Collecting, Measuring, and Understanding Contaminant Concentrations in the Marine Environment

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Contents

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Acronyms and Abbreviation

AFRAC	African Accreditation Cooperation
APAC	Asia-Pacific Accreditation Cooperation
ARAC	Arab Accreditation Cooperation
BAF	Bioaccumulation factors
BCF	Bioconcentration factors
CCCs	Criteria continuous concentrations
CMCs	Criteria maximum concentrations
DO	Dissolved oxygen
GLP	Good laboratory practise
EA	European Accreditation
ERLs	Environmental risk limits
EQS	Environmental quality standards
IAAC	Inter-America Accreditation Cooperation
ICP-MS	Inductively coupled plasma mass spectrometry
ILAC	International Laboratory Accreditation Cooperation
LOD	Limit of detection
LOR	Limit of reporting
MRA	Mutual recognition agreement
NATA	National Association of Testing Authorities Australia
NOAA	National Oceanic and Atmospheric Administration
NTAC	National Technical Advisory Committee
OECD	Organisation of Economic and Cooperation and Development
PFOS	Perfluorooctanesulfonic acid
PFOA	Perfluorooctanoic acid
QA	Quality assurance
QC	Quality control
QCs	Quality control samples
RHTs	Recommended holding times
SADCA	South African Development Community Cooperation in Accreditation
SPM	Suspended particulate matter
US EPA	United States Environmental Protection Authority
USA	United States of America
WQC	Water quality criteria

2.1 Introduction

A large part of marine pollution studies is about collecting, analysing, and interpreting the concentrations of contaminants in the environment. This involves field and laboratory work to collect and analyse the samples. Some analyses are completed directly in the field (i.e. in situ). From the process of collection through to the final analyses, there are many **quality assurance and quality control (QA/QC)** steps that are required, which, when used properly, ensure sample integrity and the reliability of results, therefore, resulting in meaningful interpretations and conclusions. Ultimately, following correct **sampling** and **analytical procedures** facilitates an accurate understanding of risk to marine organisms, ecosystems, and human health. This chapter provides a general introduction to procedures for identifying contamination in marine environments. This may not be a chapter that you read from beginning to end, but rather one that you will use as a valuable resource when putting together a sampling program. It will also help you understand what analyses may be complementary to the sampling effort in order to interpret the behaviour of contaminants, and how concentrations relate to guideline values. Table 2.1 highlights some useful references that provide expanded detail for you to investigate further if you find yourself needing detailed knowledge of sampling and analytical protocols. Information on determining organism, population, and ecosystem responses to contaminants (ecotoxicology) is also provided in ▶ Chapter 3.

2.2 Defining the Purpose of the Research

The approach used for site selection during field sampling and assessment should be **informed by the research question**. For this reason, sampling programs may differ between studies for logical and justifiable reasons. However, mistakes can be made, particularly in interpreting results if the sampling program is not well designed. Im-

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Table 2.1 Selected text resources regarding environmental sampling and analyses

Reference details
Baird, R. and Bridgewater. L. (2017). *Standard Methods for the Examination of Water and Wastewater.* 23rd Edition. Washington, American Public Health Association. P 1 545
Blasco, J. and Tovar-Sanchez. A. eds., (2023). *Marine Analytical Chemistry*. Cham, Springer Nature. P 455
US Department of the Interior and US Geologic Survey. (2015). *National Field Manual for the Collection of Water-Quality Data.* Available at: ▶ http://water.usgs.gov/owq/FieldManual/. [Accessed June 14 2021]
Mudroch, A. and Macknight, S.D. (1994). *Handbook of Techniques for Aquatic Sediments Sampling.* 2nd Edition. Boca Raton: CRC Press. P 256
Simpson S.L. and Batley G.E. eds., (2016). *Sediment Quality Assessment – A Practical Guide.* 2nd Edition. Clayton South: CSIRO Publishing. P 360

agine designing a program that aims to determine the extent of contamination from a mine tailings disposal pipeline. You would likely consider designing a spatial sampling program that investigates sites at various and increasing distances from the source (pipeline outfall point) in a grid or radial pattern and include replicate samples of the waters, sediments, and/or biota. You could thereby gain an understanding of the overall footprint of the contamination impact. In choosing the sites, it would also be useful to consider potential environmental factors and temporal changes (e.g. where and how currents and tides move water and factors affecting the transport, settlement, and resuspension of sediments). It is useful to complete literature searches during the initial phase of the research project to gain insights into the locations of interest and site-specific detail which will inform the design of a good study program. Useful information may include historical data on contamination events and recorded concentrations, previous studies at the location and/or similar locations, as well as physicochemical and biological information including bathymetry, current and tide patterns, sediment characteristics, habitat types, and species composition.

When biota is included in a sampling program, consideration must be given to selecting a suitable range of target species. Species with sessile or sedentary life cycles (e.g. most adult bivalves) will prove useful when relating body concentrations of contaminants to the chronic exposure regime at particular sites. By contrast, a species with a large range (e.g. tuna) might be just passing through a contaminated site and we would have limited understanding of past exposure, thus making it difficult to identify the source of the body burden (amount of contaminant measured in the tissue of the organism). Such data would, therefore, not be representative of the actual sampling site.

Setting up a sampling program requires questions or hypotheses to be established that can be answered with planned data collection. I have seen sampling programs with serious effort committed to sampling contaminants in pelagic fish from sites at selected distances from a contamination source. These types of data are costly to obtain and the results are difficult to interpret because they are not clearly linked to site conditions since most pelagic fish have a relatively large area in which they roam.

In some studies, part of the interest in sampling fish is related to contaminant consumption and human health impacts and there are very good reasons for being concerned with contaminant concentrations in edible fish. A good place to obtain samples of fish intended for human consumption in communities close to impact sites is from local markets or from local fishermen who collect fish from their fishing grounds. These samples may be quite different from sites selected in a sampling program focussed on distance from a contaminant source.

2.3 Transport and Storage of Contaminants

All contaminants originate from a source and are distributed around the environment by physical forces such as winds, tides, upwelling, downwelling, currents, ocean circulation, rainfall, groundwater movement, and surface runoff. Throughout these distribution processes, biota come into contact with contaminants and may accumulate and transport them. The size and density of **solid particles** influence their distribution and the contaminants that bind to them. In general, heavy or larger particles settle out first and deposit in higher energy environments compared to fine particles like clay. Clays (diameter < 2 μm) may remain in suspension for months or years and have a high surface area to volume ratio, and, therfore greater adsorptive capacity for contaminants (Reichelt-Brushett et al. 2017). Fine particles can potentially transport bound contaminants many kilometres from the original source (Figure 2.1).

The **solubility** of a contaminant also influences its distribution. Water-soluble substances will move readily in the marine environment as they will be dissolved

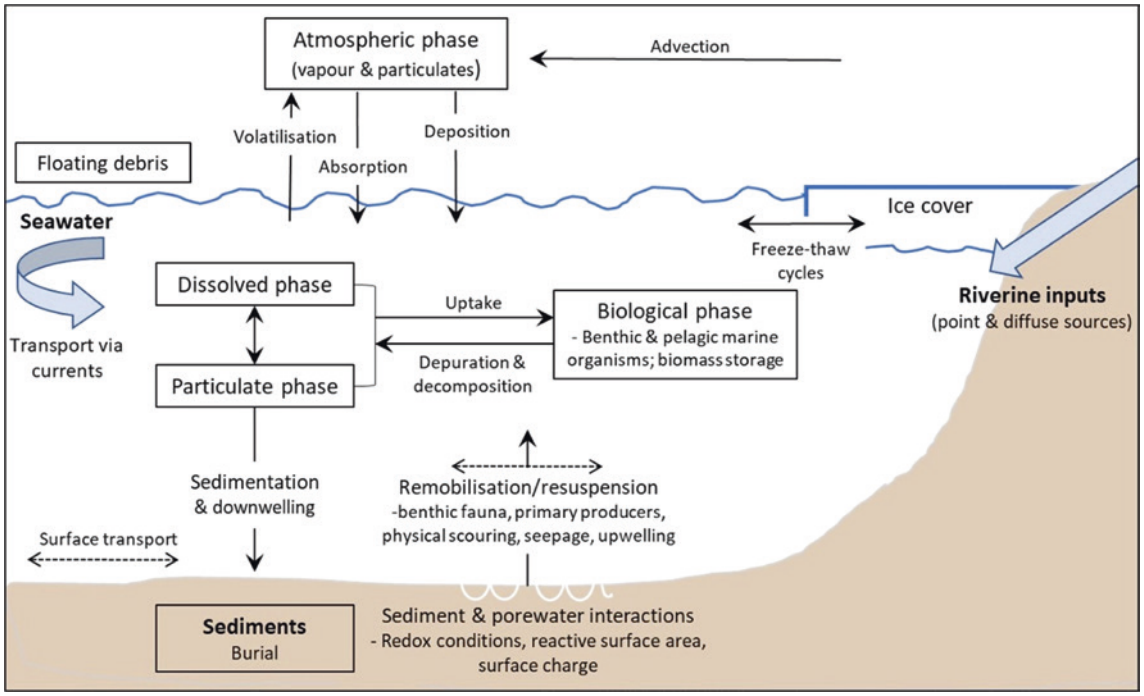

Figure 2.1 Marine contaminant distribution and storage in the environment. *Image*: A. Reichelt-Brushett and K. Summer

throughout the water column and transported with currents and tides. Some water-soluble substances, such as metal ions, are charged and will adsorb to particulates (▶ Chapter 5). Similarly, insoluble substances will more commonly be associated with sediments, or float on the water surface.

Organisms interact with contaminants from different **physical compartments** (e.g. water, sediment, and biota) how they do so will influence the rate and pathway of contaminant uptake. For example, a filter-feeding organism such as an oyster will filter large volumes of water and suspended particles through its system, whilst a polychaete worm will have a close affiliation with the sediments in which it burrows. The **trophic transfer** of some contaminants is also an important consideration. Different organisms will take up contaminants via different uptake pathways; some contaminants may be stored in body tissue, whilst others may be metabolised and excreted.

2.4 Developing a Sampling Program

2.4.1 Define Locations, Sites, and Replicates

A sampling program should define terms related to the sampling effort, and usually, a design is set up to ensure the suitability of the collected data for statistical analyses. Consider the approach in Figure 2.2; the study program has five locations, within each location, there are three sites, and within each site, there are three replicate samples (e.g. replicate sediment samples). In other words, the term **replicate** is explained as a function of **site**, the site is explained as a function of **location**, and the locations are within a study program. The definition of these words (or similar) should be locked in as part of the program. Ideally, there should be a minimum of three replicates and these must be true replicates (i.e. sediments collected from three different grab samples taken at each site, not three sediment samples from a single grab sample (this is called **pseudo replication**). Likewise, three tissue samples from a single fish is not true field replication (repeat samples like this may be useful in another context such as to ensure QA/QC in the laboratory). Upon collection, although it may seem obvious and be simple, it is critical that samples are clearly and correctly labelled to ensure that this detail is not lost and can be interpreted later.

2.4.2 Sampling Plan

Care needs to be taken to ensure that **sample integrity** is not compromised by the process of collection, transport, and storage. Suitable and appropriate equipment needs to be available to collect different types of samples. Equipment used in the field should be appropriately cleaned and calibrated; calibration, maintenance

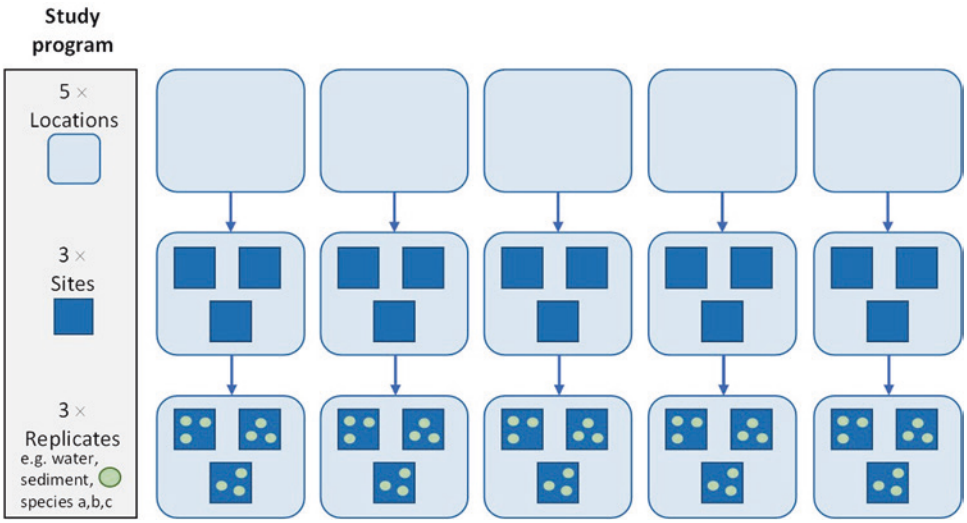

Figure 2.2 A simple study program design is comprised of replicates within sampling sites, within locations-use of correct and consistent terminology is important. Replicates are comprised of one sample type and should be reproduced for different types of samples such as water, sediment, and organisms. *Image*: A. Reichelt-Brushett and K. Summer

schedules, and repairs should be completed and recorded in related log books. Equipment should be stored clean and according to manufacturer recommendations. During sampling trips, planning for enough **storage space** is important. Much of the time samples may be stored on ice and frozen immediately on return to the laboratory and prior to analysis. Some samples may require more rigorous **storage protocols**, such as; storing at -80 °C, fixing in acetone, immediate acidification, or storage in the dark. Text and tables later in this chapter provide details related to sample storage requirements for different types of analysis.

It is essential to determine the amount of material required for all intended analyses, and that samples are stored appropriately for the needs of specific analyses or pre-treated in the field if required. There are similar but different sampling protocols for different environmental compartments (i.e. waters, sediment, and biota). These protocols are put in place to avoid contaminating a sample with field equipment, compromising the physicochemistry, and to ensure the stability of a sample matrix. These procedures prevent contaminant loss, sample degradation, and transformation of chemical matrixes.

Sampling is costly, in terms of both time and resources, and needs to be carefully considered within a **budget** that is most often limited and defined. For this reason, it is important to determine the number of specialised people and support staff required to complete the sampling in a safe manner (i.e. estimate the amount of time required for each task at each site, and consider how much sampling is achievable each day).

Most organisations require risk assessments to be completed prior to field work. These assessments help identify potential risks and allow for the development of **safe practices and procedures** to avoid injury. Consider staff qualifications such as a boat licence, coxswain licence, level of SCUBA diving qualifications, first aid, and resuscitation certifications. These types of qualifications are a valuable part of a marine scientist's capabilities and employability. On large research vessels, there may be specialist teams attached to the operation of a given vessel that support the logistics of expert sampling.

2.5 Units of Measurement

As technology advances, so do instrument capabilities and the speed and accuracy of analyses. It is easier now than ever before to obtain fast and accurate measurements of very low contaminant concentrations, with limits of detection for some elements now in the part per trillion (ng/L) range. It is essential to know your **units** of concentration and what they mean (Table 2.2) and remember:

One part per million (ppm) is equal to 1/1000000 of the whole:

$1\ \text{ppm} = 1/1000000 = 0.000001 = 1 \times 10^{-6}$

1 ppm is equal to 0.0001%

1 ppm is equal to 1000 ppb (part per billion)

At times, concentrations may be reported in **molarity**. To convert from molarity to ppm (mg/L), take molarity (with units mol/L), and multiply it by the molar mass (with units g/mol) you get g/L. Just multiply g/L by 1000 to convert g to mg, and you have ppm (in mg/L of water).

Table 2.2 Common units used for reporting concentrations of contaminants (liquids use per L and solids use per kg) (see also Appendix I). Created by K. Summer

Extended unit	Abbreviation option 1	Abbreviation option 2	Scientific notation	Context
Percent	%	–	1×10^{-2}	Parts per hundred
1 g per Litre 1 g per kilogram	%	–	1×10^{-3}	Parts per thousand Per-mille
1 mg per Litre 1 mg per kilogram	1 mg/L 1 mg/kg	1 mg L^{-1} 1 mg kg^{-1}	1×10^{-6}	Parts per million (ppm)
1 µg per Litre 1 µg per kilogram	1 µg/L 1 µg/kg	1 µg L^{-1} 1 µg kg^{-1}	1×10^{-9}	Parts per billion (ppb)
1 nanogram per Litre 1 nanogram per kilogram	1 ng/L 1 ng/kg	1 ng L^{-1} 1 ng kg^{-1}	1×10^{-12}	Parts per trillion (ppt)
1 picogram per Litre 1 picogram per kilogram	1 pg/L 1 pg/kg	1 pg L^{-1} 1 pg L^{-1}	1×10^{-15}	Parts per quadrillion (ppq)

We must also keep in mind that, in seawater, a concentration of 1.00 mg/L≠1.00 ppm since the density of seawater is 1.035 kg/L. Hence, in theory:

$$1.00\,\text{mg/L seawater} = 1.00\,\text{mg/L} \times 1\,\text{L}/1.035\,\text{kg}$$
$$= 0.966\,\text{mg/kg or } 0.966\,\text{ppm}$$

In reality, most reported concentrations of contaminants in seawater do not take the density of seawater into consideration, probably due to the very minor actual difference and the complexity that would arise when sampling estuarine environments, where salinity varies in time and space.

2.6 Water Sampling and Analysis

Water generally contains low levels of contaminants and for this reason, small errors caused by poor sampling and/or analytical processes can cause large relative impacts on the final measured concentrations and compromise correct interpretations. Table 2.3 provides some details about procedures and analytical tools for different types of water analyses. Due to the behaviour of different classes of chemical contaminants, it is usual practice for samples to be collected in different types of containers so that the material the containers are made of doesn't interact with the sample. For example, some parameters such as chlorophyll *a* will photodegrade, and therefore, need to be protected from light on collection (usually by using opaque containers or wrapping containers in foil). Other parameters will require pretreatment such as filtration and/or acidification at the time of collection in order to stabilise the sample prior to storage. Containers used in sample collection and laboratory analysis should be acid washed prior to use for later metal analysis procedures, and ethanol washed prior to use for later organic chemical analysis.

2.6.1 Surface Water

Sampling water at the water surface is fairly easy but a few key points should be remembered:

- Containers for sampling should be rinsed three times with water that is to be collected.
- For dissolved contaminants, water should be collected just below the surface and not specifically from the water–air interface.
- The bottle should remain capped until it is fully submerged, the cap can then be removed, the bottle filled, and the cap replaced under the water. Exceptions to this would be if the sampling effort was specifically focused on floating material (i.e. not dissolved) such as oils or microplastics.

Some analyses can be completed in situ using various probes and detectors including pH, dissolved oxygen, temperature, turbidity, conductivity, redoxpotential, total dissolved solids, chlorophyll *a,* and pressure. **Data loggers** can be deployed for long time periods for continuous or high-frequency analysis. The data is either stored within the instrument until retrieval and downloading or is delivered in real time using phone or satellite systems. More advanced **field equipment** enables measurements of parameters including labile ions and trace metals, but the detection limits can be much higher than those available in laboratory analyses, and therefore, the data may only be useful for broad screening. Deployed equipment can be damaged by vandalism, biofouling, rough seas, floods, and bad weather; therefore, systems need to be in place to minimise such risks.

Sampling the interface of the water and atmosphere is also important for some studies. Floating material such as debris, nanoplastics, and films or slicks

Table 2.3 Approaches for the analyses of some contaminants in seawater, techniques, sample collection and storage. Created by K. Summer

Contaminant/ analyses class	Specific analyses	Typical instrumentation/ method (LOD)	Sample volume required	Sample container	Sample storage	Maximum storage time
Metals and metalloids	Total, dissolved	ICP–MS (0.5–5 µg/L; metal dependent)	10 mL	Polycarbonate	0.45 µm filtration; acidify with conc. HNO_3; R	6 mo (28 d for Hg)
	Acid extractable	ICP–MS (0.5–5 µg/L; metal dependent)	10 mL	Polycarbonate	Acidify with conc. HNO_3; R	6 mo (28 d for Hg)
	Speciation	HPLC–ICP–MS, GC–MS (low ng/L)	10 mL–1 L; compound/method dependent	Polycarbonate for metals/metalloids Glass for organometallics	R; may require dilution/further preparation	14 d
Organic contaminants	Pesticides	HPLC, HPLC-FLD (0.2–10 µg/L–compound/ method dependent)	Up to 1 L; compound/method dependent	Glass solvent-rinsed amber bottles; PTFE-lined caps and septa; fill to neck	Preserve (e.g., ascorbic acid, $Na_2S_2O_3$) if necessary (dependant on sample redox conditions); LS; R	28 d
	Hydrocarbons (e.g. PAHs, TPHs, BTEX, oil/ grease)	HPLC–ICP–MS + UVD and/or FLD; GC–MS + FID (0.5–2 µg/L); HEGM (2 mg/L)	2–40 mL (PAH, BTEX, TPH C6-C9); 1L (TPH C10-C36); 500 mL oil/grease	G solvent-rinsed amber bottle; PTFE-lined caps and septa; do not pre-rinse with sample	Acidify with HCl/H_2SO_4 if analysis delayed; LS; R	7 d
	Surfactants	HPLC–ICP–MS (0.1 mg/L)	100 mL	Glass	R; avoid foam formation	2 d
Pharmaceuticals	Specific drugs	HPLC–ICP–MS (1–2000 ng/L; depending on compound)	500 mL	Glass PTFE-lined caps and septa;	Immediately dechlorinate using 50 mg ascorbic acid/L sample and add 1 g NaN_3/L sample as biocide; R; LS	28 d
Nutrients/trophic status	Nitrogen and phosphorous (total)	Persulfate-FIA (2 µg/L)	50 mL	Acid-washed P/G vials	Acidify with H_2SO_4/HCl; R	28 d
	Chlorophyll-a	HPLC; EF (5 µg/L)	500 mL	Opaque P/G container; filter to remove algae	Cool/R (2 d) or F (28 d); LS	2 d, 28 d
	BOD	DO meter, incubation bottles	500 mL	Clean glass bottles or disposable plastic BOD bottles with stoppers	LS during incubation period; cool	24 h
Nano/micro-particles	Nano-materials (1–100 nm)	HPLC–ICP–MS; variable dependent on type	1 L or potentially greater volumes, then filter	Plastic (inorganic) or Glass (organic constituents)	LS; depends on particle type	Depends on particle type
	Micro-plastics (<5 mm)	WPO-DS-GA; ATR-FTIR; (0.1 g/L)	1 L	Glass; whole sample or surface net capture (mesh size depending on desired size fraction), record transect length	Rinse from net/preserve with 70% ethanol; Cool; LS	Depends on particle type

(continued)

Table 2.3 (continued)

Contaminant/ analyses class	Specific analyses	Typical instrumentation/ method (LOD)	Sample volume required	Sample container	Sample storage	Maximum storage time
Physicochemical analyses	e.g. DO, pH, EC, temperature, turbidity	Relevant calibrated meters and probes (single/multi-parameter)	20–500 mL (parameter dependent)	Plastic or lass; analyses generally performed on-site	Cool	6 h–28 d, depending on parameter
	TOC/DOC, TSS	Oven-dried TSS	50 mL 250 mL (depends on clarity)	Plastic or glass; filter to 0.45 µm for DOC	R; LS	28 d
	Alkalinity	HCl/H_2SO_4 titration (1 mg/L)	100 mL	Plastic or glass	R	14 d
Gases	e.g. CO_2, CH_4	CRDS			Generally analysed on-site	
Radionuclides	e.g. ^{222}Rn, ^{131}I and stable isotopes ^{12}C, ^{13}C	HPGe; GFPC (1 – 100 pCi/L)	20 mL – 18 L (depending on analyses)	Plastic or glass	Acidify with H_2SO_4/HCl; R	6 mo (8 d ^{222}Rn, 14d ^{131}I)
Pathogens	e.g. *E. coli*	Cell culture, microscopy (cfu/100 mL); HPLC–ICP–MS	100 mL	Plastic or glass	R	96 h

Sources and examples: Batley and Gardener (1977); SA and SNZ (1998); Takeuchi et al. (2000); Rovedatti et al. (2001); US EPA (2001); Anderson et al. (2002); Schultz et al. (2003); Niyogi and Wood (2004); Smith (2006); Becker (2008); Hassellöv et al. (2008); Gattuso et al. (2010); Kahru and Dubourguier (2010); Hirai et al. (2011); Buesseler et al. (2012); Kroon et al. (2012); Moynihan et al. (2012); Chen et al. (2013); Maher et al. (2015); Masura et al. (2015); Downs et al. (2016); Viršek et al. (2016); Baird et al. (2017); Rosentreter et al. (2017); Reichelt-Brushett et al. (2017)

F = freeze, R = refrigerate (transport on ice, store < 4 °C), LS = light sensitive (store in dark/foil wrapped), ATR-FTIR: attenuated total reflectance fourier-transform infrared spectroscopy; BOD: biochemical oxygen demand; BTEX: benzene, toluene, ethylbenzene and xylene; CRDS: cavity ring down spectroscopy; EDTA: ethylenediaminetetraacetic acid; EF: acetone-HCl pigment extraction and fluorometric determination; FID: flame ionisation detector; FLD: fluorescence detector; GFPC: gas flow proportional chamber; HEGM: hexane extractable gravimetric method; HPLC–ICP–MS: high performance liquid chromatography coupled with ICP–MS; partition of compounds based on transfer rate differences between stationary phase (column) and mobile phase (gas/liquid); HPGe: high purity germanium detection; ICP–MS: inductively coupled mass spectrometry; element identification and quantification based on atomic mass; LLE-GC/HPLC: liquid–liquid extraction (chloroform) coupled with gas chromatography or high performance liquid chromatography; LOD: limit of detection; Persulfate-FIA: persulfate digestion with flow injection analyser; PFOA/PFOS: perfluorooctanoic acid/perfluorooctane sulfonate; PTFE: polytetrafluoroethylene, TOC: total organic carbon; TPHs: total petroleum hydrocarbons; UVD: ultra-violet detector; WPO-DS-GA: wet peroxide oxidation of organic material, density separation, gravimetric analysis

of oil will be present at this boundary layer. Sampling is different for solid and liquid materials, and sampling procedures that involve sieving or filtration need to consider the effort per unit area of sea surface sampled. Adsorption discs can be used to collect contaminants from liquid samples, but some techniques can be weather dependent (e.g. as oils degrade they can become more solid than liquid). Measuring gas fluxes between the water and air requires different measurement and quantification approaches.

2.6.2 Water from Depth

There is a range of equipment available for collecting water samples at **depth** and the best method will depend on the depth required and the vessel available. Not surprisingly, generally the deeper the sample the costlier the sample collection process. For sampling down to a depth of about 10 m depth, a weighted tube can be deployed and a pump used to draw water up from depth with the sample being taken after a calibrated pumping period, depending on the depth being sampled. Beyond this, Niskin bottles or similar vessels (e.g. Knudsen, Nansen, and Rosette Friedinger samplers) are used which are deployed open, a messenger is sent to shut and seal the container, and a volume of water is bought to the surface in the sealed bottle for sampling (Mudroch and Macknight 1994). SCUBA divers can take samples at depths up to about 30 m. Sample collections from deeper than about 100 m are best achieved by robotic sampling devices attached to powered undersea vessels. Figure 2.3 provides some examples of different water sampling devices.

2.6.3 Pore Water and Groundwater

Pore water or **groundwater** is the water that occupies the space between sediment or soil particles, making up about 5% of the volume of surface sediments (e.g. Presley et al. 1980). It can move through sediments and interacts with the contaminant load in the sediment; it is often a place of anoxic and reducing physicochemical conditions. These parameters influence contaminant behaviour, and some contaminants that would normally bind to sediment particles mobilise into the

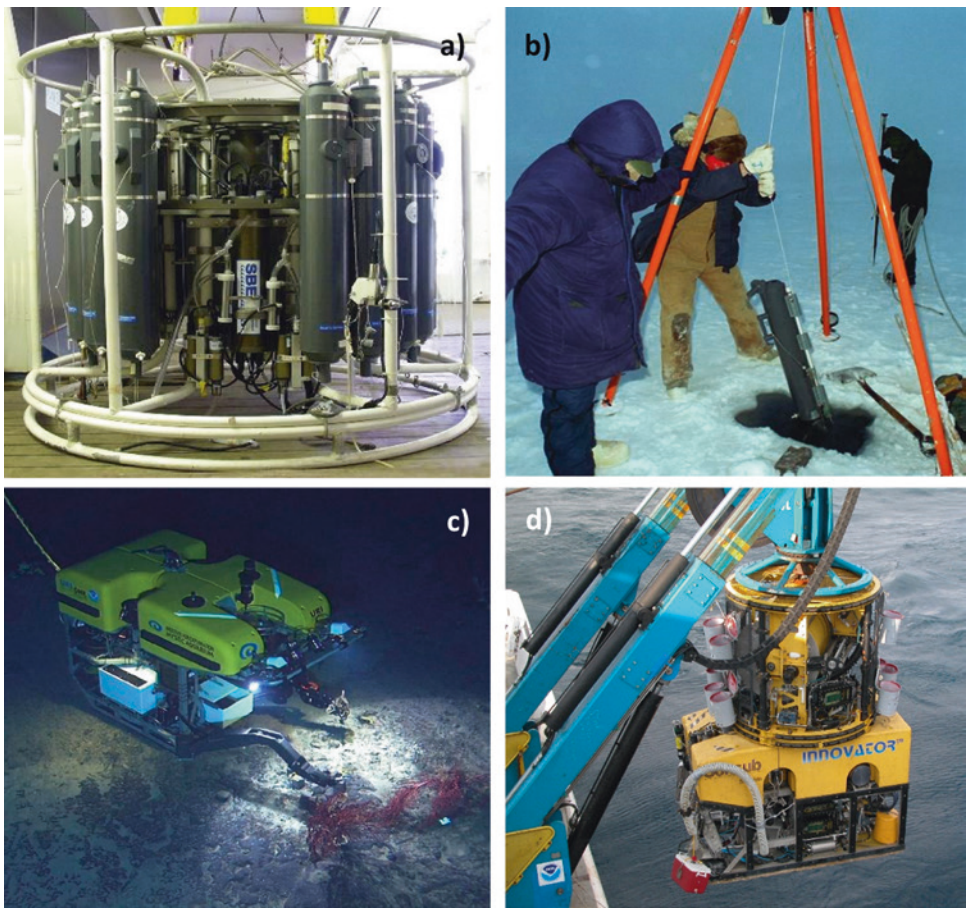

Figure 2.3 Underwater sampling devices **a** a Niskin bottle rosette (*Photo*: Hanness Grobe. Creative Commons: CC-BY-SA-2.5), **b** Lowering a Niskin bottle (*Photo*: Hanness Grobe. Creative Commons: CC-BY-SA-2.5), **c** remotely operated underwater vehicle (*Source to Photo*: Mountains in the Sea Research Team; the IFE Crew; and NOAA/OAR/OER. NOAA Photo Library, Flickr), **d** a tethered management system atop a remotely operated vehicle (*Photo*: Gulf of Mexico Deep Sea Habitats Expedition/NOAA/OAR/OER CC By 2.0)

pore water. As a result, pore water can be highly contaminated and an important transport route for contaminants (Chapman et al. 1998; Simpson et al. 2016). Characteristics of the sediment particles and macro-biological structures, such as plant roots and burrows of benthic organisms, can increase the reactive surface area of the sediment and the pore water volume. Benthic organisms can be exposed to pore water, however, many burrowing species have well-aerated burrows that maintain a micro-layer of oxic sediment within their habitat which acts as a barrier to the anoxic sediment chemistry.

2.7 Sediment Sampling and Analysis

Adsorption of contaminants onto sediment surfaces plays an important role in the removal of contaminants from water. The capacity for contaminants to bind to surfaces will depend on the size, composition, and abundance of the particles, concentration of other ions in the solution, the type of charge associated with the contaminant, hydrophobicity, and the pH of the solution. Particles with bound contaminants eventually settle in low-energy environments and these **depositional areas** may have enriched contaminant loads. Once particles are settled and become sediments, the surrounding pore water chemistry may change and influence the adsorption/desorption behaviour. Adsorption and **desorption** are important mechanisms that influence the solubility, mobility, and dispersion of contaminants. The way contaminants behave is dynamic and influenced by many factors, some of which are highlighted in ◘ Table 2.4.

There is much discussion in the scientific literature about how to treat sediment samples and the effects that such treatments have on analytical results (e.g. Ajayi and Vanloon 1989; Markert 2008; Simpson and Batley 2016; Csuros 2018) (◘ Table 2.5). As with water samples, sediment samples destined for organic contaminant analysis should not come into contact with plastics and instead should be stored in aluminium foil or amber glass containers. Sediment samples for metal analysis can be stored in clean plastic bags or containers. An additional effort may be required to minimise geochemical changes in sediment resulting from oxidation processes in the newly-exposed sediments, especially where sequential or partial extraction analyses are to be performed. When metal speciation and/or toxicity studies are important, samples should be collected and immediately stored in nitrogen-sealed bags prior to analysis. During sample processing, the use of nitrogen sparring or a nitrogen atmosphere glove box may be justified to avoid sample oxidation. The care given to avoiding sediment oxidation will depend on the analyte/s of interest. ◘ Table 2.6 provides a snapshot of general techniques for sediment sampling and processing.

2.7.1 Surface Sediments

The top 15 cm of sediment is the primary area of sediment and water interaction and biological activity. Such interactions can also occur deeper in a sediment profile as a result of ground water movement, deeply-burrowing organisms, and natural (e.g. extreme weather) and artificial (e.g. dredging) disturbances. Surficial sediments are generally of most interest in sampling sediment contamination and sampling methods are designed to collect these surficial sediments. There are various types of grab samplers available for sediment collection. The **Van Veen grab** sampler (◘ Figure 2.4) is arguably the most commonly used sediment-sampling device; other options include: the Birge-Ekman Sampler, Ponar Grab Sampler, Smith-Mcintyre Grab Sampler, and Petersen Grab Sampler, all with various benefits and applications (Mudroch and Macknight 1994; Simpson et al. 2016). They all work on a similar principle: the grab sampler is lowered slowly through the water (either by hand or hydraulic winch) until landing on the sediment surface. The release of weight tension on the device from landing triggers the release of the pin that allows the jaws to close containing a sediment sample. Expert SCUBA divers are able to minimise disturbance whilst collecting surface sediment samples which can be particularly useful in studies of the sediment–water interface (Mudroch and Macknight 1994). Sediment sampling in extremely deep waters requires mechanised and usually remotely operated equipment.

2.7.2 Sediment Cores

Sediment cores taken from low-energy depositional sites can provide a wealth of historical information about contaminant loadings over time, and analyses can determine valuable pre-contamination reference points. The inclusion of age dating such as carbon dating can also provide a chronology and historical time series (Reichelt-Brushett et al. 2017). Such a time series may be linked to historical events that have occurred at the sites and locations of interest. Finding suitable sites that are not constricted by habitat types (e.g. mangrove roots, biogenic solids such as coral reefs), physical impediments to sampling (e.g. river stones), or impacted by disturbance events can be challenging. It is best to target low-energy environments with a sediment accumulation rate of mm to cm per year; a high rate of sediment accumulation limits the duration of the deposition history within a given length of core.

Similar to grab samplers, there is a range of core sampling devices such as gravity corers, box corers, piston corers, vibra corers, and boomerang corers (Mudroch and Macknight 1994; Batley and Simpson 2016), and as the name suggests, they are designed to retrieve

Table 2.4 Some examples of how sediment characteristics can influence contaminant loads, and measures used to mitigate errors in data interpretation

Physicochemical parameter	Influence on contaminant behaviour	Considerations in sample processing and interpretation
Mineralogy	Adsorption–desorption potential (also related to cation exchange capacity); influences contaminant storage/mobility	Complete X-ray diffraction and X-ray fluorescence analysis to determine mineralogy
Grain size	Finer-sized particles have a greater surface area to volume ratio, and therefore a higher capacity for surface adsorption and chemical reactions; grain size is also related to particle (and bound contaminant) distribution; negative charges dominate clay surfaces to which positively charged cations in solution are readily adsorbed	Normalisation[a] of contaminants with grain size fraction; filter water samples according to operationally defined processes to clarify grain size of interest
Colloids particles	Negative charges on clays are much greater than positive charges, and positively charged cations in solution are adsorbed onto clays	Filter water samples; use operationally defined processes to clarify grain size of interest
Salinity gradients	Common in estuaries: a steep ionic gradient destabilises fine suspensions of colloidal material and causes the suspension suspended particles to flocculate, carrying with it them the bound contaminants	Measure salinity at sampling sites; note variability between wet and dry seasons
pH and Redox	Both parameters influence the mobility/immobility of contaminants (particularly metals) in sediment–water systems	Measure pH and redox to assist with interpretation and risk assessment
Total organic carbon (TOC)	Humic substances in sediment TOC pools strongly bind contaminants and influence the partitioning of organic and inorganic contaminants within sediment matrices; major determinant of bioavailability	Normalisation of contaminants with TOC content; measure when TOC exceeds 1%

[a] for the purpose of comparison between sites

Table 2.5 Treatment methods for sediment samples and purposes for doing so

Treatment	Procedure	Purpose	Example of use
Homogenisation	Use large pre-cleaned glass bowl; debris documented and removed (e.g., shells, wood, stones, seagrass); should be performed quickly and efficiently to reduce sample oxidation	Obtain representative samples	ANZG (2018)
Compositing	Sub-sample combination; use equipment made of inert/non-contaminating materials; process within 24 h of collection; multiple replicate samples should be taken as opposed to compositing where sediment disturbance needs to be minimised	Determine broad site characteristics; if large sample volumes required; depends on sediment heterogeneity, desired analytical resolution/study objectives	
Sieving	Dry press-sieving is preferred using a 2 mm mesh sieve; not recommended as can substantially alter sample physicochemical characteristics (use forceps as an alternative for small sample volumes)	Remove organisms and debris	ANZG (2018)
Pore-water collection	In situ (peeper chambers, suction); laboratory methods (centrifugation, pressurisation, suction); require 1–2 kg sediment sample or 500 mL pore water; analyse as soon as possible as chemistry will change substantially	Expected to be in equilibrium with sediment; understand partitioning of contaminants within sediment matrix; may reflect groundwater; toxicity testing	Pagano et al. (2017)
Preparation of elutriates	1:4 sediment:water; shaken for 1 h prior to centrifugation and analyses	Evaluate aqueous extraction of suspended sediment to assess effects of contaminant resuspension during disturbance events (e.g. by dredging, bioturbation, storms)	Lesueur et al. (2015)
Spiking	Wet methods are recommended over dry; jar rolling (large vol, 2 h) hand mixing (small vol); ensure homogenous mixing (confirm by replication) and sufficient equilibration time (2 h–28 d); measure physicochemical parameters; determine moisture content to normalise dry weight concentration	Chemical addition to determine recovery rates (QA/QC); toxicity testing	Simpson et al. (2004)

Table preparation assisted by K. Summer and P. Howe
Sources: ASTM (2000), US EPA (2001), Simpson and Batley (2016)

Table 2.6 Approaches for the analyses of contaminants in sediments including sample collection and storage procedures

Contaminant/ analyses class	Specific analyses	Recommended preparation and instrumentation (LOD)	Collection container, amount and storage[a–c]	Preferred maximum storage time
Metals and metalloids	Total/acid extractable	HNO_3/HCl acid digestion at 85 °C for 1 h; detection by ICP–MS (0.2–1 mg/kg)	P; 20 g; F	6 mo (6 wk for Hg)
	Operationally defined bio-available	1.0 M HCl acid extraction at 25 °C for 1 h; detection by ICP–MS (0.2–1 mg/kg)	P; 20 g; F	6 mo (6 wk for Hg)
	Speciation	Extraction prior to analysis by HPLC–ICP-–MS (0.2–1 mg/kg)	P (metal/metalloid) G (organometallics); 20 g; F	6 mo (6 wk for Hg)
Non-metallic contaminants	Acid-volatile sulfides (AVS)	PT; spectrophotometry	Allow 10% headspace; F	28 d
	Ammonia	ASE	R	28 d
Organic contaminants	e.g., pesticides, hydrocarbons, surfactants, phenols, cyanides, pharmaceuticals, and PCPs	Extraction[a] prior to analysis generally by HPLC–ICP–MS (µg–mg/kg)	250 g–1 kg; G amber or foil wrapped with PTFE- lined caps/septa; F	7 d (before extraction), 30 d (after extraction)
Nutrients and organic material	Nitrogen and phosphorous (total)	Extraction[a] followed by persulfate-FIA (mg/kg)	P/G; R; 20 g	28 d
	Stable C, N isotope ratios	Elemental analyser-IRMS	P/G; F	28 d
	TOC	Wet oxidation-titration; combustion-IR; GC-FID (µg/kg)	P/G; R; 20 g; remove larger organic debris (>2 mm)	28 d
Nano/micro-particles	Nano-materials (1–100 nm)	Extraction[a] followed by HPLC–ICP–MS; variable dependent on type (see)	P (inorganic) or G (organic constituents)	6–12 mo
	Micro-plastics (<5 mm)	WPO-DS-GA; microscopy	G; sieved to remove > 5 mm plastics	Not defined
Physicochemical analyses	Particle size analysis/texture, bulk density/porosity	LDA; may be impregnated with epoxy or polyester resins	P/G; 300 g	Not defined

(continued)

Table 2.6 (continued)

Contaminant/ analyses class	Specific analyses	Recommended preparation and instrumentation (LOD)	Collection container, amount and storage[a–c]	Preferred maximum storage time
	pH and redox potential	pH/ORP electrode	Generally in situ	
	Water content	Oven dried at 40 °C for 24–48 h; wet mass-dry mass (g/cm^3)		28 d
	Radionuclides (e.g., ^{7}B, ^{210}Pb, ^{222}Rn) and stable isotopes	HPGe; GFPC; IRMS (1–100 pCi/L)	P/G; 50 g	Variable
Biological analyses	Pathogens	Cell culture; microscopy; DNA extraction-bioinformatics; variable depending on the organism	P/G; R/F	96 h-28 d

Table preparation assisted by K. Summer and P. Howe

Sources and examples: Ankley et al. (1990), Chapman et al. (1998), ASTM (2000), Petrović et al. (2001), US EPA (2001), Hassellöv et al. (2008), Bainbridge et al. (2012), Zhang (2014), O'Reilly et al. (2015), Koziorowska et al. (2016), Simpson and Batley (2016), Brady and Weil (2016), Al-Mur et al. (2017), Nascimento et al. (2017), Reichelt-Brushett et al. (2017), Liu et al. (2018)

P = plastic (polyethylene/polypropylene), G = glass; F = freeze, R = refrigerate (transport on ice, store < 4 °C), LS = light sensitive (store in dark/foil wrapped); [a]extraction methods may include Soxhlet, sonication, centrifugation, supercritical fluid, accelerated solvent, and/or microwave-assisted extraction. ASE: ammonia-selective electrode; GC-FID: gas chromatography-flame ionisation detector; GFPC: gas flow proportional chamber; HPGe: high purity germanium detection; HPLC–ICP–MS: high performance liquid chromatography coupled with ICP–MS; ICP–MS: inductively coupled mass spectrometry; IR: infrared detection; IRMS: isotope ratio mass spectrometry; LDA: laser diffraction analysis; NMR: nuclear magnetic resonance; PCPs: personal care products; Persulfate-FIA: persulfate digestion with flow injection analyser WPO-DS-GA: wet peroxide oxidation of organic material, density separation, gravimetric analysis

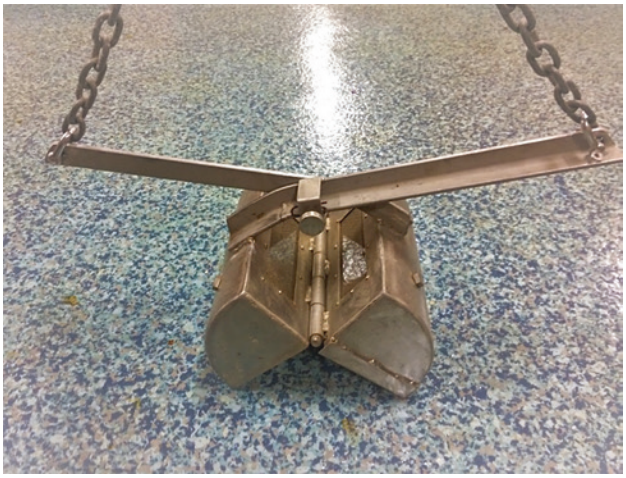

Figure 2.4 A Van Veen grab sampler shown open. *Photo*: A. Reichelt-Brushett

an intact sediment core sample. There is normally a cutting head on the end that is pushed into the sediment, the core barrel which can be of various lengths, a weighted collar, and a sealing mechanism. Shallow-water, hand-operated corers can easily be made with equipment from local hardware stores (care should be taken to avoid material that could be a potential contamination source of the analytes of interest). There is a range of suitable mechanised deployment options for mid-range water depths and SCUBA divers can collect sediment cores to a depth of around 30 m. For deeper waters of around 50–80 m, sophisticated oceanographic sampling equipment is required.

Coring devices vary in width and capacity to successfully sample sediments with differing physical features such as variable grain size. A wide core will provide more sediment for analyses at each depth interval but will be heavy and harder to manage than a narrow core. Deeper sediments (> 50 cm from the sediment–water interface) usually have less water content than shallower sediments which increases the sediment-to-water ratio. Specialised equipment (e.g. penetrometers, acoustic surveys) may be used to understand specific physical sediment characteristics at different sites, and hence aid in the sampling design (Mudroch and Macknight 1994; Simpson and Batley 2016).

2.7.3 Suspended Particulate Matter (SPM)

There is interest in measuring contaminant loads associated with SPM. The interest lies in the particulate matter as an exposure route to biota, and in understanding contaminant transport, dispersion, and relocation through ecosystems (Mudroch and Macknight 1994; Simpson and Kumar 2016). As noted previously, suspended sediments are sites of adsorption for contaminants and therefore influence their cycling through the environment and commonly make up the bulk of SPM. Suspended particles can range in size from colloids (< 0.05 µm) to particles > 2 mm (Mudroch and Macknight 1994). There is considerable research delineating what is truly particulate and what is dissolved. Commonly, but arguably, operationally defined suspended particulates are those that are captured on a 0.45-µm filter and the filtrate is the dissolved fraction. The dissolved fraction, < 0.45 µm, can be further classified (Table 2.7). Suspended sediments can be collected in various ways such as grab sampling, pump samplers, sediment traps, and integrating samplers (Batley and Simpson 2016). Water sampling devices are suitable for collecting SPM but samples require filtration on collection. Sediment traps and settling containers can also be deployed in situ, but their success, and our ability to make direct comparisons between sites, will depend on local turbulence, current, and tide conditions/interactions.

Complexities with Estuarine Waters

Estuaries are a mixing zone between seawater and fresh water. Within the mixing zone, often referred to as a **salt water wedge**, a steep ionic gradient destabi-

Table 2.7 Operationally defined size classes and the range of chemical forms potentially present within each class

Chemical form	Size class
Dissolved	< 1 nm
'Dissolved' organic chelates e.g. weak binding ligands	1 nm–0.2 µm
Biogenic and organic colloids and particles e.g. detritus,faecal pellets, and humic and Fulvic substances	0.05 µm–0.45 µm
Inorganic colloids and particulates e.g. clay platelets detrital alumno-silicates	0.01 µm–0.45 µm

Adapted from von der Heyden and Roychoudhury (2015)

lises fine suspensions of colloidal material and causes the suspended particles to **flocculate**, carrying with it the bound contaminants. A pH gradient between the fresh and marine water may also exist. Sedimentation in an estuary is not only controlled by flow rates, but is also electrolytically driven by divalent-cations (commonly Mg^{2+}, Fe^{2+}, and Ca^{2+}) bridging between fine (negatively charged) particles causing flocculation. **Sediment suspensions** may also be continually reworked by the physical effects of tidal currents and wind action on the water surface to produce characteristic turbidity, known as the **turbidity maximum**. The region of turbidity maximum is exceptional in regard to the many chemical reactions involved in shifting phase between dissolved and particulate forms.

2.8 Biota Sampling

How Biotaorganisms interact with the abiotic environment influences contaminant **exposure and uptake pathways**. Uptake of contaminants by organisms also depends on numerous physicochemical factors such as chemical speciation, partitioning, and degradability (Connell et al. 1999; Maher et al. 2016). Biological variables (e.g. species, habitat, physiology, feeding habits, age, etc.) can play major roles in uptake, and environmental factors such as season may also alter the distribution and availability of contaminants (Connell et al. 1999; Maher et al. 2016). What is clear is that an understanding of the biological and ecological characteristics of a given organism is essential to understand contaminant loads in that organism. The following definitions outline the differences between bioaccumulation, bioconcentration, and biomagnification (see also ▶ Chapter 7):

Bioconcentration: The process whereby chemicals enter aquatic organisms through the gills or epithelial tissue directly from the water (or surrounding environmental medium) and become more concentrated in the organism than in the surrounding environmental medium (water, soil, etc.).

Bioaccumulation: Chemical uptake by an organism, attributable to both bioconcentration and dietary accumulation. Bioaccumulation is related to organism-specific rates of uptake, metabolism, and elimination, and occurs when a substance is absorbed at a faster rate than it is lost.

Biomagnification: The process whereby tissue concentrations of a bioaccumulated chemical increase with successively higher levels in a food chain (at least two trophic levels) (▶ Chapter 7). This phenomenon is rare; however, those specific contaminants that do biomagnify pose serious environmental problems, and consequently, receive great publicity. Contaminants known to biomagnify include:

- chlorinated hydrocarbons;
- insecticides (e.g. DDT group and cyclodienes—dieldrin);
- non-insecticides (e.g. PCBs—hydraulic fluids, heat-transfer fluids); and
- some organometallic compounds (e.g. methylmercury [MeHg], tributyltin [TBT]).

These contaminants characteristically have a high lipid solubility (i.e. high K_{ow} value; see ▶ Chapter 7 for further explanation), and therefore, a strong affinity to accumulate in biological tissue with high-fat content (including adipose tissue/blubber, white muscle, and some organs). They are stable and persistent within the organism, and accumulation can lead to disease and mortality in higher order predators.

Bioavailability is another common term that refers to the fraction of an element (or compound) that is available to be taken up by an organism. The entry pathway of a contaminant into an organism (e.g. via water, sediment, food, etc.) will also influence the bioavailability. Metals that are weakly bound to sediment particles are bioavailable. However, some contaminants are very strongly adsorbed to sediment particles or bound within the lattice structure of the particle: they will not be reactive within the organism and will likely pass through the organism with the particle.

2.8.1 Tissue Sampling

Sampling of organisms to determine contaminant loads in tissues involves firstly identifying and collecting representative species found at the range of sites in a sampling program. Consideration should be given to the need for depuration of gut contents, particularly if the organism is going to be acid digested whole for analysis. Often specific tissues will be dissected from the organism for separate analysis, typically; tissue, liver, gill, and gonads, but specifics will depend on the research question. In the dissection process, it is important to develop a procedure that avoids contamination of the tissue samples, even between tissue types. To minimise the transfer of contaminants between different tissue types during storage, dissections are best done at the time of sampling and prior to freezing and storage. ◘ Table 2.8 provides some guidelines and considerations for tissue sampling and analysis. Sample processing and analytical procedures are similar to those used for sediment.

Table 2.8 Analyses of marine contaminants: general considerations, rationale, and requirements for biota samples

Traits	Considerations	Example references
Biology/ecology		
Organism type	Depends on resources and research question (e.g. intensive study, ongoing biomonitoring programs, toxicity testing, community/ecosystem, contaminant/s of interest, human consumption); organism should be abundant, socially and/or ecologically important, representative, and biology/taxonomy well-understood	US EPA (2000), (2002), Lu (2005), Bricker et al. (2014)
Organism size, age, life stage etc.	Related to organism sensitivity, rates of BC, BA, BM; different uptake, metabolism and elimination pathways depending on developmental stage and physiology; should be standardised for comparability	Walker et al. (2012)
Biotic interactions	Consider tropic level and predator–prey relationships; BM- increased tissue concentrations with trophic level by virtue of contaminant persistence (maximum BM in apex predators)	Kelly et al. (2009)
Abiotic interactions: habitat, ecological niche	Consider pelagic, benthic, sediment-dwelling; related to contaminant exposure and uptake pathways; filter/deposit feeding enhances contaminant exposure	Walker et al. (2012)
Behaviour, distribution and life cycle traits	Consider sessile, sedentary, mobile characteristics, migration, reproduction and influences on exposures, sensitivity, contaminant transfer to offspring	Russell et al. (1999)
Sample type	Contaminant concentrations vary between different tissue types and organs, living and non-living tissues, symbiont-host organisms	Reichelt-Brushett and McOrist (2003), Maher et al. (2016)
Live/dead organism	Tissue sample: live- biopsy (non-lethal; limitations to sample type and quantity), dead- necropsy; determines equipment and procedures	Cagnazzi et al. (2019)
Permits and approvals	Ensure necessary permits and ethics approval are obtained prior to sampling	NHMRC (2013)
Equipment and sample collection	Analytical grade/acid-washed containers P/G (inorganics) (zip-lock bags/containers) or G or foil (organics); stainless steel HHI, biopsy needle or gun-dart system, PPE; equipment cleaned of adhering material and washed with deionised water and methanol between samples (new scalpel blades); collection devices and equipment dependent on sample type- may require additional resources (e.g. boat, personnel, aquaria)	US EPA (1994), (2000)
Sample storage and preparation	Dissection and cleaning using ambient seawater or deionised water; store on ice in field and freeze; if analyses delayed > 24 h store in liquid nitrogen whilst in field and freeze -80 °C; preparation and extraction for specific analyses similar to Table 2.3 (sediments); do not freeze–thaw-freeze	US EPA (1994), (2000)
Whole organism	Small organisms (e.g. shellfish, anemones, larvae); often used in toxicity testing; *in situ* biomonitoring (e.g., shellfish); biochemical analyses (e.g. enzyme activity)	US EPA (1994), (2000)
Tissue analysis		
Muscle, fat/blubber	Analyses of inorganic and organic contaminants	Cagnazzi et al. (2019), Gilbert et al. (2015a, 2015b)
Gills	Primary sites of contaminant contact, uptake, deposition, gas/ion exchange; identification of ultrastructural changes caused by contaminants	Sweidan et al. (2015)

(continued)

Table 2.8 (continued)

Traits	Considerations	Example references
Organs	Animal organs e.g. liver, kidney; analyses of lipid-soluble organic contaminants; understanding contaminant compartmentalisation, metabolism, secondary metabolites and excretion; sample from same portion of organ (e.g. top left lobe of liver) as contaminant distribution varies	US EPA (1994)
Fluids	e.g. urine- analyses of aqueous contaminants, metabolism and excretion; e.g. blood- lipid-soluble contaminant storage, assessment of contaminant effects on endocrine and immune systems	Nomiyama et al. (2014)
Reproductive organs/tissues, milk	e.g. gonads, eggs; understand maternal contaminant transfer and genotoxicity	Russell et al. (1999)
Other structures	e.g. hair, feathers, skin; indicators of whole-body metal burden	Finger et al. (2015)
Microbiology	e.g. bacteria, viruses, protozoa; pathogenic organisms and changes to beneficial microbial communities associated with toxicity and disease	Kamp et al. (2015), Gissi et al. (2019)
DNA	Isolated from frozen sample; genetic lesions indicate toxicity	Downs et al. (2016)

Table preparation assisted by K. Summer
BC: bioconcentration (concentration in organism via surrounding environmental media), BA: bioaccumulation (BC + dietary accumulation), BM: biomagnification (increased concentration with successive trophic levels); P = plastic (polyethylene/polypropylene), G = glass, acid washed and rinsed using deionised water and solvent, dried and sealed between cleaning and collection; In general, the shorter the time that elapses between sample collection and analysis, the more reliable will be the analytical results. HHI: stainless steel hand-held implements (e.g. sterile knives, scissors; dissecting scalpel, forceps, needles, and trays), MeHg: methylmercury, OCs: organochlorine pesticides, PCBs: polychlorinated biphenyls, PPE: personal protective equipment, including non-vinyl gloves

2

2.8.2 Biomonitors

The rate of uptake and depuration of a chemical will influence its toxicity, and all **uptake pathways** (through water, food, sediment, etc.) contribute to chemical concentrations in an organism. If we understand **chemical uptake rates,** uptake pathways, and depuration rates of a contaminant by an organism, we can potentially use living organisms as monitors of the environment. This use of organisms in environmental assessment is termed biomonitoring and is an established and growing field of research in ecosystem risk assessment. Biomonitoring studies provide a longer-term integration of environmental contaminants compared to single time and point sampling of abiotic compartments. Biomonitoring studies may include chemical loads in organism tissues, changes in biochemical, physiological, morphological, or behavioural aspects of organisms, as well as ecological aspects such as species diversity and abundance (Connell et al. 1999).

Biomonitoring studies provide an integrated assessment of conditions over time, whereas water samples are usually a snapshot in time.

Requisites for organisms used in bioaccumulation studies:

- easy to identify and preferably established knowledge of biology and ecology;
- geographically widespread;
- not highly specialised in habitat;
- wide tolerance to environmental conditions (e.g. temperature, O_2, salinity);
- common and abundant;
- sedentary or relatively immobile;
- relatively large in size;
- long-lived (ageing methods established);
- hardy animal in the lab (for controlled experiments); and
- high concentration factor for the pollutant under study.

Organisms within a survey should exhibit the same correlation between the pollutant level and that of the surrounding medium. However, before data can be interpreted, the following questions need to be addressed:

- How rapidly is the contaminant taken up?
- How quickly is it lost/depurated?
- Can the organism exercise control over uptake and/or loss?
- Is the pollutant differentially distributed within the organism (e.g. flesh vs. liver for fish, flesh vs. carapace for prawns)?

Biomarkers should not be mixed up with biomonitors. Biomarkers are endpoints that can be used to define a potential effect of contaminants on organisms in the environment, and are employed in laboratory-based ecotoxicological testing (Connell et al. 1999; Taylor and Maher 2016). Details on ecotoxicological studies are provided in ▶ Chapter 3.

2.8.3 Collecting Pelagic Species

Various technique can be used to collect pelagic biota with equipment often targeting a particular size class. Importantly, the same approaches should be used across all sites. Field staff need to have suitable taxonomic knowledge to ensure the correct species are collected. Plankton tows are suitable for small species including both plankton and nekton communities. There are many regular fishing devices, such as traps, rods, and nets, which can be purchased off the shelf for use or adapted for sampling. You may also find and capture some species using snorkel or SCUBA. Consider the potential benefits of selecting a range of species that comprise of trophic levels.

2.8.4 Collecting Benthic Species

Sediment grab samplers (◘ Figure 2.4) and pipe dredge samplers can be used to collect benthic species (see also Maher et al. 2016). Sediments may need to be sieved to retrieve specimens and samples should be rinsed (and dissected if necessary) before storage. You may also locate and collect specimens by snorkelling or SCUBA diving or even on foot at shorelines and in intertidal areas.

Box 2.1: NOAA Mussel Watch Program, United States of America

Dr. Pelli Howe, Environmental Scientist.

Since commencement in 1986, the United States of America (USA) National Oceanic and Atmospheric Administration (NOAA) Mussel Watch Program has become one of the world's longest, and arguably most successful, continuous ecosystem monitoring efforts. It was designed to provide data on the spatial distribution and temporal trends of contaminants in coastal marine and estuarine environments of the United States of America, including Alaska, Puerto Rico, and Hawaii (O'Connor, 1998). The program is based on annual collections of resident mussels and oysters and comprises almost 300 monitoring sites between 10 and 100 km apart (◘ Figure 2.5). Tissue analyses of over 140 organic and inorganic

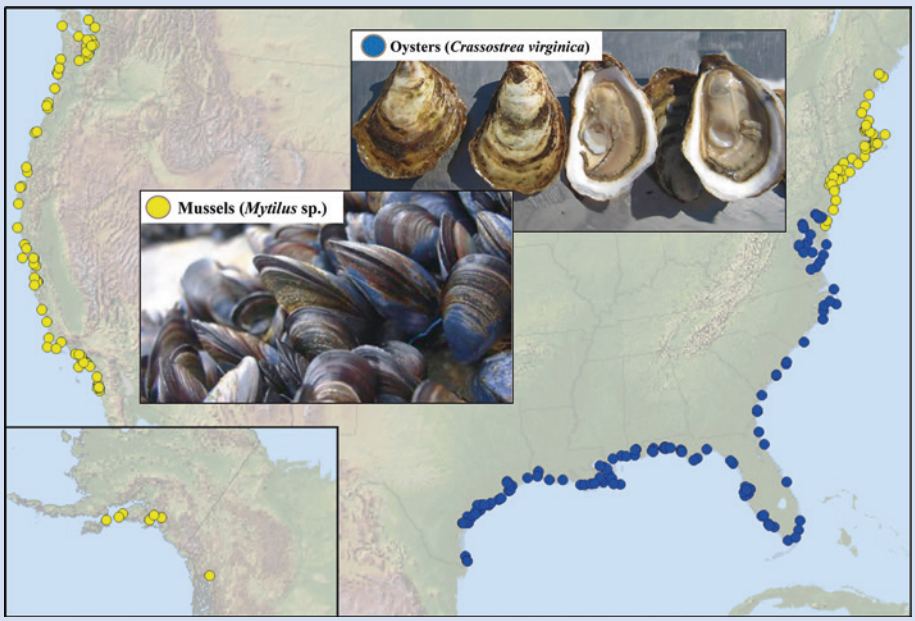

Figure 2.5 ▶ Box 2.1: Distribution of marine bivalve species and sampling locations comprising the Mussel Watch Program throughout coastal and estuarine environments of the United States. Adapted from Kimbrough et al. (2008) by P. Howe

compounds and a rigorous QA/QC process is employed among analytical laboratories to ensure data accuracy and comparability (Kimbrough et al. 2008). Samples are also stored to enable retrospective analyses for new and emerging contaminants of concern.

Bivalves are commonly used as indicators of water and sediment quality as they readily bioconcentrate and bioaccumulate contaminants by virtue of filter feeding (Melwani et al. 2014). They are sedentary and therefore representative of a given location, widely distributed, and have stable populations that can withstand repeated sampling (Farrington et al. 2016). Many are also commercially important seafood species. Mussel Watch data is useful for characterising the impact of marine contaminants at local, regional, and national scales and helping to understand current and emerging contaminants, potential food safety risks, and can be used to evaluate the efficacy of management and remediation strategies (Kimbrough et al. 2008).

Such long-term and extensive sampling efforts are costly and difficult to sustain. The success of the Mussel Watch Program can be attributed to collaboration between national and state governments, regional and local groups, private sector partners, and citizen scientists who aid in collection (Kimbrough et al. 2008). One justified criticism is that not all contaminants are readily bioconcentrated/bioaccumulated (e.g. those with high water-solubility) and are therefore not addressed by the program (Farrington et al. 2016). Furthermore, large scale geographic comparisons are constrained by differences in target species and environmental factors which may influence bioaccumulation and bioconcentration rates (Farrington et al. 2016). Nonetheless, the program provides valuable information for decision making. See Kimbrough et al. (2008) for further information and data summaries.

2.9 Quality Assurance and Quality Control

2.9.1 NATA Registration and Other Global Systems

To standardise quality assurance and quality control, a diverse range of tools can be applied (e.g. calibration services, inspection organisations, certified reference materials, and providers of proficiency testing). Companies provide these services and products to help ensure that users have confidence in their results. Laboratory accrediting organisations conduct regular audits of member laboratories to ensure that a high standard is maintained. Accreditation is a valuable tool for effective policy making, it contributes to maintaining fair markets, and improves regulation and governance in diverse areas including; food production, environmental protection, healthcare, construction, and waste management.

In Australia, the National Association of Testing Authorities, Australia (NATA) performs this role, and monitors compliance with the Organisation of Economic and Cooperation and Development OECD prin-

ciples of Good Laboratory Practise (GLP). This is a public company which has a memorandum of understanding with Federal and State Governments, who recommend (and in many cases enforce) the engagement of NATA-accredited organisations for certain services. Acquiring and maintaining NATA-accreditation requires organisations that provide analytical services to establish and uphold high quality, strictly standardised techniques, analyses, instrumentation, use of certified reference materials, data management, and consistently prove that exceptional quality assurance and control measures are in place and being used effectively. Therefore, NATA-accredited organisations offer the community an assurance of confidence and trust in their services and/or products, facilitate trade, and improve tendering success.

International accreditation agreements exist and provide mutual recognition, to which NATA is a signatory. NATA is one of around 100 accreditation bodies worldwide that are signatories to the International Laboratory Accreditation Cooperation (ILAC) Mutual Recognition Agreement (MRA). This minimises trade barriers between accredited organisations. The ILAC is for accreditation bodies that involve calibration, testing (environment and medical), inspection, and proficiency testing providers. The ILAC offers independent evaluation of conformity to recognised standards, and works closely with regional co-operation bodies such as the Asia–Pacific Accreditation Cooperation (APAC), European Accreditation (EA), Inter-America Accreditation Cooperation IAAC in the Americas, the African Accreditation Cooperation (AFRAC), the Arab Accreditation Cooperation (ARAC), and the South African Development Community Cooperation in Accreditation (SADCA). In 2018, more than 10,500 inspection bodies and almost 76,500 laboratories were accredited by ILAC MRA signatories.

2.9.2 Chain of Custody

Reliable reporting of analytical results requires a great deal of care in handling samples and is an important requirement for accreditation. A **chain of custody** accurately documents the movement of samples through an organisation, from collection and submission for analyses, transfer between sections of an organisation, preparation, analysis, and storage of samples, and reporting of results. Strict practices ensure that samples are not mislaid or mislabelled (or not labelled), that holding times are appropriate, and enable samples to be easily located at all times. As you can imagine, an unlabelled or mislabelled sample container with a nondescript sample in a busy laboratory is extremely problematic. Each stage of the chain of custody requires appropriate sample storage and handling.

2.9.3 Sample Storage and Integrity

Some parameters should ideally be measured in the field as they are likely to change during collection, transport, and storage, including:

- temperature;
- pH;
- conductivity;
- redox (reduction/oxidation potential);
- dissolved oxygen;
- turbidity; and
- chloride.

Field measurements may not always be possible for a range of reasons, and nor may they be ideal, as much more accurate measurements may be available using laboratory instruments. If samples are to be collected and transported to a laboratory, the techniques and materials used for the collection are important for the integrity of the sample. Sample collection methods have been developed and optimised over many years of research to minimise potential changes during transport (see Tables 2.1, 2.5, and 2.7). The collection method should be carefully chosen with consideration of the target analyte/s and the overall objectives of the sampling. These must be understood and strictly adhered to by all involved.

Strict protocols exist for accredited analytical laboratories to ensure that sample handling and storage maintain sample integrity. Obviously, appropriate handling and storage differ for different types of samples, and also depend upon the type of analyses that will be conducted. General protocols for samples include:

- ensuring that sample containers cannot break or leak and cause cross-contamination;
- filtering in the field is mandatory for many tests;
- minimising the exposure of samples to air is critical for many tests;
- most samples should be chilled to < 4 °C or < 6 °C (depending on the analyte/s of interest) on collection. There are also cases where samples need to be stored at -20 °C or -80 °C;
- some samples need to be treated with preservation chemicals on collection; and
- strict adherence to established recommended holding times (RHTs) for different samples and for different analyses.

2.9.4 Step to Ensure Analytical Certainty

Certified Reference Materials

As mentioned previously, manufacturers of certified reference materials require accreditation, and so must maintain an exceptionally high and consistent standard. They guarantee their product to the analytical lab-

oratories that use them to maintain their own QA/QC. Reference materials of a known substance and concentration provide a **reference sample** and are prepared in the sample way as all other samples. The analytical results of reference materials are used to ensure that the sample preparation and analyses have been conducted correctly. For example, certified reference sediment is used alongside sediment samples for analyses of trace elements by inductively coupled plasma mass spectrometry (ICP–MS); the concentrations in the reference sediment are known (and are certified by the manufacturer), and so any significant deviation (e.g. ± 10%) from the expected concentrations will alert the operator to a potential problem.

The ILAC defines five types of reference materials:

- physicochemical reference substances;
- matrix reference materials;
- pure substances;
- standard solutions and gas mixtures; and
- artefacts or objects.

Spiked Additions

Another means of maintaining QA/QC is through spiked additions of known substances at known concentrations to randomly chosen samples. This is a method used to ensure that analytical instruments are calibrated properly and are functioning normally. Accredited laboratories will, for example, add a known volume of a known solution to a duplicate of a sample that is being analysed normally. The software is then programmed to recognise the appropriate increase in concentration in the spiked sample compared to the unspiked sample and will flag unexpected problem results. The operator must then identify the problem, which may not always be easy. The first step is to carefully spike and analyse the sample again in order to discount human error in the preparation of the spiked sample (e.g. incorrect ratio volume of spike solution to sample). Next, the spiked solution should be carefully remade to discount this as the source of the error. If the results still seem erroneous, it may be that the sample contains substances that interact with the spiked solution and interfere with the analysis. As a final check to discount a non-instrument-related problem, a different sample should be spiked. If none of these steps resolve the discrepancy between the concentration in the spiked addition and the concentration measured by the instrument, then there is a problem with the instrument and/or the calibration, and all sample analyses are ceased until this is resolved. Spiked additions are generally used every 10 or so samples to enable reasonably immediate identification of possible errors in the data. For the same reason, samples are analysed in duplicate at a similar frequency. If the result of a spiked or duplicated sample is inconsistent with the expected result, all the samples that have been analysed since the last correct measurement need to be reanalysed.

2.9.5 Detection Limits

Analytical laboratories have minimum detection limits, which generally depend on the instrumentation that is available. These are usually reported as the limit of detection (LOD), or the limit of reporting (LOR). LOR is a value below which the laboratory cannot confirm the repeatability of the result. Although laboratory instruments and equipment also have upper limits to the concentrations that they can reliably measure (and which may be governed by the calibration), if samples present very high concentrations they can be diluted prior to analyses. Dilutions up to 10,000 times may need to be done on some samples to enable analyses, but this introduces potential errors. The operator needs to be aware of the limitations of the instrumentation, for example, analysing samples with very high concentrations of some substances can severely contaminate the instrument as well as all other samples that are analysed subsequently.

2.9.6 Dealing with Difficult Samples

Seawater has a very different chemical composition than fresh water (▶ Chapter 1), and for many types of analyses, an entirely different method is required. Analyses of seawater samples by ICP–MS, for example, are complicated by the usually very low concentrations of trace elements, and by the very high salt content, which can cause complex interferences. These interference problems have mostly been overcome by advancements in instrument design. There may also be different analytes in the same sample that require different pre-treatment and instrument operations. Nutrient analyses of soils and sediments may be required for total nitrogen and total phosphorous, and also for relevant nitrogen species (e.g. nitrate, nitrate, ammonia) and phosphorous (e.g. orthophosphate) species. Analyses of total nutrients require pre-treatment via chemicals and autoclave digestion, whereas analyses of nutrient species do not. Hence, the different sample matrix requires the instrument to be calibrated and operated differently for total nitrogen and phosphorus as compared to their species.

2.9.7 Dealing with Novel Contaminants

The rapidly increasing number and quantity of new and emerging contaminants are challenging for analytical scientists. It is difficult to develop reliable and accurate testing methods at the same pace as new contaminants are being identified, although efforts con-

tinue (e.g. Liu et al. 2015a, 2015b) (▶ Chapter 13). Without analytical methods to identify the presence and concentration of novel contaminants, their toxicity and environmental behaviour cannot be investigated and their effects on the environment will remain unknown.

2.10 Identifying Contamination

As discussed in ▶ Chapter 1, a contaminant is a substance that is present in unnaturally high concentrations (i.e. above background concentrations). For all synthetic substances, this is any measured concentration, whilst for naturally occurring substances, the background concentration will vary with location. In aquatic systems, some substances are far more toxic in seawater than in fresh water, and vice versa, and the levels of contamination that may have negative effects on organisms and ecosystems differ greatly. Many substances are naturally present in different types of ecosystems at very different concentrations. The same concentrations of nutrients, for example, could indicate contamination in oligotrophic marine waters (e.g. coral reefs), but might be a normal background concentration in an estuaries.

2.10.1 Determining Background Concentrations

By definition, the assessment of contamination depends on **knowledge of the normal**, or **background concentrations**. Whilst most synthetic substances have no normal background concentration, there are exceptions to this with contaminants (such as DDT) that are now distributed globally.

In Australia state-based environmental protection agencies describe background concentrations as being natural or ambient:

- **Natural**—the amount of a chemical substance that is naturally occurring and is derived/originated from natural processes (e.g. erosion and dissolution of minerals), and is related to specific human activities or sources. The concentrations will depend on a wide range of factors such as the geology, geography, topography, and biological and chemical characteristics of the receiving environments.
- **Ambient**—the concentration of a chemical substance that is representative of the surrounding area and is not from a single source (e.g. widespread diffusion, historical activities). If the determination of the natural background concentration is not possible due to long-term human impacts, the ambient background concentration still provides a means of identifying increases due to future inputs.

In the absence of background concentration data, reference sites are often used. Appropriate **reference sites** must have similar physicochemical conditions and not be impacted. Samples from reference sites should be taken at the same time as samples from the study site, handled in the same manner, and preferably analysed by the same laboratory. Samples collected for the purpose of determining background concentrations should not be combined. Reference sites are selected on a case-by-case basis. Careful collection of samples for determining background concentrations is critical, since this information will be used to identify contamination (e.g. Crommentuijn et al. 2000).

Water

Sampling to determine background concentrations in water requires the following considerations:

- **samples should be taken upstream or up current (if relevant)**—awareness of conditions such as inflow, outflow, and currents;
- **recent rainfall or extended dry periods**—storm events may result in short-lived changes in water quality that may not be representative of background concentrations, and concentrations of potential contaminants may also not be representative of typical background concentrations following unusually dry periods; and
- **water quality parameters** (e.g. pH, hardness, conductivity, temperature, suspended and total dissolved solids, and dissolved oxygen)—should be measured prior to and during sampling to provide assurance of the stability of the system at the time of sampling.

Sediment

Sampling for the purpose of determining background concentrations in soils and sediments requires the following considerations:

- the samples should be taken from relatively undisturbed sites at a higher elevation and upwind of the study site;
- sediments should have similar lithology as the study area;
- samples should have no odour or staining; and
- reference sites should be geographically, chemically, physically, and biologically similar to the impact site.

Activities or events that result in sediment deposition and their frequency and intensity need to be understood to help interpret geochemical signatures of contaminants in sediments and sediment cores. For example, inputs into estuaries that are derived from broad-scale agriculture activities in river catchments may have a deposition record linked to pulse rainfall events.

A range of information is required to fully characterise an area of interest and identify when measured concentrations exceed normal background levels and these may vary considerably throughout a study site. By using approaches like sediment normalisation to determine regional geochemical baselines, a more integrated understanding of contaminant concentrations over space and time can be achieved.

Biota

It may be important to determine background concentrations of contaminants in Biota. This is particularly relevant for biomonitoring, whereby it is necessary to understand the naturally occurring concentrations of potential contaminants in organisms to enable the identification of an increased body burden. Oysters, for example, are often used as biomonitors to measure environmental concentrations of metals. As the normal concentrations of metals in oysters tissue may vary depending on geological location, it is important that background concentrations are determined in areas where oysters are being used as biomonitors (e.g. Scanes and Roach, 1999).

2.10.2 Normalising Techniques

It is common to normalise the total contaminant concentration to the organic carbon content in sediments for hydrophobic organic compounds (Simpson and Batley, 2016). It is a useful approach to establish differences in organism exposure because the organic carbon is important in establishing the equilibrium between the solid and liquid phases of sediments (Di Toro et al. 1991) and takes account of the relative partitioning between pore water, organic carbon, and Biota (Simpson and Batley, 2016). Contaminants may also be normalised to the sediment grain size either by analysis of selective sediment grain size fractions or by completing post-extraction normalisation procedures (e.g. Birch and Snowdon, 2004). It is also a standard procedure to remove sediment particles > 2 mm as part of sample processing prior to analysis (ANZG, 2018). For Biota sampling, hydrophobic organic compound concentrations may also be normalised to lipid content. Consideration should be given to normalisation procedures prior to sampling but also once early results are available. It is helpful to ensure that some portion of the sample remains intact and well stored in case retrospective sampling needs to be undertaken.

2.10.3 Understanding Degradation

Following the distribution of contaminants in the environment, some compounds (mainly organic compounds) degrade over time. As the compounds degrade or break down, they generally become less toxic, but there are cases where the degradation products are actually more toxic than the original compound. The herbicide diuron (1,1-dimethyl, 3-(3',4'-dichlorophenyl) urea) is used in agriculture for weed control around water bodies and is a component of marine antifouling paints. There is evidence that most of the degradation products of diuron are much more toxic than the parent molecule (Tixier et al. 2001; Giacomazzi and Cochet, 2004). For further details on degradation, see Chapters 7 and 8.

2.10.4 Using Guideline Values

Water, Biota, and sediment quality guidelines or trigger values provide a tool for assessing whether a given chemical or physical stressor is likely to cause unacceptable harm to a specific community value (e.g. human or agricultural health, recreation, or ecological protection). As environmental conditions are dynamic and infinitely variable, site-specific guidelines are always the most appropriate, but are not always available, in which case non-site-specific values are used (ANZG, 2018).

Water Quality Criteria (WQC) are defined and expressed differently throughout the world. Australia, New Zealand, and the United States, and more recently China and South Africa, use the term WQC or Water Quality Guideline (WQG). The first WQC was published in America in 1968 by the National Technical Advisory Committee (NTAC) and has been continually revised by the United States Environmental Protection Agency (US EPA) since 1972. The most recent WQC published by the US EPA lists 120 priority pollutants, 43 nonpriority pollutants, and 23 pollutants with organoleptic (i.e. taste and odour) effects (US EPA, 2009). The US EPA WQC provides:

- **criteria maximum concentrations (CMCs)**, which are the estimated highest concentrations of a substance in surface water to which brief exposure is not predicted to cause unacceptable effects on aquatic ecosystems; and
- **criteria continuous concentrations (CCCs)**, which are estimations of the concentrations to which an aquatic ecosystem can be indefinitely exposed without experiencing unacceptable effects.

However, for the majority of these pollutants, only concentrations that are relevant to human health (e.g. by exposure or ingestion) are provided.

Environmental risk limits (ERLs) are used to derive environmental quality standards (EQS) in several countries (e.g. the Netherlands; Crommentuijn et al. 2000). ERLs include negligible concentrations, maximum per-

missible concentrations, maximum concentrations that are considered acceptable for ecosystem protection, serious risk concentrations, and maximum permissible concentrations.

Guideline values for aquatic ecosystems may be based on reference-site data, field-effects data, or laboratory-effects data. Increasingly, importance is placed on using multiple lines of evidence (i.e. a combination of at least two of these data types) (See Chapters 3 and 7 for further details on how guideline values are developed).

2.10.5 Development of Guidelines for New and Emerging Contaminants

For the benefit of human and ecological health, in recent years a lot of research effort has focussed on new and emerging contaminants (▶ Chapter 13). This is critically important as the number and quantity of new chemicals are increasing rapidly. You may be aware of numerous examples of substances that were not known to be toxic until well after they caused devastating effects, such as DDT and the Minamata mercury poisoning event. This point should be considered when determining the amount of research effort that should be directed towards developing methods for measuring and assessing the toxicity of new and emerging contaminants.

Water and sediment quality guidelines and trigger values provide tools for assessing potential impacts of a wide range of contaminants, and arriving at meaningful estimates of these values takes dedicated time and effort from people with a wide range of expertise. As mentioned earlier, there are no analytical techniques for many emerging contaminants, and this must be resolved before environmental toxicologists, analysts, and policymakers can even begin to estimate the risks of new and emerging contaminants.

2.11 Summary

The first step in understanding marine pollution is understanding the contaminants in the environment. Before we can investigate the effects or potential effects of contaminants, we need to be able to measure them, which requires sampling. The sampling design (e.g. location(s), sites (e.g. reference sites, number of sites), sample number/frequency, sampling methods) will depend on the **purpose of the research**. The quality of the sampling will become irrelevant if the sampling is not designed in a way that can provide meaningful data. After the research purpose has been clearly defined, the sampling program can be designed.

The **accuracy**, and therefore, relevance, of research findings involving environmental samples depends on several consecutive processes. If any one of these processes is not carried out correctly, it can jeopardise the results, regardless of how well every other process was conducted. The importance of maintaining the **integrity** of samples begins with sampling, transport, and storage, prior to analyses. The accurate analysis depends on correct sample **handling**, processing and pre-treatment, preparation for analysis, operation of instrumentation, instrumentation accuracy/calibration, and finally data **analyses**, **interpretation,** and **reporting**. Most of these stages have several elements.

Accurate measurement of contaminants in environmental samples, alongside an understanding of the effects of such contaminants, allows, finally, for an ability to identify the presence and degree of contamination, and provide guidance for policy and regulation to protect environmental and human health. This entire process obviously requires a lot of **time** and **effort** from a wide range of highly **trained people** with a wide range of **expertise**, and even more so in the case of new and emerging contaminants.

2.12 Study Questions and Activities

1. Imagine you were designing a sampling program to assess the extent of contamination from a toxic chemical spill. Try and list in order the steps you would take to develop the program. It is expected that you would include at least 10 steps.
2. Using ◘ Table 2.6, determine how much sediment sample that would be required to collect from each site to complete the following analyses and explain how you would store your samples on collection. Analyses to be completed: total trace metals, TOC, pesticides, and grain size.
3. You are about to embark on a field trip to sample sediments at 27 sites for metals and pesticides, you will also be collecting physicochemical water quality data at each site and will need to determine sediment grain size and TOC for each sample. Using the guiding principles described in this chapter, create a checklist of all your sample collection equipment. Assume that there are no shops nearby and you need to be 100% self-contained (i.e. don't forget plenty of permanent markers and all those other minor, but essential, items).

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