Determination of trace metal concentrations in marine waters

CSIRO provides a specialist capability for baseline sampling and analysis for metals and metalloids at ultratrace concentrations

The analysis of metals and metalloids at ultratrace concentrations in marine waters is acknowledged to be technically challenging and necessitates the application of rigorous protocols for all components of the sampling and analysis to ensure the accuracy of results.

In most coastal waters unimpacted by anthropogenic discharges, metal concentrations are sub-µg/L (part per trillion) (Table 1). While in near-shore waters or harbours and estuaries, concentrations are usually below the ANZECC/ARMCANZ (2000) water quality guideline values (GV) at low µg/L concentrations. The generation of reliable baseline data requires the use of state-of-the-art protocols for preparation of sampling containers and equipment, sample collection ('clean hands/dirty hands' sampling protocols), sample preservation and ensuring adequate blanks and replicates are collected in the field, and adequate analytical QA/QC (Ahlers et al., 1990). Accurate quantification at sub-µg/L concentrations cannot be achieved routinely using standard inductively coupled plasma atomic emission spectrometry (ICP-AES) and ICP-mass spectrometric techniques (IC)-MS) techniques (Table 2). It is typically necessary to use a preliminary pre-concentration step. Access to a Class-100 clean laboratory is essential to minimise sample contamination during laboratory manipulations.

The CSIRO Centre for Environmental Contaminants Research (CECR) situated at Lucas Heights, Sydney, has NATA-accreditation and quarantine-approved premises (QAP, certified by Biosecurity Australia) for its highly proficient specialist capabilities in ultratrace dissolved metal and metal speciation analyses. This capability has been applied in a wide range of studies both within Australia and internationally within the Asia-Pacific region, particularly in relation to baseline assessment and due-diligence monitoring for proposed or operating industries.

Through independent, and international, proficiency programs, CSIRO ensures the accuracy and highest quality of its NATA-accredited laboratory. We consistently rank very highly by world standards. To ensure the highest level of quality assurance, certified reference materials for trace metals in marine waters are analysed routinely, along with spike-recoveries, sample replicates and blanks for all procedural stages.

Table 1. Typical dissolved concentrations in urban-industrialised harbour and coastal- ocean waters

Metal or metalloid	Marine waters (µg/L)[a]		Water quality GV[b] (µg/L)		Notes
	Industrial harbours	Coastal and ocean	99% PC	95% PC	
Ag	0.0001-0.08	<0.0001-0.001	0.8	1.5	
Al	<0.5-50	0.03-0.15		15 [c]	Consider colloidal forms if pH <8
As	1-40	0.5-1.5			Speciation influences GV
Cd	0.001-0.5	<0.001-0.08	0.7	5.5	
Co	0.01-2	0.0003-0.01	0.005	1	
Cr	0.1-0.5	0.03-0.3	0.14	4.4	GV for Cr(VI)
Cu	0.5-10	0.02-0.07	0.3	1.3	
Hg	0.001	<0.0001-0.01	0.1	0.4	
Mn	0.3-30	0.02-8			
Ni	0.1-12	0.1-0.2	7	70	
Pb	<0.002-3	<0.001-0.2	2.2	4.4	
Se	0.02-0.1	0.05-0.1			
V	1.8-2	0.6-1.6	50	100	
Zn	0.5-20	0.01-0.5	7	15	

[a] Apte et al. (1998); Hatje et al. (2003); Angel et al. (2010); McAlpine et al. (2003). [b] The water quality GVs are represented by 95% and 99% species protection concentrations (PC) (ANZECC/ARMCANZ, 2000). [C] Golding et al. (2014) CSIRO report (unpublished).

Table 2. Comparison of limits of detection (LOD) of for metals and metalloids in marine waters

Typical limit of detection (µg/L)						
Technique	ICP-AES	ICP-MS	ICP-AES	ICP-MS	ICP-MS	HG-AAS, GF-AAS and CV-AFS [d]
Sample pre-treatment	Standard addition	Dilution	Standard addition	Solvent-extraction	Dilution	Multiple techniques
Element	Unsuitable LOD for marine waters		Suitable LODs and certified CRMs[c]			
Ag	1	1	-	-	-	0.003[b,e]
Al	-	-	1[b]	-	1[b]	-
As	2	[a]	-	-	-	0.05[d]
Cd	1	[a]	-	0.001	-	-
Co	2	[a]	-	0.001	-	-
Cr	1	-	-	-	0.1	0.1[e]
Cr VI	1	-	-	-	-	0.1[b,e]
Cu	2	0.1	-	0.01	-	-
Fe	1	-	-	-	0.1	-
Hg	-	-	-	-	-	0.0001[f]
Mo	-	-	-	-	0.1	-
Mn	-	[a]	0.1	-	-	-
Ni	1	0.1	-	0.01	-	-
Pb	2	0.1	-	0.01	-	-
Se	-	[a]	-	-	-	0.03[b,d]
V	-	-	-	-	0.1	-
Zn	1	1	-	-	-	-

[a] Seawater matrix results in biased results. [b] No certified reference material is available for these concentrations.
[c] Certified Reference Materials: National Research Council Canada CRMs CASS-5 (near-shore), NASS-5 (coastal) and SLEW-3 (estuarine) seawaters. [d] HG-AAS = Hydride Generation Atomic Absorption Spectrometry.
[e] GF-AAS = Graphite Furnace AAS. [f] CV-AFS = Cold Vapour Atomic Fluorescence Spectrometry.

CSIRO's accredited analytical laboratory

NATA

WORLD RECOGNISED ACCREDITATION

Quarantine Approved Premises (QAPs)

Specialist applications

CSIRO undertakes NATA-accredited ultratrace metals testing as part of water quality and environmental impact assessments (EIA) for both industry and regulators, including:

- baseline trace metal surveys for metals in estuarine, coastal or oceanic waters;
- ultratrace analyses for samples (with sampling advice and provision of bottles if required);
- process-related studies to understand chemical fate and transformations;
- metal speciation (including methyl-mercury) and bioavailability assessments
- ecotoxicological studies to link metal exposure with effects and derive site-specific guidelines.

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CSIRO Land and Water, Centre for Environmental Contaminants Research
Contact Drs Simon Apte and Stuart Simpson Phone: +61 2 9710 6838 and 97106807
Email Simon.Apte@csiro.au and Stuart.Simpson@csiro.au;
http://www.csiro.au/science/Contaminant-chemistry-and-ecotoxicology