a survey of dissolved and total metals concentrations in Port of Lyttelton water in June 2013

Sources of metals to Port of Lyttelton water

- *Stormwater*
- *Leaching from port structures*
- *Leaching from vessel hulls*
- *Dry dock discharge*
- *Runoff from port structures*
- *Re-suspended metal contaminated sediment*

Methods

Sites

Surface water was collected from fifteen sites within the operational area of the Port of Lyttelton and a site within Lyttelton Harbour/Whakaraupō. The sites sampled are shown in Figure 1 and details are provided in Appendix 1. The sites include both historical and current Environment Canterbury water quality monitoring sites and two new sites that were added for the purpose of this investigation.

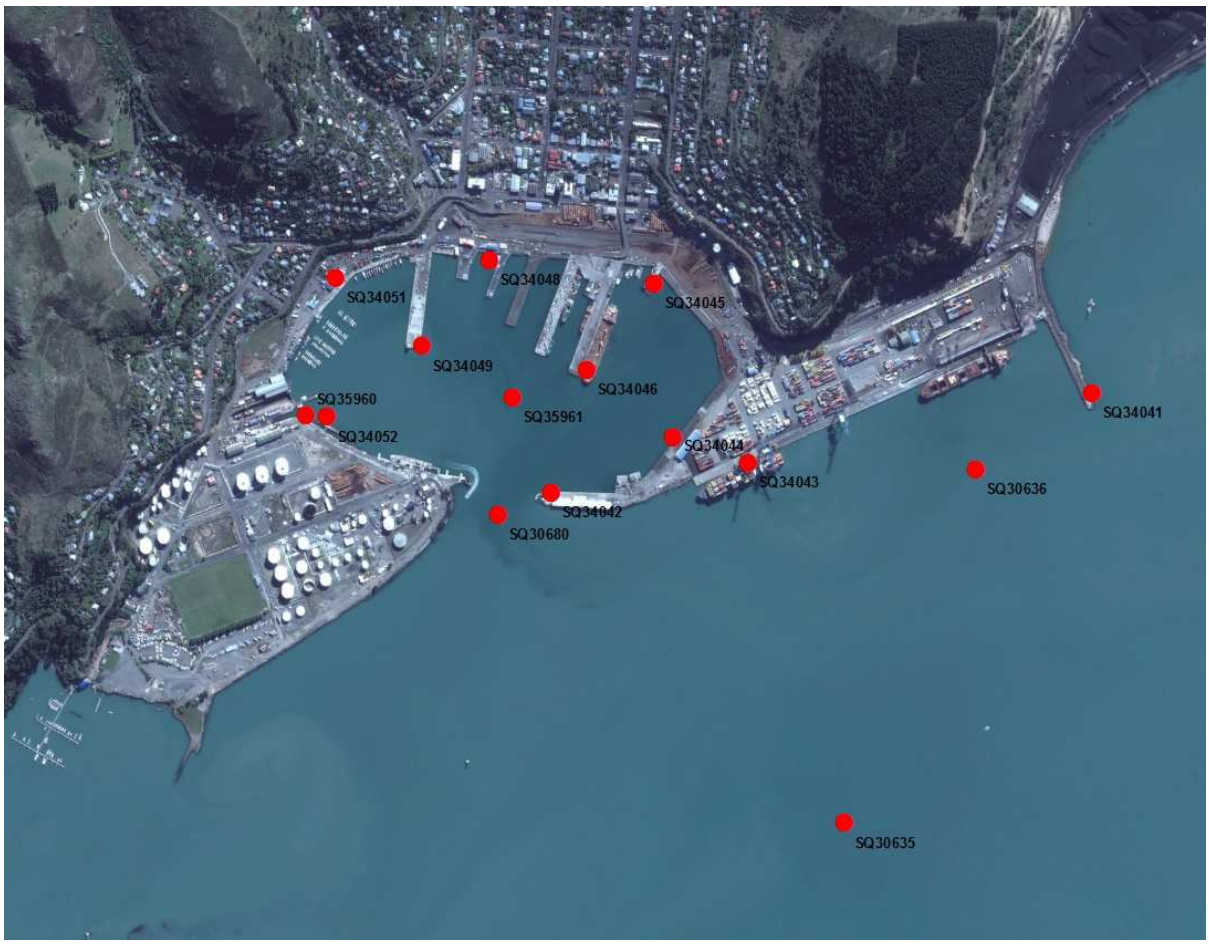

Figure 1 Sampling sites

Sampling details

Sampling details are provided in Table 1.

Table 1 Time and conditions at time of, and prior to, sampling

	18th June	26th June
Time of HT at Lyttelton	1132	0626
Time of Sampling	1325-1423	935-1050
Wind direction and strength	E, light	SW, light/calm
Rainfall[1] (mm) 1 day prior	37.4	0
Rainfall (mm) 2 days prior	48.2	0
Rainfall (mm) 3 days prior	3.8	0
Rainfall (mm) 4 days prior	0	0.6

Sample analyses and field data
Hill Laboratories analysed the samples. Details of the analysis methods including the analytical level of detection are provided in Appendix 2. Each sample was analysed to determine the dissolved and total concentrations of cadmium, chromium, copper, lead, nickel, zinc and mercury. Dibutyltin, Triphenyltin and Tributyltin and total suspended solid concentrations were also measured. At the time of sampling water temperature and salinity were measured using a field meter.

Results

Field data

At all sites the water was slightly warmer on 18th June than 26th of June (Table 2). The time of day of sampling may account for this difference.

On the 18 June the salinity at sites ranged from 26.4 to 32.9. On 26 June the salinity at sites ranged from 32.1 – 32.9. At 14 of the fifteen sites there was a difference in salinity between sampling periods. There was no difference in salinity at the eastern-most sampling station of Sticking Point. At other sites located outside of the breakwaters there was at most a salinity difference of 0.5 between 18 and 26 June. Between the breakwaters there was a salinity difference of 2.7 between the two sampling occasions. At all other sites within the port the difference in salinity between sampling occasions ranged from 1.5 (at the site just inside the breakwater) to 6.4 (at the site near the dry dock). The lower salinity at the 14 sites on the 18th than on the 26th of June indicates the input of freshwater into the port. We have made the assumption that the larger the salinity difference between sampling occasions at a site, the closer the site is to a freshwater input i.e. a stormwater or other discharge point, or the more freshwater it receives compared to other sites.

There is no pattern in total suspended solids concentrations between sampling occasions at sites. Two sites showed no difference between sampling occasions while another two sites showed a difference of 1g/m^3. Seven sites had total suspended solids concentrations that

[1] Measured by LPC

were higher on the 18th than 26th, while four sites had concentrations that were higher on the 26th than the 18th of June.

Table 2 Salinity, water temperature and total suspended concentrations at the sites

Site	Date sampled	Salinity	Water Temperature	Total Suspended Solids
		ppt	℃	g/m3
SQ30635	18-Jun-13	32.3	10.3	11
	26-Jun-13	32.8	9.2	10
SQ30636	18-Jun-13	32.4	10.5	14
	26-Jun-13	32.8	9.2	9
SQ30680	18-Jun-13	30	10.3	8
	26-Jun-13	32.7	9.2	10
SQ34041	18-Jun-13	32.9	10.6	23
	26-Jun-13	32.9	9.4	14
SQ34042	18-Jun-13	31.1	10.3	7
	26-Jun-13	32.6	9.2	7
SQ34043	18-Jun-13	32.2	10.5	14
	26-Jun-13	32.4	8.9	12
SQ34044	18-Jun-13	30.5	10.3	6
	26-Jun-13	32.1	8.7	< 3
SQ34045	18-Jun-13	30.4	10.2	15
	26-Jun-13	32.5	9.2	5
SQ34046	18-Jun-13	29.7	10.2	10
	26-Jun-13	32.5	9.2	8
SQ34048	18-Jun-13	28.2	10.3	7
	26-Jun-13	32.3	9.2	4
SQ34049	18-Jun-13	28.5	10.3	7
	26-Jun-13	32.6	9.3	10
SQ34051	18-Jun-13	27.7	10.1	11
	26-Jun-13	32.6	9.4	12
SQ34052	18-Jun-13	27.9	10.3	9
	26-Jun-13	32.7	9.5	20
SQ35960	18-Jun-13	26.4	10.2	10
	26-Jun-13	32.8	9.5	19
SQ35961	18-Jun-13	28.9	10.3	6
	26-Jun-13	32.5	9.1	6

Metal concentrations

The laboratory analytical levels of detection are provided in Appendix 2. The majority of results were below the analytical level of detection. For some metals all results were below the analytical level of detection and at one site all metal concentrations were below the analytical level of detection. All above the analytical level of detection results are presented in Table 3.

Table 3 Metal concentrations at sampling sites

site	Date sampled	Total Cadmium mg/L	Total Chromium (III) mg/L	Total Chromium mg/L	Dissolved Copper mg/L	Total Copper mg/L	Dissolved Nickel mg/L	Total Lead mg/L	Dissolved Zinc mg/L	Total Zinc mg/L	Triphenyltin (as Sn) mg/L
SQ30635	18-Jun-13										
	26-Jun-13										
SQ30636	18-Jun-13			0.0012							
	26-Jun-13										
SQ30680	18-Jun-13				0.0014	0.0022					
	26-Jun-13										
SQ34041	18-Jun-13		0.0017	0.0017		0.0014		0.0012			
	26-Jun-13										
SQ34042	18-Jun-13				0.0013	0.0021					
	26-Jun-13										
SQ34043	18-Jun-13					0.004					
	26-Jun-13										
SQ34044	18-Jun-13				0.0016	0.0024					
	26-Jun-13				0.001						
SQ34045	18-Jun-13			0.0014	0.0021	0.0038			0.004	0.0105	
	26-Jun-13				0.0015					0.0043	
SQ34046	18-Jun-13				0.0019	0.0035					
	26-Jun-13				0.001						
SQ34048	18-Jun-13				0.0024	0.0088			0.004	0.0078	0.0001
	26-Jun-13									0.0043	
SQ34049	18-Jun-13				0.0023	0.0046			0.006	0.007	
	26-Jun-13					0.0015					
SQ34051	18-Jun-13				0.0025	0.0051			0.004	0.0066	
	26-Jun-13				0.0014	0.0013			0.004	0.0049	
SQ34052	18-Jun-13	0.00026			0.0019	0.0046				0.0056	
	26-Jun-13					0.0015	0.012				
SQ35960	18-Jun-13				0.0033	0.0075			0.006	0.0131	
	26-Jun-13				0.0025	0.0065			0.008	0.0086	
SQ35961	18-Jun-13				0.0019	0.0049				0.0043	
	26-Jun-13										

Metal concentrations were compared to the ANZECC (2000) trigger values for dissolved metals providing protection for 80%, 90% and 95% of species. These trigger values are presented in Table 4. There are no ANZECC (2000) trigger values for total metal concentrations in water.

There were dissolved concentrations above the analytical level of detection for copper, nickel and zinc. All dissolved nickel and zinc concentrations are lower than the trigger values providing protection for 95% of species. Dissolved copper concentrations at some sites were above trigger values (Table 5, Figures 2 and 3).

Table 4 ANZECC (2000) trigger values (mg/L) for dissolved metals to provide protection for 80%, 90% and 95% of species

Metal	80%	90%	95%
Cu	0.008	0.003	0.0013
Ni	0.56	0.2	0.07
Zn	0.043	0.023	0.015

Table 5 Recorded copper concentrations compared to trigger values

site	Date sampled	Dissolved Copper mg/L
SQ30680	18-Jun-13	0.0014
	26-Jun-13	
SQ34044	18-Jun-13	0.0016
	26-Jun-13	0.001
SQ34045	18-Jun-13	0.0021
	26-Jun-13	0.0015
SQ34046	18-Jun-13	0.0019
	26-Jun-13	0.001
SQ34048	18-Jun-13	0.0024
	26-Jun-13	
SQ34049	18-Jun-13	0.0023
	26-Jun-13	
SQ34051	18-Jun-13	0.0025
	26-Jun-13	0.0014
SQ34052	18-Jun-13	0.0019
	26-Jun-13	
SQ35960	18-Jun-13	0.0033
	26-Jun-13	0.0025
SQ35961	18-Jun-13	0.0019
	26-Jun-13	
	value higher than 90% trigger value	
	value higher than 95% trigger value	

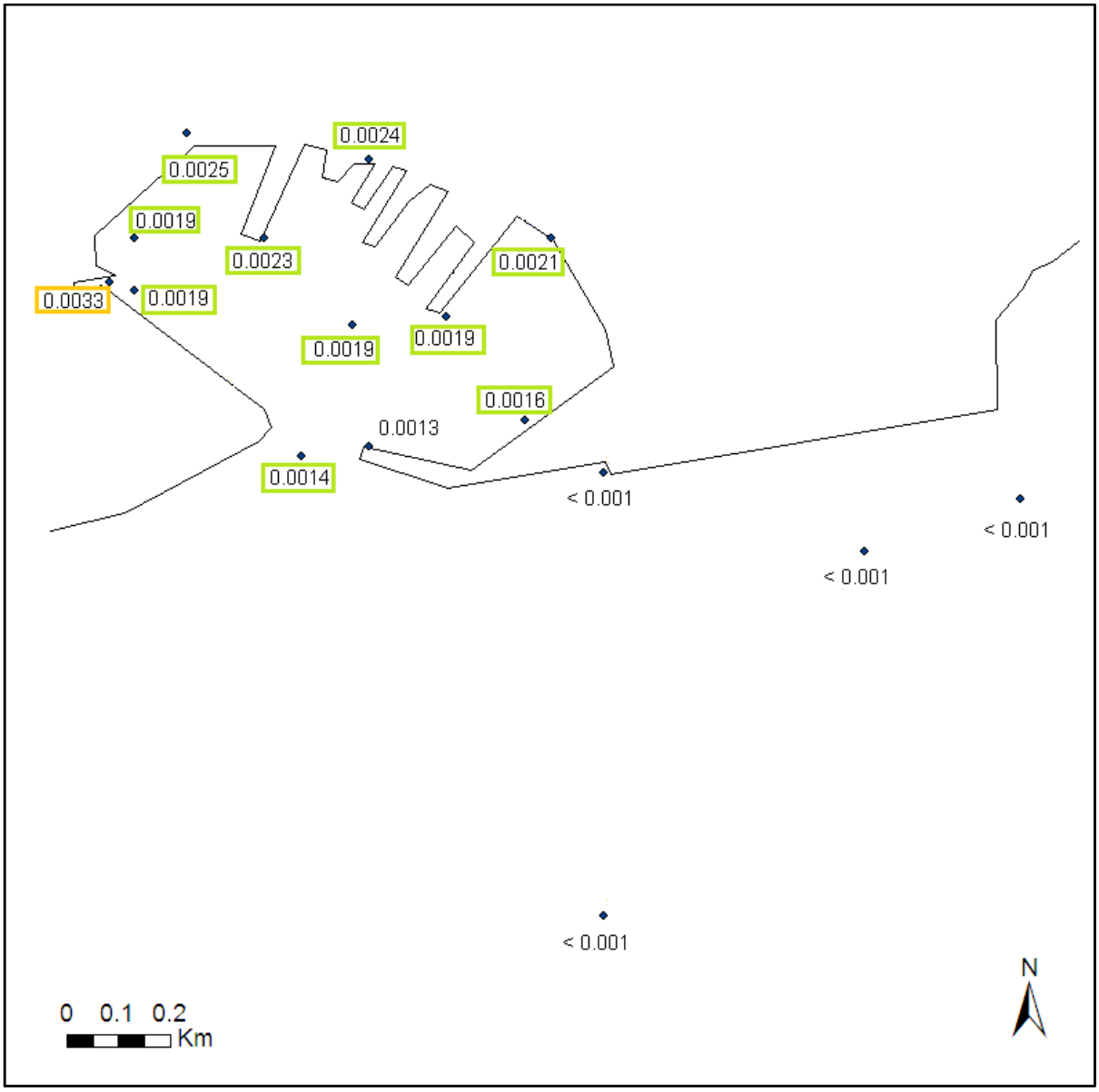

Figure 2 Dissolved copper concentrations (mg/L) at sites on 18 June 2013

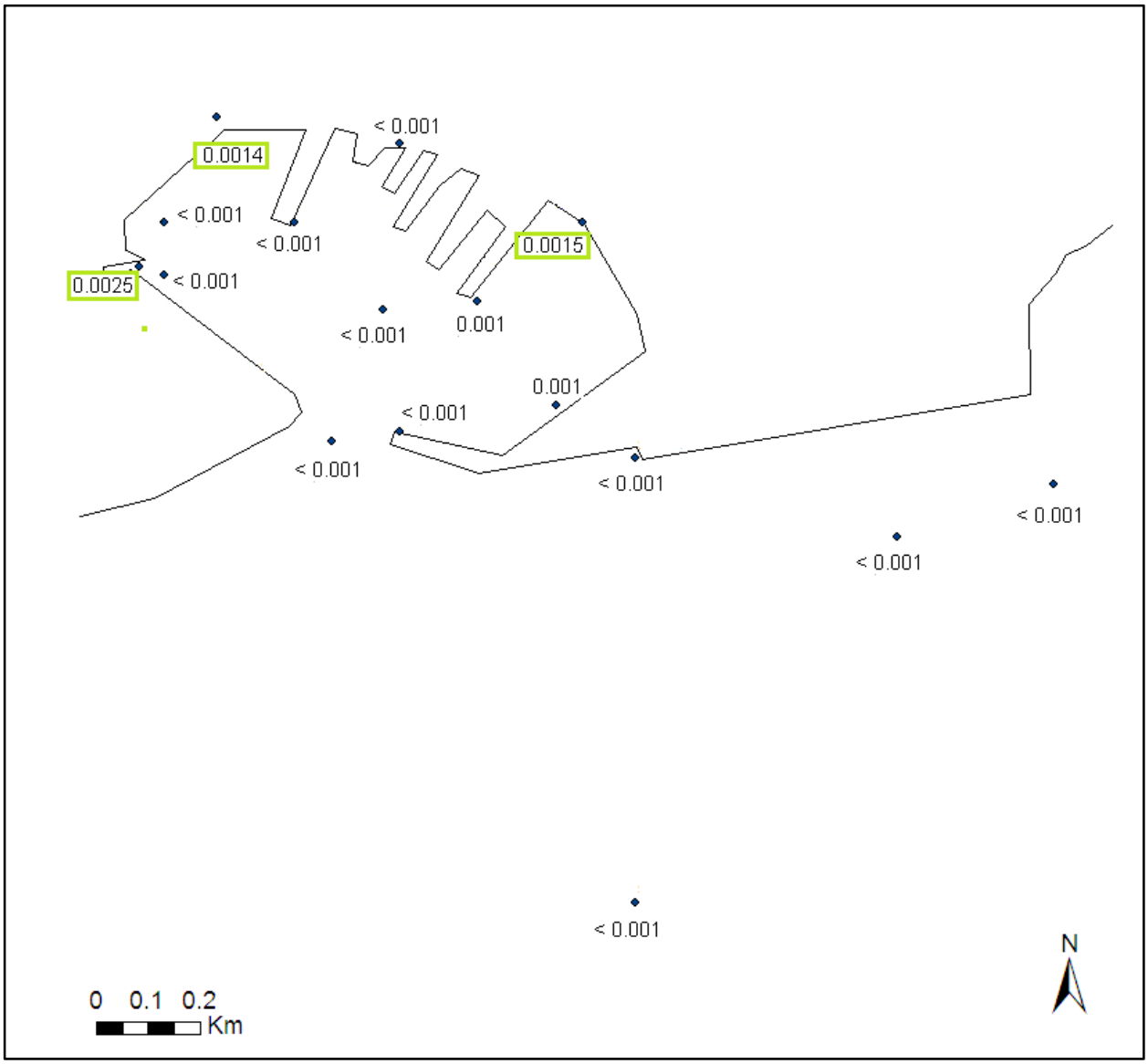

Figure 3 Dissolved copper concentrations (mg/L) at sites on 26 June 2013

On 18 June above the analytical level of detection for:

- dissolved zinc concentrations occurred at four sites
- dissolved nickel concentrations did not occur at any sites
- dissolved copper concentrations occurred at ten sites.

On 26 June above the analytical level of detection for:

- dissolved zinc concentrations occurred at two sites
- dissolved nickel concentrations occurred at one site
- dissolved copper concentrations occurred at five sites.

The highest dissolved copper and zinc concentrations occurred at the site in the area near the discharge from the dry dock. Dissolved concentrations were typically higher at sites

adjacent to land compared to those at sites further from land. The results indicate that dissolved zinc and copper concentrations within the inner port are influenced by rainfall. Stormwater and runoff from port facilities likely accounts for the metal concentrations recorded on 18 June. We do not know if the dry dock was in use on the 18th and if there was a discharge from the dry dock at the time of sampling. We attribute the dissolved copper concentration between the breakwaters on 18 June to stormwater flowing from the pipe that discharges to the port from the western breakwater.

At all sites beyond the entrance to the inner port the dissolved copper and zinc concentrations were below the analytical level of detection. This result suggests that any dissolved and total copper and zinc that flows out of the inner port becomes diluted within a short distance of the port entrance/structures.

Appendix 1 Site details

Site name	Site ID	Site Easting	Site Northing
Lyttelton Harbour midway Lyttelton/Diamond Harbour	SQ30635	1577697	5170592
Lyttelton Harbour off Cashin Quay	SQ30636	1578197	5171292
Lyttelton Harbour Port entrance	SQ30680	1577117	5171475
Lyttelton Harbour End of Sticking Pt Breakwater	SQ34041	1578497	5171392
Lyttelton Harbour End of Z Berth near Lighthouse	SQ34042	1577247	5171492
Lyttelton Harbour Cashin Quay Container Terminal	SQ34043	1577697	5171442
Lyttelton Harbour Gladstone Pier Docking Area	SQ34044	1577547	5171542
Lyttelton Harbour Beside Fox II Mooring	SQ34045	1577597	5171892
Lyttelton Harbour Off end of N0.2 Wharf	SQ34046	1577397	5171742
Lyttelton Harbour Between N0.5 & N0.6 Wharfs	SQ34048	1577247	5172042
Lyttelton Harbour Off end of N0.7 Wharf	SQ34049	1577047	5171892
Lyttelton Harbour Between Fishing Boats & Yachts	SQ34051	1576897	5172092
Lyttelton Harbour Beside Cattle Jetty	SQ34052	1576797	5171792
Lyttelton Harbour Dry Dock	SQ35960	1576750	5171807
Lyttelton Harbour Mid Port	SQ35961	1577218	5171725

Appendix 2 Analytical methods

Test	Method description	Default detection limit (g/m³)
Tributyl Tin Trace in Water samples by GCMS	Solvent extraction, ethylation, SPE cleanup, GC-MS SIM analysis	
Total Digestion of saline samples	Nitric acid digestion. APHA 3030 E 22nd ed. 2012 (modified)	
Total Suspended Solids	Saline sample. Filtration using Whatman 934 AH, Advantec GC-50 or equivalent filters (nominal pore size 1.2 - 1.5 µm), gravimetric determination. APHA 2540 D 21st ed. 2005.	3
Filtration for dissolved metals analysis	Sample filtration through 0.45µm membrane filter and preservation with nitric acid. APHA 3030 B 21st ed. 2005.	
Dissolved Cadmium	Filtered sample, ICP-MS, ultratrace level. APHA 3125 B 21st ed. 2005	0.0002
Total Cadmium	Nitric acid digestion, ICP-MS, ultratrace level. APHA 3125 B 21st ed. 2005	0.00021
Dissolved Chromium (III)	Calculation: Total Dissolved Chromium - chromium (VI).	0.0010
Total Chromium (III)	Calculation: Total Chromium - chromium (VI).	0.0010
Hexavalent Chromium	Diphenylcarbazide colorimetry. Discrete Analyser. APHA 3500 Cr B (modified from manual anaylsis) 21st ed. 2005.	0.0010
Dissolved Chromium	Filtered sample, ICP-MS with dynamic reaction cell, ultratrace level. APHA 3125 B 21st ed. 2005	0.0010
Total Chromium	Nitric acid digestion, ICP-MS with dynamic reaction cell, ultratrace level. APHA 3125 B 21st ed. 2005	0.0011
Dissolved Copper	Filtered sample, ICP-MS with dynamic reaction cell, ultratrace level. APHA 3125 B 21st ed. 2005	0.0010
Total Copper	Nitric acid digestion, ICP-MS with dynamic reaction cell, ultratrace level. APHA 3125 B 21st ed. 2005	0.0011
Dissolved Lead	Filtered sample, ICP-MS, ultratrace level. APHA 3125 B 21st ed. 2005	0.0010
Total Lead	Nitric acid digestion, ICP-MS, ultratrace level. APHA 3125 B 21st ed. 2005	0.0011
Dissolved Mercury	0.45µm filtration, bromine oxidation followed by atomic fluorescence. US EPA Method 245.7 , Feb 2005.	0.00008

Total Mercury	Bromine Oxidation followed by atomic fluorescence. US EPA Method 245.7 , Feb 2005.	0.00008
Dissolved Nickel	Filtered sample, ICP-MS, ultratrace level. APHA 3125 B 21st ed. 2005	0.006
Total Nickel	Nitric acid digestion, ICP-MS, ultratrace level. APHA 3125 B 21st ed. 2005	0.0063
Dissolved Zinc	Filtered sample, ICP-MS with dynamic reaction cell, ultratrace. APHA 3125 B 21st ed. 2005	0.004
Total Zinc	Nitric acid digestion, ICP-MS with dynamic reaction cell, ultratrace. APHA 3125 B 21st ed. 2005	0.0042