Marine: sampling of water and sediment chemistry

Version 1.0

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Contents

Inventory and monitoring toolbox: marine

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Department of Conservation
Te Papa Atawhai

Synopsis

This section gives a summary of the application, most common approaches, key considerations and requirements associated with this methodology. For full details of how to perform sampling for water and sediment chemistry, please refer to the final section: 'Full details of technique and best practice'.

Within the context of this method, water and sediment 'quality' refers to chemical properties relating to estuarine and coastal ecosystem function (for chemical properties related to contamination, refer to 'Marine: sampling environmental contaminants'—doccm-2903042)[1]. The chemical character of coastal and marine water and sediments is closely related to local geology, hydrography and climate, as well as sources of nutrient loading. Sampling chemical properties in sediment and water is used to measure and understand the condition of the environment, and enables managers to examine changes in condition and ascertain risks to estuarine and coastal habitats. Chemical composition of sediment and water contribute to ecological processes, such as nutrient cycling, organic matter remineralisation, primary production, oxygenation, carbon dioxide flux and denitrification efficiency. Chemical and biological sampling provide an understanding of the ecosystem function and the relationship between ecological and chemical processes. Changes in levels of contaminants and biological processes can provide early indication of shifts in the functioning of the wider ecosystem beyond what is expected naturally.

Ocean acidification is the ongoing decrease in the pH of the Earth's oceans, caused by the uptake of carbon dioxide (CO_2) from the atmosphere (Caldeira & Wickett 2003). Ocean acidification is a key issue that is predicted to alter a number of key chemical and ecological processes. However, this issue is beyond the scope of this method—more information can be found at www.carim.nz.

Typical chemical properties analysed in sediment and water are outlined in Table 1. The most common methods for sampling chemical concentrations in sediment and water are:

1) Instrumentation that collects data electronically using sensors that are deployed into water or sediment.

2) Physical collection of sediment and water samples that are sent to professional laboratories to determine concentrations or levels. Sampling water and sediment to determine chemical composition is commonly conducted by scientists and government organisations (i.e. regional councils) for various purposes. These may include state of the environment monitoring, resource consent condition monitoring, recourse consent assessment of environmental effects and various scientific studies.

This document outlines methods for field collection and appropriate storage and transport for post-laboratory processing of water and sediment samples. The chemical variables, arrangement of

[1] http://www.doc.govt.nz/documents/science-and-technical/inventory-monitoring/im-toolbox-marine-sampling-environmental-contaminants.pdf

sites, number of samples per site, volume of samples and frequency of sampling will be determined by the objectives of the monitoring study. Typically, sampling is repeated monthly, quarterly, biannually or annually and can be used in long-term monitoring. A robust sampling design should complement water and sediment chemistry sample collection with the collection of covariate data (sediment type, grain size, plankton counts etc.) to describe variability within the study and aid in the analysis and interpretation of sampling data.

Analysis of chemical properties can help inform the status of components involved in ecological processes that support ecosystem functioning (e.g. nutrient cycling, carbon dioxide flux etc.), and or impact assessments and changes in the long-term condition of the study site. To determine if chemical levels are ecologically meaningful and represent departures from a natural state, they are often compared against expected levels of the chemical property required for the specified process (e.g. oxygen and carbon dioxide for photosynthesis) and/or historical data to assess change in the long-term condition of the study area. This is often achieved by generating percentile distributions that can be used as threshold values against which incoming data can be compared. Alternatively, chemical and physical properties levels can be compared against threshold values presented within the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC 2000). Often threshold values for a given study are pulled from several sources relevant to each chemical property and often are site specific. For example, the *Canadian Sediment Quality Guidelines for the Protection of Aquatic Life* were developed by the Canadian Council of Ministers of the Environment (CCME 2002) as broadly protective tools to support the functioning of healthy aquatic ecosystems. They are based on field research programmes that have demonstrated associations between chemicals and biological effects by establishing cause-and-effect relationships in several case studies.

Regardless of the study approach and interpretation of chemical levels (assessing ecosystem functioning, temporal change or threshold values/guidelines), results will lend to decisions about future monitoring and implementing management actions.

Examples of questions that water and sediment chemistry sampling can be applied to include:

- What are the chemical levels at a specific site, and how do they compare to the levels at other sites within New Zealand?
- What are the temporal changes in chemical properties of water and or sediment of estuary, freshwater or coastal environments?
- What are the dissolved oxygen levels at the surface and at depth, and are these levels near to having sub-lethal effects on benthic fish (typically < 30% dissolved oxygen)?
- What are the levels of nitrogen near a recently implemented sea-run salmon farm, and how do these nitrogen levels change over time and space?

Key considerations for water and sediment sampling include:

- Cost
- The availability of historical data

- Current gaps in data and future data requirements given current and potential future pressures
- What to sample
- Which variable(s) to analyse
- Number and or volume of samples to collect (proper replication)
- Spatial arrangement of sampling
- Any covariate information to be recorded concurrently
- Skill level required of personnel
- Equipment and other resources required
- Temporal replication
- How the results of the study will be interpreted and/or analysed (e.g. compared to historical data, chemical levels at other sites, water quality standards)

Table 1. Types of chemical properties measured in water and sediment (excluding contaminants, which are covered in 'Marine: sampling environmental contaminants'—doccm-2903042).

Chemical property	Description	Water	Sediment
Salinity	The amount of salts dissolved in water. It is usually measured in PSU (practical salinity unit), which is a unit based on the properties of seawater conductivity. It is equivalent to per thousand or g/kg of water.	✓	
pH	A figure expressing the acidity or alkalinity of a solution on a logarithmic scale on which 7 is neutral, lower values are more acid and higher values more alkaline. The pH is equal to $-\log_{10} c$, where c is the hydrogen ion concentration in moles per litre (mol/L). pH can be measured using sensors attached to equipment lowered into the water column, or water samples can be collected and tested in a laboratory.	✓	
Sediment grain size distribution	The distribution of sediment grain size in a sample of sediment. Typically, sediment would be measured in millimetres or on the phi scale. Volume of sediment within size class categories is used to classify sediment on the Wentworth scale (e.g. muddy sand). Particle size distribution is either measured by dry sediment sieving or laser defraction. Laser analysis can only be undertaken on particles less than 2 mm; particles over 2 mm can be measured using sieves and data merged later.		✓
Biological/biochemical oxygen demand (BOD)	The amount of dissolved oxygen consumed in a waterbody by biological processes breaking down organic matter. BOD is used by some councils as a measure of the amount of organic pollution in water.	✓	
Total suspended solids (TSS)	The dry weight of particles trapped by a filter. It is a water quality parameter used, for example, to assess the quality of wastewater after treatment in a wastewater treatment plant.	✓	

Chemical property	Description	Water	Sediment
Dissolved oxygen	The oxygen that is dissolved in water. The oxygen dissolves from the air–water interface and photosynthesis from phytoplankton, seagrass and macroalgae. It is usually measured as oxygen concentration (mg/L) and dissolved oxygen saturation (%).	✓	
Chlorophyll-*a* and fluorescence	Chlorophyll-*a* and fluorescence (dominated by fluorescence of phytoplankton pigments) refers to the amount of phytoplankton in the water column. Chlorophyll-*a* (Chla) is usually presented as concentrations (mg Chla/m^3) often by depth over time.	✓	
Turbidity	The amount of particulates in the water. High turbidity can be caused by heavy rainfall, disturbance of the riverbed or bank by heavy machinery, or through direct discharges. Usually measured in nephelometric turbidity units (NTUs), a measurement of light scatter.	✓	
Total suspended solids	The amount of particles in the water column measured in ppm, mg/L, g/L and %.	✓	
Photosynthetically active radiation (PAR)	The amount of light/radiation available for photosynthesis between 400–700 nm. PAR is measured as m^{-2} s^{-2}.	✓	
Dissolved reactive silicon (DRSi)	The amount of silicon dissolved in water. The amount of silica in the water reflects a combination of input from run-off and the biological fixation of phytoplankton skeletons, which are deposited and then dissolved into the water. Generally measured in µmol/L, g/m^3 (the same as mg/L) or parts per billion (ppb). 1 ppb = 0.001 g/m^3.	✓	
Dissolved reactive phosphorous (DRP)	The dissolved (soluble) phosphorus compounds in water that are readily available for use by plants and algae. DRP concentrations are an indication of a waterbody's ability to support nuisance algal or plant growths (algal blooms). Generally measured in µmol/L, g/m^3 (the same as mg/L) or parts per billion (ppb). 1 ppb = 0.001 g/m^3.	✓	
Nitrate (NO_3-N)	The amount of nitrate in water. Nitrate is a highly soluble molecule made up of nitrogen and oxygen with the chemical formula NO_3. It is a very important plant fertiliser but because it is highly water soluble—it leaches through soils very easily, particularly after heavy rainfall. It is one of the most common contaminants in waterways in rural and urban areas. NO_3-N can be transformed to other forms of nitrogen. Sources of NO_3-N include excessive application of inorganic fertiliser, septic tanks and leaking sewage systems. Nitrate also enters waterways as a result of nitrification of the ammonia in animal waste by bacteria in soil. Generally measured in µmol/L, g/m^3 (the same as mg/L) or parts per billion (ppb). 1 ppb = 0.001 g/m^3.	✓	✓

Chemical property	Description	Water	Sediment
Ammoniacal nitrogen (NH_4-N)	The amount of ammoniacal nitrogen in water. Ammoniacal nitrogen (NH_4-N), also often called 'ammonium', covers two forms of nitrogen: ammonia (NH_3) and ammonium (NH_4). NH_4-N can be transformed to other forms of nitrogen and is a very important plant fertiliser but is less mobile in the soil than nitrate-nitrogen. It enters waterways primarily through point source discharges, such as raw sewage or dairy shed effluent. It is toxic to aquatic life at high concentrations. Generally measured in µmol/L, g/m^3 (the same as mg/L) or parts per billion (ppb). 1 ppb = 0.001 g/m^3.	✓	✓
Dissolved organic nitrogen	The amount of organic nitrogen dissolved in water. Nitrogen in high concentrations can over-stimulate algal growth causing eutrophication. Generally measured in µmol/L, g/m^3 (the same as mg/L) or parts per billion (ppb). 1 ppb = 0.001 g/m^3.	✓	✓
Dissolved organic carbon	The amount of organic carbon dissolved in water. Carbon levels give an indication of the amount of carbon consumed in photosynthesis and released from remineralisation. Generally measured in µmol/L, g/m^3 (the same as mg/L) or parts per billion (ppb). 1 ppb = 0.001 g/m^3.	✓	
Particulate carbon (PC)	The amount of particulate carbon in water. Carbon levels give an indication of the amount of carbon consumed in photosynthesis and released from remineralisation.	✓	
Particulate nitrogen (PN)	The amount of particulate nitrogen in water. Excessive particulates can cause oxygen consumption potentially leading to anoxic events. Generally measured in g/m^3 (the same as mg/L) or parts per billion (ppb). 1 ppb = 0.001 g/m^3.	✓	
Total nitrogen (TN)	The amount of total nitrogen in water. TN is used in photosynthesis, but in excess can over-stimulate algal growth causing eutrophication. Generally measured in g/m^3 (the same as mg/L) or parts per billion (ppb). 1 ppb = 0.001 g/m^3.	✓	✓
Apparent redox potential discontinuity (aRPD)	The depth of the aRPD boundary is one index of redox potential discontinuity (RPD), or the extent of oxygenation within sediments. Eutrophication is often initiated by excessive nutrient input resulting in plankton and algal blooms, which can have adverse effects on the water column and underlying sediments. Generally measured in mm or cm depth from the surface of the sediment.		✓

Assumptions

- Sites are representative of the wider coastal environment or gradient or effect that is to be analysed and determined.
- Sites and samples are statistically independent.
- Sampling effort is similar across sites, locations and/or sampling occasions.
- The chemical properties of interest can be sampled and processed with sufficient accuracy for the research or survey objectives.
- The number of samples collected is appropriate to capture natural variability.

Advantages

- This method is amenable to implementation on beaches, freshwater, estuarine, coastal and marine environments, both within and outside marine reserves throughout New Zealand.
- Sampling is repeatable over time.
- Can be used in long-term monitoring.
- Methods are recognised and utilised nationally for environmental monitoring so that comparisons outside the specific study area can be made.
- The method is amenable to the collection of covariate data regarding the physical environment.
- Requires only basic equipment (except when using a water profiler).
- Sample collection is relatively easy to accomplish.
- Random sampling of an area is possible.
- The number of samples to collect is adaptable to the study area, although a minimum number should be calculated prior to sampling.
- Samples can be stratified to encompass various water depths and/or distance from a source of investigation.

Disadvantages

- Only provides a snapshot of the biogeochemical system, with subsequent surveys required to add temporal variation.
- May be costly to process samples in a contracted laboratory.
- Sampling times may be restricted by tidal cycle and adverse weather.
- Effects-related results may be masked by environmental conditions at the time of sampling.

Suitability for inventory

This method is not suitable for inventories because of the temporal variability in water and sediment chemistry.

Suitability for monitoring

This method is well suited to monitoring a wide range of chemical attributes due to the ability to replicate the same method over time and space with a high level of consistency. Changes in concentrations of interested variables can be used to assess the condition of an area, track change over time and advise management strategies.

Skills

Undertaking assessment of the chemical properties of coastal waters and sediments requires a specific skill set enabling effective survey design, implementation, sample analysis, data analysis and reporting results. These skills include:

Pre-survey:

- Survey design skills for determining the number of replicates, power analysis, stratification (if any) and placement of replicates, and what variables are to be recorded.
- GIS knowledge for the planning of field locations and sites.
- Transfer of site coordinates to portable GPS.
- Where appropriate, dive-planning skills (e.g. max depth and times) and knowledge of relevant standard operating procedures.
- Setting up the software and membranes on a water profiler (when and if applicable).
- Coordination skills to ensure all sample containers are appropriate for analysis planned (e.g. some types of heavy metal analysis require acid-washed glass).

In the field:

- Good fitness is needed as access to some sites may require walking considerable distances carrying sampling equipment across sand, gravel or rocky beaches.
- Knowledge of appropriate health and safety protocols (including SCUBA safety regulations certification where relevant).
- The skills to record and securely manage data.
- Use of portable GPS.
- Ability to preserve, package and ship samples as required for specific processing.

Data analysis:

- Basic statistical skills for analysing chemistry results from laboratory testing.
- Familiarity with statistical packages (*R* recommended).
- Appropriate storage of data.

Interpretation:

- Knowledge of chemical oceanography will allow interpretation of the significance of any changes identified and identification of potential confounding factors.
- Ecological knowledge will allow correlation of biological and chemical factors and inferences of possible effects of any changes seen in chemical properties.
- Knowledge of ecology and chemistry is required to develop future management recommendations, identification of possible confounding factors and recommendations of future analysis.

Dissemination:

- Scientific writing and presentation skills are required to disseminate results concisely.

Resources

Survey work requires a minimum of two people for safety reasons. When operating off a vessel, three may be required. In addition to the usual SCUBA diving gear and associated safety equipment (when required), this section describes the specific gear required for sampling environmental contaminants.

- Comprehensive first-aid kit.
- Communications (cell-phone or handheld radio).
- Protective gloves.
- Appropriate clothing and footwear (boots, waders or wetsuit).
- Sunscreen, hat, insect repellent and plenty of snacks and water.
- Wet weather gear and warm items of clothing as weather can change quickly.
- General field equipment, including pencils, slates, waterproof paper.
- Clipboard with pre-prepared data sheets printed on waterproof paper. Figure 1 shows a generic sediment sample data sheet; however, this data sheet will need to be adjusted to fit the survey objectives and specific data objectives. The data sheet will need to be printed and filled out in the field (see 'Full details of technique and best practice').
- GPS unit and map for site location.
- Water profiler (conductivity-temperature-depth (CTD), Sonde, handheld probe).
- Waterproof camera.
- Scoop, corer or sediment sampler for sediment sampling (ensure the material of scoop will not contaminate samples).
- Bucket, water sampler bottle (e.g. Van Dorn) and/or hose system.
- Pre-labelled containers for sediments and water for laboratory analysis.
- Sharpies or permanent markers for sample labelling.
- Ice or cooler.
- Vessel and associated personnel if needed.
- For sampling requiring the use of divers, all equipment and personnel necessary for the safety of divers will be required as outlined in DOC's 'Scientific diving and snorkelling technical document' (doccm-237640).[2]

[2] http://www.doc.govt.nz/documents/science-and-technical/inventory-monitoring/im-toolbox-marine-scientific-diving-and-snorkelling-technical-document.pdf

Sampling of Water and Sediment Chemistry Metadata			
Survey Objectives: to be filled in prior to printing			
Survey Name:		Location:	Vessel:
Office Contact:	Survey Leader Name:	Contractor Name:	Recorder:
Event Date:	Event Time:	Site Name:	Site Latitude: Site Longitude:
Protection Status:	Weather:	Tide:	Tidal Zone:
Analysis Type:	Water Profiler:	Site Notes:	

Sampling of Water and Sediment Chemistry Data									
Sample ID	Replicate Within Site	Sample Latitude	Sample Longitude	Abiotic	Biotic	Sample Variable	Sample Aggregate	Aggregate Size	Sample Depth

Figure 1. Example of a generic sediment field sampling data sheet ('Sampling of water and sediment chemistry—data sheet'—doccm-5446874).[3] Note: This may need to be adjusted depending on the specific survey objectives, design and covariate data.

[3] http://www.doc.govt.nz/documents/science-and-technical/inventory-monitoring/im-toolbox-marine-sampling-of-water-and-sediment-chemistry-data-sheet.docx

Minimum attributes

Consistent measurement and recording of these attributes is critical for the implementation of the method. Other attributes may be optional depending on your objective. For more information, refer to 'Full details of technique and best practice'.

DOC staff should complete a 'Standard inventory and monitoring project plan' (docdm-146272)[4].

Once back from the field, enter your data into a spreadsheet. The importance of entering data using correct formatting cannot be stressed enough. You should have one line per sample collected. Each of these lines should also include the data presented in Table 2 and any associated covariate data. By using this formatting method, each sample collected during the survey will have clear metadata associated with it.

Table 2. Minimum data attributes to be recorded for water and sediment chemistry sampling.

Database field	Description	Value
Survey Objectives	A statement of the goals and objectives of the survey, with reference as to how the survey method will achieve the stated objectives.	Unlimited text
Survey Name	A name for this survey. Allows for differentiation of surveys conducted at different dates at similar location (e.g. Poor Knights Feb 2015).	Short text
Location	General locality where the sampling occurred (e.g. Wellington Harbour).	Short text
Vessel	Vessel used to collect samples, if appropriate.	Unlimited text
Office Contact	Name (first name + surname) of the key contact in DOC office who was related to this survey.	Short text
Survey Leader Name	Name (first name + surname) of the person in charge of this survey.	Short text
Contractor Name	Name of person/company contracted to carry out the survey, if applicable.	Short text
Recorder	Name of the person who recorded the transect data.	Unlimited text
Event Date	Date of sampling.	Date (dd/mm/yyyy)
Event Time	Time at which the sample was collected.	Time in 24 h format (hh:mm)
Site Name	Site within *Location* where the sampling occurred.	Short text

[4] http://www.doc.govt.nz/Documents/science-and-technical/inventory-monitoring/im-toolbox-standard-inventory-and-monitoring-project-plan.doc

Site Latitude	Decimal degree latitude for the site (WGS84) (e.g. latitude for Wellington Conservation House is −41.289904).	Number with up to 6 digits after decimal. Values are between −90 and 90, but typically negative for New Zealand.
Site Longitude	Decimal degree longitude for the site (WGS84) (e.g. longitude for Wellington Conservation House is 174.775043).	Number with up to 6 digits after decimal. Values are between 0 and 360.
Protection Status	Indicates the protection status of the area sampled.	One of the six values: • Marine reserve (type 1 MPA) • Type 2 MPA • Mātaitai • Taiāpure • Other protection • No protection
Weather	Description of the atmospheric conditions (wind, sea state, swell, etc.).	Unlimited text
Tide	Simplified tidal level at the time of sampling.	One of the four values: • Low • Medium • High • Undetermined
Tidal Zone	Intertidal, Subtidal	Unlimited text
Analysis Type	Type of analysis the samples are being collected for.	E.g. salinity, total suspended solids, dissolved organic nitrogen etc.
Water Profiler	Make, model, serial number of water profiler used, if applicable.	Unlimited text
Site Notes	Any general notes relating to *Site Name.*	Unlimited text
Sample ID	A unique identifier during this survey for this specific sample.	Unique number
Replicate Within Site	Number of replicate within the site, starting at 1 and up to the number of samples achieved at that particular site. Note that if only one sample was achieved per site, then this field takes the value 1 throughout.	Integer
Sample Latitude	Decimal degree latitude for the sample within the site (WGS84).	Number with up to 6 digits after decimal. Values are between −90 and 90, but typically negative for New Zealand.
Sample Longitude	Decimal degree longitude for the sample within the site (WGS84).	Number with up to 6 digits after decimal. Values are between 0 and 360.
Abiotic	A description of the physical component of the benthos (silt, mud, gravel, shell hash, boulder, etc.).	Short text
Biotic	A description of the dominant habitat-creating organisms associated with the	Short text

	benthos (*Ecklonia*, red algae, Crustose Corraline Algae, Mytilidae, Pinnidae, etc.).	
Sample Variable	The type of sample being collected (e.g. sediment type, water).	Unlimited text
Sample Aggregate	Is the sample an aggregate of a number of smaller samples?	Yes or No
Aggregate Size	Number of samples that have contributed to an aggregate sample.	Integer
Sample Depth	Depth at which the sample is collected. For water samples this is depth below water surface; for sediment samples this is depth below sediment surface.	Integer

Optional attributes

It is recommended that you collect any additional covariate data that may aid in the interpretation of contaminant data. Covariate data could include:

- Depth at which the sample was collected if sampling is occurring sub-tidally
- Temperature, pH, dissolved oxygen, conductivity, tidal level, current, distance from structures (e.g. aquaculture facilities, sewage treatment plants etc.)
- A description of abiotic and biotic habitat within the vicinity of sample collection
- Sediment grain size, smell and colour, apparent redox potential discontinuity (aRPD) for sediment chemistry sampling
- Plankton counts
- Associated epifauna or infauna with target sample
- Whether any images were taken, and reference numbers for images for linking with the sample number
- Any additional notes that may be useful for future surveys or for interpretation of the results

Data storage

DOC is currently developing a national database to hold and provide access to data collected from marine reserve monitoring in New Zealand. The aims of the database are to:

- Support consistent standards in national marine reserve monitoring programmes for marine environmental quality
- Coordinate and optimise marine reserve monitoring in New Zealand
- Provide a high-quality monitoring dataset for New Zealand’s marine reserves

Once operational, this methodology will be updated with a description of how to lodge data within the national database. In the interim, data should be recorded within the spreadsheets associated with this methodology. It is essential that all raw data sheets are completed, digitised and backed

up. Raw data and associated metadata should be entered into databases/spreadsheets in a standardised format.

Data should be stored in a way that can be easily understood by a third party. To avoid repeating the metadata multiple times, the data could also be subdivided into two sections, the first one describing the metadata associated with the survey and the second comprising the sample data itself. A field with unique values should be created to make the link between the two sections. Each field recorded should be defined to remove any ambiguity in its meaning and use.

The metadata should also include a description of the monitoring objectives and any information that will allow someone unfamiliar with the monitoring to interpret the data and replicate the methodology. Data should be arranged so that each row represents one sample, with the corresponding data regarding site, replicate number and contaminant values arranged into columns. Ideally, all data should be located within a single database to facilitate ease of access.

For internal DOC monitoring, information pertaining to each survey within a marine reserve and resultant data/reports should be entered into the Marine Protected Area Monitoring and Research (MPAMAR) data sheet[5] so there is an easily accessible account of the survey.

Analysis, interpretation and reporting

Seek advice from a statistician or suitably experienced person prior to undertaking any analysis. Ideally, statistical advice should be sought prior to any data collection to ensure that the design of the data collection is robust and suitable for answering the question at hand. For quality control, the data should be checked for correct counts or volume per sample area, and pre-labelled containers and bags should be checked to remove any errors in data entry.

Data analysis

The type of analysis most applicable to the data will largely be determined by the research question, and whether additional supporting information (such as physical conditions or biological/physical habitat variables) has been collected or is available. The common method for summarising and presenting water and sediment chemistry data is to calculate the mean concentration level and corresponding statistical variance. Concentrations from each replicate sample for a site are summed and an average calculated for that site. Statistical variance provides a measure of how the data are distributed around the mean. These means can be compared to historical data for that site, other sites within the study, increasing distances from point source pollution site (e.g. sewage outfall), ANZECC thresholds, chemical property specific thresholds and/or risk indicators. Statistics can be applied to test for differences in chemical levels between locations and between years. Depending on the questions, data distribution, and the hypotheses

[5] 'MPAMAR metadata—national' (doccm-1163829): http://www.doc.govt.nz/documents/science-and-technical/inventory-monitoring/im-toolbox-marine-MPAMAR-metadata-national.xls

underpinning the monitoring, time series analysis, regression analysis and analysis of variance (ANOVA) may be appropriate statistical tests.

Interpretation

Interpretation of results should be performed with the assistance of a statistician as well as consideration of the major driving forces operating within the system. At this stage, it should be determined whether the objectives of the original data collection have been achieved and whether the data are sufficient to answer those questions outlined prior to the initial surveys.

Reporting

Reporting will largely be governed by the duration of the monitoring and data collection. If data collection is ongoing, regular reports should be submitted at 3–5-year intervals, whereas for short-term (< 2 years in duration) data collection, reports should be submitted within a year of the final data collection.

Case study A

Case study A: Coastal water quality and ecology of the Wellington region: state and trends (Oliver & Milne 2012)

Synopsis

Greater Wellington Regional Council conducts broad- and fine-scale ecological monitoring to ascertain estuarine condition in several estuaries within the Wellington region. The estuary monitoring process consists of three components developed from the National Estuary Monitoring Protocol (Robertson et al. 2002), of which the fine-scale monitoring component included monitoring of chemical indicators of sediment and water (the other two components being ecological vulnerability assessments and broad-scale habitat mapping). This synopsis focuses on sediment and water chemistry attributes from fine-scale monitoring at Pāuatahanui Arm and Onepoto Arm of Porirua Harbour over a four-year period. Pāuatahanui Arm and Onepoto Arm have had high to moderate modification, and adjacent land-use includes pasture, urban development, and exotic and native forests (see key estuary characteristics, Table 3). Sediment samples were collected and analysed for a suite of variables to include organic content, nitrogen and phosphorous concentrations and sediment oxygenation. These variables are considered key indicators for eutrophication levels, one of the key variables in assessing ecosystem health (Robertson et al. 2002). The results from this study are compared against the Wriggle Coastal Management set of ‘condition indices’ or ‘ratings’, which are based on a combination of expert opinion from extensive monitoring of estuaries in New Zealand and consideration of international literature (Stevens & Robertson 2006). The sediment results suggested the estuary was in a ‘transitional state’ in regard to eutrophication, therefore to better understand eutrophication levels and establish a baseline of nutrient and chlorophyll-*a* concentrations, physio-chemical water sampling was initiated in 2011.

Overall, results from 2008 and 2011 established a baseline of estuary condition for Porirua Harbour, against which change and future impacts can be measured.

Objective

- Conduct fine-scale monitoring of physical, chemical and biological indicators of the water and sediment to detect spatial and temporal changes in the condition of the Pāuatahanui Arm and Onepoto Arm in Porirua Harbour.

Table 3. Key features of the Pāuatahanui and Onepoto arms of the Porirua Harbour Estuary. (Modified from Oliver & Milne 2012.)

	Porirua Harbour	
	Pāuatahanui Arm	**Onepoto Arm**
Estuary type	Tidal lagoon	Tidal lagoon
Estuary area (ha)	450–470	240–250
Depth (m)	1–2*	1–3
Catchment area (km^2)	109	65
Catchment land uses (% cover dominant land uses)	Pasture (61%), exotic forest (18%), native forest (14%), urban (6%)	Pasture (39%), urban (36%), native forest/scrub (18%)
Major tributaries	Pāuatahanui and Horokiri streams	Porirua Stream
Degree of modification	Moderate	High
Survey years	2008, 2009, 2010, 2011†	

Notes:
* A maximum water depth of 10 m has been recorded in the main channel.
† Reduced in scope following completion of initial baseline in 2010.

Sampling design and methods

- Fine-scale monitoring is based on the methods described in the National Estuary Monitoring Protocol (Robertson et al. 2002).
- Four fine-scale sediment sampling sites were selected in the intertidal zone, two within each arm of Porirua Harbour, and sampled annually from 2008–2011 (Figure 2, top).
- Each site was divided into 12 equal-sized plots; a sediment sample was a composite of samples from 10 randomly selected plots. A minimum of three replicate sediment samples were collected at each site.
- Samples were collected for sediment grain size (texture), nutrient and organic content (total nitrogen, total phosphorous and total organic carbon), heavy metal concentrations, and benthic fauna abundance and diversity using a core.
- Colour and texture were described and oxygenation (average apparent redox potential discontinuity (aRPD) depth) were recorded (Figure 3).
- The data from this study were synthesised and compared to fine-scale estuary condition ratings (Robertson & Stevens 2006). Select ratings pertinent to this case study are illustrated in Figure 4. The ratings are based on a review of estuary monitoring data,

guideline criteria and expert opinion. They are designed to be used in combination with each other (usually involving expert input) when evaluating overall estuary condition and deciding on appropriate management.

- In 2011, water samples were collected monthly on a mid-ebb tide from six sites in Porirua Harbour (Figure 2, bottom) and analysed for temperature, pH, salinity, conductivity, dissolved oxygen, turbidity, total suspended solids (TSS), soluble and total nitrogen and phosphorus, and chlorophyll-*a*.
- Chilled sediment and water samples were sent to R.J. Hill Laboratories for analysis. Refer to Table 4 and Table 5 for sediment and water analytical methods.

a.

b.

Figure 2. Location of sample sites within Porirua Harbour. (a) Sediment sites from fine-scale monitoring. (b) Water sampling locations. (Modified from Oliver & Milne 2012.)

Figure 3. Sediment core samples taken from Site B in the upper Onepoto Arm of Porirua Harbour in 2008 (left) and 2010—note the shallower aRPD depth in 2010. (Taken from Oliver & Milne 2012.)

Table 4. Estuarine sediment quality analytical methods. (Modified from Oliver & Milne 2012.)

Determinant	Method	Detection limit
Sediment particle/grain size (2 mm, 63 µm–2 mm, and < 63 µm fractions)	Air dried at 35°C and sieving using 2 mm and 63 µm sieves, gravimetry (calculation by difference)	0.1 g/100 g dry wt
Total organic carbon (TOC)	Acid pre-treatment to remove carbonates if present, Elementar Combustion Analyser	0.05 g/100 g dry wt
Total recoverable phosphorus	Nitric/Hydrochloric acid digestion, ICP-MS, screen level, US EPA 200.2	40 mg/kg dry wt
Total nitrogen	Catalytic Combustion (900°C, O_2), separation, Thermal Conductivity Detector [Elementar Analyser]	0.05 g/100 g dry wt

Table 5. Porirua Harbour water quality analytical methods. (Taken from Oliver & Milne 2012.)

Determinant	Method	Detection limit
Electrical conductivity (EC)	Saline water, Conductivity meter, 25°C. APHA 2510 B 21st Ed. 2005.	0.10 mS/m
Salinity	Meter, no temp. compensation. APHA 2520 B 21st Ed. 2005.	0.2 ppt
Turbidity	Saline sample. Analysis using a Hach 2100N, Turbidity meter. APHA 2130 B 21st ed. 2005.	0.10 NTU
Total suspended solids (TSS)	Filtration using Whatman 934 AH, Advantec GC-50 or equivalent filters (nominal pore size 1.2–1.5µm), gravimetric determination. APHA 2540 D 21st Ed. 2005.	2 mg/L
Total ammoniacal nitrogen	Saline, filtered sample. Phenol/hypochlorite colorimetry. Discrete Analyser. (NH_4-N = NH_4+-N + NH_3-N). APHA 4500NH_3 F (modified from manual analysis) 21st Ed. 2005.	0.01 mg/L

Nitrite nitrogen (Nitrite-N)	Saline sample. Automated Azo dye colorimetry, Flow injection analyser. APHA 4500-NO_3-I (Proposed) 21st Ed. 2005.	0.002 mg/L
Nitrate nitrogen (Nitrate-N)	Calculation: (Nitrate-N + Nitrite-N) – NO_2N.	0.002 mg/L
Nitrate-N + Nitrite-N	Saline sample. Total oxidised nitrogen. Automated cadmium reduction, Flow injection analyser. APHA 4500-NO_3-I (Proposed) 21st Ed. 2005.	0.002 mg/L
Total Kjeldahl nitrogen (TKN)	Total Kjeldahl digestion (sulphuric acid with copper sulphate catalyst), phenol/hypochlorite colorimetry. Discrete Analyser. APHA 4500-N_{org} C. (modified) 4500 NH_3 F (modified) 21st Ed. 2005.	0.1 mg/L
Total nitrogen	Calculation: TKN + Nitrate-N + Nitrite-N.	0.05 mg/L
Dissolved reactive phosphorus	Filtered sample. Molybdenum blue colorimetry. Discrete Analyser. APHA 4500-P E (modified from manual analysis) 21st Ed. 2005.	0.004 mg/L
Total phosphorus	Total phosphorus digestion (acid persulphate), ascorbic acid colorimetry. Discrete Analyser. APHA 4500-P E (modified from manual analysis) 21st Ed. 2005.	0.004 mg/L
Chlorophyll-*a*	Acetone extraction. Spectroscopy. APHA 10200 H 21st Ed. 2005 (modified).	0.003 mg/L

Total Organic Carbon

Estuaries with high sediment organic content can result in anoxic sediments and bottom water, release of excessive nutrients and adverse impacts to biota - all symptoms of eutrophication.

TOTAL ORGANIC CARBON CONDITION RATING

RATING	DEFINITION	RECOMMENDED RESPONSE
Very Good	<1%	Monitor at 5 year intervals after baseline established
Good	1-2%	Monitor at 5 year intervals after baseline established
Fair	2-5%	Monitor at 2 year intervals and manage source
Poor	>5%	Monitor at 2 year intervals and manage source
Early Warning Trigger	>1.3 x Mean of highest baseline year	Initiate Evaluation and Response Plan

Redox Potential Discontinuity

The RPD is the grey layer between the oxygenated yellow-brown sediments near the surface and the deeper anoxic black sediments. It is an effective ecological barrier for most but not all sediment-dwelling species. A rising RPD will force most macrofauna towards the sediment surface to where oxygen is available. The depth of the RPD layer is a critical estuary condition indicator in that it provides a measure of whether nutrient enrichment in the estuary exceeds levels causing nuisance anoxic conditions in the surface sediments. The majority of the other indicators (e.g. macroalgal blooms, soft muds, sediment organic carbon, TP, and TN) are less critical, in that they can be elevated, but not necessarily causing sediment anoxia and adverse impacts on aquatic life. Knowing if the surface sediments are moving towards anoxia (i.e. RPD close to the surface) is important for two main reasons:

1. As the RPD layer gets close to the surface, a "tipping point" is reached where the pool of sediment nutrients (which can be large), suddenly becomes available to fuel algal blooms and to worsen sediment conditions.
2. Anoxic sediments contain toxic sulphides and very little aquatic life.

The tendency for sediments to become anoxic is much greater if the sediments are muddy. In sandy porous sediments, the RPD layer is usually relatively deep (>3cm) and is maintained primarily by current or wave action that pumps oxygenated water into the sediments. In finer silt/clay sediments, physical diffusion limits oxygen penetration to <1cm (Jørgensen and Revsbech 1985) unless bioturbation by infauna oxygenates the sediments.

RPD CONDITION RATING

RATING	DEFINITION	RECOMMENDED RESPONSE
Very Good	>10cm depth below surface	Monitor at 5 year intervals after baseline established
Good	3-10cm depth below sediment surface	Monitor at 5 year intervals after baseline established
Fair	1-3cm depth below sediment surface	Monitor at 5 year intervals. Initiate Evaluation & Response Plan
Poor	<1cm depth below sediment surface	Monitor at 2 year intervals. Initiate Evaluation & Response Plan
Early Warning Trigger	>1.3 x Mean of highest baseline year	Initiate Evaluation and Response Plan

Total Phosphorus

In shallow estuaries like Freshwater the sediment compartment is often the largest nutrient pool in the system, and phosphorus exchange between the water column and sediments can play a large role in determining trophic status and the growth of algae.

TOTAL PHOSPHORUS CONDITION RATING

RATING	DEFINITION	RECOMMENDED RESPONSE
Very Good	<200mg/kg	Monitor at 5 year intervals after baseline established
Good	200-500mg/kg	Monitor at 5 year intervals after baseline established
Fair	500-1000mg/kg	Monitor at 2 year intervals and manage source
Poor	>1000mg/kg	Monitor at 2 year intervals and manage source
Early Warning Trigger	>1.3 x Mean of highest baseline year	Initiate Evaluation and Response Plan

Total Nitrogen

In shallow estuaries like Freshwater, the sediment compartment is often the largest nutrient pool in the system, and nitrogen exchange between the water column and sediments can play a large role in determining trophic status and the growth of algae.

TOTAL NITROGEN CONDITION RATING

RATING	DEFINITION	RECOMMENDED RESPONSE
Very Good	<500mg/kg	Monitor at 5 year intervals after baseline established
Good	500-2000mg/kg	Monitor at 5 year intervals after baseline established
Fair	2000-4000mg/kg	Monitor at 2 year intervals and manage source
Poor	>4000mg/kg	Monitor at 2 year intervals and manage source
Early Warning Trigger	>1.3 x Mean of highest baseline year	Initiate Evaluation and Response Plan

Figure 4. Condition ratings text and tables reproduced from reports prepared for Greater Wellington by Wriggle Coastal Management. (Modified from Oliver & Milne 2012.)

Results

- aRPD depth decreased over time in Pāuatahanui Arm and Onepoto Arm. In 2011, aRPD depth was 1 cm, which is the shallowest oxygenated layer since monitoring began in 2008. The aRPD depths were considered poor for Pāuatahanui Arm and poor to fair for Onepoto Arm compared to the condition ratings (Table 6).
- Organic content in both arms was considered very low (< 1%) compared to condition ratings (Table 6).
- Nitrogen and phosphorous levels were considered low to moderate in both arms of the estuary (Table 6).
- Benthic communities within both arms were considered healthy and diverse across all years, with increased presence of opportunistic species that are tolerant of moderate levels of organic enrichment. This finding initiated water sampling.
- Inner harbour sites experience higher levels of freshwater and stormwater inputs than outer harbour sites and therefore showed more variability. Concentrations of phosphorus, nitrogen and chlorophyll-*a* were all consistently low at the outer harbour site (E1) compared to inner harbour sites (Table 7).
- Chlorophyll-*a* varied seasonally at some sites, peaking in March and April 2011 at site O2 (Table 7).

Table 6. Estuary nutrient enrichment condition ratings for Porirua Harbour based on annual fine-scale monitoring, undertaken between 2008 and 2011 (*n* = 1–4). (Modified from Oliver & Milne 2012.)

Estuary issue	Indicator	Porirua Harbour							
		Pāuatahanui Arm				Onepoto Arm			
		2008	2009	2010	2011*	2008	2009	2010	2011*
Nutrient enrichment	Nuisance macroalgae cover (% estuary area with >50% cover)	Very Low (<1%)	Low (10%)	Low (7%)	Low (7%)	Moderate (41%)	Moderate (34%)	Moderate (23%)	Moderate (22%)
	Organic content (TOC)	Very Low (<1%)			Not tested	Very Low (<1%)			Not tested
	Nutrient content (N and P)	Low–Moderate			Not tested	Low–Moderate			Not tested
	aRPD depth (cm)	Good (3–4)	Fair–Good (1–4)	Poor (1)	Poor (1)	Good (2.5–6)	Fair (2–3)	Fair (1–1.5)	Fair (1–1.4)
	Macrofauna (organic enrichment)	Slightly enriched			Not assessed	Slightly enriched			Not assessed

Note:
* 2011 surveys reduced in scope following completion of initial baseline in 2010.

Table 7. Median (and range)* of values for selected variables measured during monthly water sampling between January and December 2011. (Taken from Oliver & Milne 2012.)

	Porirua Harbour Entrance (E1)	Pāuatahanui Arm North (P1)	Pāuatahanui Arm East (P2)	Pāuatahanui Arm South (P3)	Onepoto Arm North (O1)	Onepoto Arm South (O2)
TSS (mg/L)	6.5 (2–51)	12.5 (5–83)	8.5 (4–210)	11 (3–67)	10 (5–45)	21.5 (9–230)
Turbidity (NTU)	2.35 (1.22–19.5)	6.6 (2–54)	3.8 (2.1–169)	5.45 (1.57–15.6)	5.75 (2.2–25)	9.5 (1.56–126)
Salinity (ppt)	34 (32–35)	32.5 (29–35)	31 (11–35)	32 (22–35)	32.5 (28–35)	30 (15.8–34)
Chlorophyll-*a* (mg/L)	0.0015 (–)	0.0015 (0.0015–0.003)	0.0015 (0.0015–0.016)	0.0015 (0.0015–0.007)	0.0015 (0.0015–0.005)	0.0015 (0.0015–0.019)
Ammoniacal nitrogen (mg/L)	0.005 (0.005–0.026)	0.005 (0.005–0.041)	0.005 (0.005–0.074)	0.005 (0.005–0.038)	0.005 (0.005–0.051)	0.0165 (0.005–0.11)
Nitrate-N + nitrite-N (mg/L)	0.002 (0.001–0.138)	0.0035 (0.001–0.12)	0.01 (0.001–0.66)	0.001 (0.001–0.23)	0.003 (0.001–0.149)	0.1335 (0.001–0.37)
Dissolved reactive phosphorus (mg/L)	0.0055 (0.002–0.012)	0.007 (0.002–0.015)	0.008 (0.002–0.017)	0.0045 (0.002–0.014)	0.005 (0.002–0.017)	0.0035 (0.002–0.019)
Total phosphorus (mg/L)	0.0155 (0.012–0.046)	0.0265 (0.015–0.09)	0.0235 (0.015–0.24)	0.025 (0.016–0.036)	0.0275 (0.02–0.053)	0.039 (0.024–0.25)

Note:
* Values reported as below the laboratory detection limit have been halved.

Limitations and points to consider

- This methodology illustrates how collection of sediment and water can be used to determine the physical and chemical properties within an estuary.
- Although sediment nutrient concentrations were relatively low, both arms support high nuisance-level macroalgae cover, which may be contributing to organic enrichment.
- Macroinvertebrate abundance and diversity (infauna and epifauna) samples were also collected, but this is not discussed in this case study.
- Sedimentation plates were also placed at the sites to examine sedimentation rates, but this is not discussed in this case study.
- Sediments and water were analysed for organic and inorganic contaminants, but this is not discussed in this case study.

References for case study A

Jørgensen, B.B.; Revsbech, N.P. 1985: Diffusive boundary layers and the oxygen uptake of sediments and detritus 1. *Limnology and Oceanography 30*(1): 111–122. https://doi.org/10.4319/lo.1985.30.1.0111

Oliver, M.D.; Milne, J.R. 2012: Coastal water quality and ecology in the Wellington region: State and trends. Greater Wellington Regional Council, Publication No. GW/EMI-T-12/144, Wellington.

http://www.gw.govt.nz/assets/Our-Environment/Environmental-monitoring/Environmental-Reporting/Coastal-water-quality-and-ecology-SoE-report.pdf

Robertson, B.M.; Gillespie, P.A.; Asher, R.A.; Frisk, S.; Keeley, N.B.; Hopkins, G.A.; Thompson, S.J.; Tuckey, B.J. 2002: Estuarine environmental assessment monitoring: A national protocol. Cawthron Institute, Sustainable Management Fund Contract No. 5096, Nelson.

Robertson, B.; Stevens, L. 2006: Southland estuaries state of the environment report 2001–2006. Report prepared for Environment Southland by Wriggle Coastal Management, Nelson.

Robertson, B.; Stevens, L. 2008: Porirua Harbour: Fine scale monitoring 2007/08. Report prepared for Greater Wellington Regional Council by Wriggle Coastal Management, Nelson.

Robertson, B.; Stevens, L. 2009; Porirua Harbour: Intertidal fine scale monitoring 2008/09. Report prepared for Greater Wellington Regional Council by Wriggle Coastal Management, Nelson.

Robertson, B.; Stevens, L. 2010: Porirua Harbour: Intertidal fine scale monitoring 2009/10. Report prepared for Greater Wellington Regional Council by Wriggle Coastal Management, Nelson.

Sorensen, P.G.; Milne, J.R. 2009: Porirua Harbour targeted intertidal sediment quality assessment. Greater Wellington Regional Council, Publication No. GW/EMI-T-09-136, Wellington.

Stevens, L.; Robertson, B. 2006: Broad scale habitat mapping of sandy beaches and river estuaries on the western Wellington coast. Report prepared for Greater Wellington Regional Council by Cawthron Institute, Report No.1035, Nelson.

Case study B

Case study B: Water quality in the Marlborough Sounds: annual monitoring report July 2014–June 2015 (Broekhuizen 2015)

Synopsis

In 2011 Marlborough District Council started a water quality monitoring programme with sites in Queen Charlotte Sound and Tory Channel. Through collaboration with New Zealand King Salmon and the National Institute of Water and Atmospheric Research (NIWA), sites were added in Pelorus Sound and Port Gore. The water quality monitoring programme was designed to monitor the trophic status of the sounds. Broekhuizen's 2015 report focuses on collating water quality monitoring data results and trends over time and does not conduct formal statistical analysis on trophic status. Water quality characteristics such as nutrients, salinity, oxygen, temperature, concentrations of suspended solids, and volatile suspended solids were measured, and data are presented as station-specific near-bed and near-surface samples as time series. Probability distributions of the measurements were also calculated to assist Council staff in identifying outliers in the data, which could be used as quality control flags or guard values for incoming data to be compared against. There were no measurements of microbiological, organic contaminants or heavy metals. This study

provides an illustration of a water quality sampling and monitoring programme that was conducted to provide data that feeds into the examination and monitoring of the trophic status of the Marlborough Sounds.

Objective

- To collect water quality monitoring data that support assessment, monitoring and management of the trophic status of the Marlborough Sounds.

Sampling design and methods

- There were 11 sampling stations in each of Pelorus Sound and Queen Charlotte Sound/Tory Channel (Figure 5).
- Sampling was conducted once a month.
- Conductivity-temperature-depth (CTD) casts (using various water profiler devices) were made at all stations. The CTD was equipped with sensors to measure depth, conductivity, temperature, dissolved oxygen, photosynthetically active radiation (PAR) and fluorescence. CTD data were post-processed to remove the upcast; only the downcast data was used. Water column salinity and density were calculated from temperature and conductivity. Data were binned into 1-metre increments.
- Water was collected for analysis at a subset of stations (four in Queen Charlotte Sound, one in Tory Channel and seven in Pelorus Sound). Water samples were collected from close to the surface and close to the seabed. In 2011–2014 near-bed samples were collected with a Van Dorn bottle that was lowered 2 m above the seabed. From 2014 onward, samples were collected with a hose sampler. The hose sampler is a simple operation: a weighted hose is lowered down to 15 m, sealed, and then pulled aboard the vessel. The water is transferred to a bucket, stirred, and the sample is drawn out of the bucket. When recovered onto the boat, a sub-sample of the water is drawn and preserved with Lugols solution. The remainder of the sample is retained in a sealed bottle and packed in ice and transferred to the NIWA water quality laboratory.
- Water samples (not Lugols-preserved samples) were analysed for salinity, temperature, dissolved reactive silicon (DRSi), dissolved reactive phosphorus (DRP), nitrate (NO_3-N), ammoniacal nitrogen (NH_4-N), dissolved organic nitrogen, dissolved organic carbon, phytoplankton and zooplankton abundance (by cell counts) and biomass, volatile suspended solids (VSS), total suspended solids (TSS), chlorophyll-*a*, particulate organic carbon (POC), particulate organic nitrogen (PON), and total nitrogen (TN; combination of dissolved and PON).
- Table 8 shows the water quality characteristics, laboratory method and detection limit.

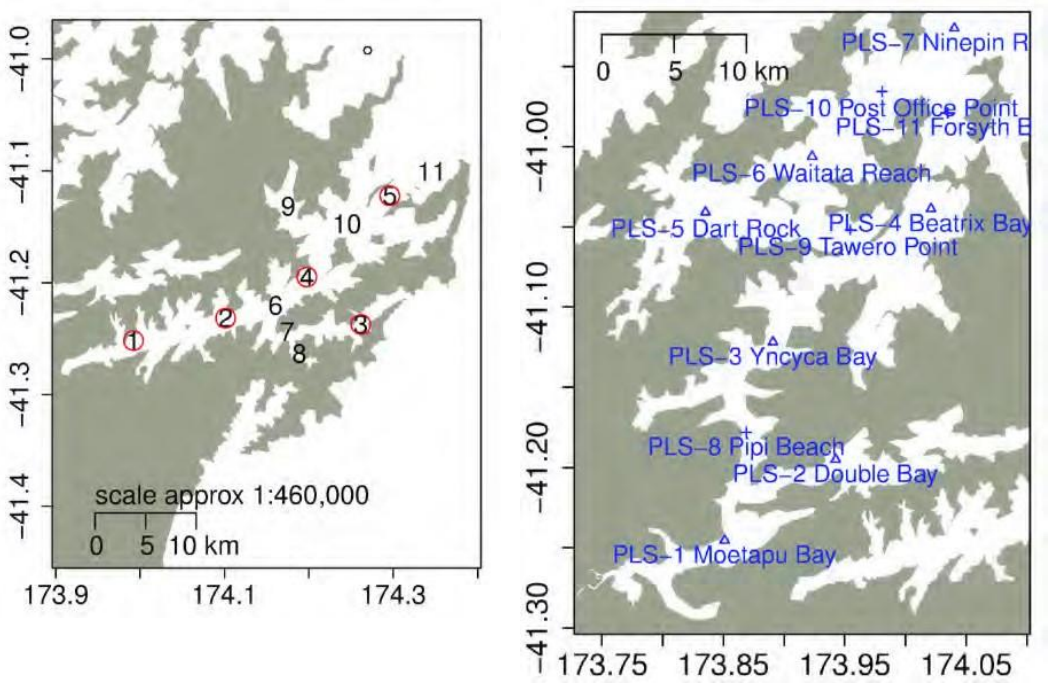

Figure 5. Locations of the Marlborough District Council sampling stations: (left) Queen Charlotte Sound/Tory Channel and Port Gore; (right) Pelorus Sound. For Queen Charlotte/Tory, circled numbers denote water-quality sampling stations, and unadorned numbers denote CTD-only stations. The black circle indicates the Port Gore sampling station. For Pelorus, water-quality stations are denoted with a triangle whilst CTD-only stations are denoted with a cross. (Taken from Broekhuizen 2015.)

Table 8. Characteristics measured in each water sample. (Modified from Broekhuizen 2015.)

Quantity	Laboratory method	Detection limit
Salinity	-	0.1 ppt
Turbidity	Turbidimeter rated against Formazin standards (APHA2130B)	0.1 Nephelometric Turbidity Units
Total suspended solids	Filtration (GF-C), drying at 104°C (APHA 2540D)	0.5 g m^{-3}
Suspended inorganic solids	Filtration (GF-C), drying at 104°C, followed by furnacing at 400°C	0.5 g (DW*-AFDW†) m^{-3}
Volatile suspended solids	TSS-SIS	0.5 g AFDW m^{-3}
Dissolved reactive silicon	Molybdosilicate/ascorbic acid reduction. APHA4500Si	1 mg Si m^{-3}
Dissolved reactive phosphorus	Simultaneous Autoanalysis (Astoria)	1 mg P m^{-3}
Dissolved organic phosphorus	TDP-DRP	1 mg P m^{-3}
Total dissolved phosphorus	Persulphate digest, molybdenum blue, FIA (Lachat)	1 mg P m^{-3}
Ammoniacal nitrogen	Simultaneous Autoanalysis (Astoria)	1 mg N m^{-3}
Nitrate+Nitrite	Simultaneous Autoanalysis (Astoria)	1 mg N m^{-3}
Total dissolved nitrogen	Persulphate digest, auto cadmium reduction, FIA (Lachat)	10 mg N m^{-3}
Dissolved organic nitrogen	TDN-NH_4N-NO_3N	1 (if NH_4N+NO_3N > 10) mg N m^{-3}
Dissolved organic nitrogen	TDN-NH_4N-NO_3N	1 (if NH_4N+NO_3N > 10) mg N m^{-3}
Chlorophyll-*a*	Filter onto GF-C filter (approx. 1.2 µm pore size); Acetone pigment extraction, spectrofluorometri *c* measurement.	0.1 mg Chla m^{-3}
Particulate organic carbon	Filtration onto GFC, acidification, Catalytic combustion @900°C, sep, TCD, Elementar C/N analyser	0.1 mg C m^{-3}
Particulate carbon	Filtration onto GFC, Catalytic combustion @900°C, sep, TCD, Elementar C/N analyser	0.1 mg C m^{-3}
Particulate nitrogen	Filtration on GF/C, Catalytic combustion @900°C, sep, TCD, Elementar C/N analyser	0.1 mg N m^{-3}

Notes:
* DW: Dry Weight
† AFDW: Ash Free Dry Weight

Results

The results presented here are results of salinity, dissolved oxygen, particulate nitrogen (PN), particulate carbon (PC), PN:PC and total nitrogen from water quality monitoring results from the Queen Charlotte Sound programme of 2014, specifically station five (QCS5). These results are not

exhaustive; many other elements were tested for. For full results see Broekhuizen (2015). It is important to note that Broekhuizen did not conduct any formal statistical analysis.

- Near-surface salinities were lower than near-bed measurements. Salinities did not exceed 30 PSU. Those measured in the laboratory tend to be slightly higher than those measured at sea throughout the sampling period (Figure 6).
- Whilst no formal cross-correlation tests were made, salinities at different sites appear to be positively correlated. Fluctuations at the Sound scale suggested that all areas sampled were responding to one or more shared drivers (rainfall runoff, evaporation, intrusions from Cook Strait).
- Near-surface dissolved oxygen concentrations were high (> 80% saturation) at all stations throughout the sampling period. Concentrations were found to be highest in spring and lowest in late summer/early autumn. As expected, oxygen concentrations decreased with depth (Figure 6).
- Particulate nitrogen, particulate carbon and PN:PC results are shown in Figure 7.
- Total nitrogen was determined as the sum of particulate and total dissolved nitrogen. Total nitrogen is illustrated in Figure 7.
- Empirical cumulative probability distributions were generated for each water quality variable measured to identify the quantity-values (usually concentrations) corresponding to the 50th (median), 95th, 98th and 100th percentiles. The data were divided into season and depth strata (near-surface versus near-bed); as such, percentile distributions can be used to set up a quality control value for incoming data. Broekhuizen suggests threshold values be set and if a value falls outside the band then it should be subject to investigation. An example histogram is shown in Figure 8.
- The report explains several instances where data were rejected, along with associated reasons (see pp. 93–96 in Broekhuizen 2015). For example, data were excluded from the results for the following reasons: sample mix up; lab analyser failed to load the samples properly; conductivity results not adequate to calculate salinity; in-field equipment failure or mishap; the water sample bottle hit the seabed causing the sample to represent abnormal turbidity values.

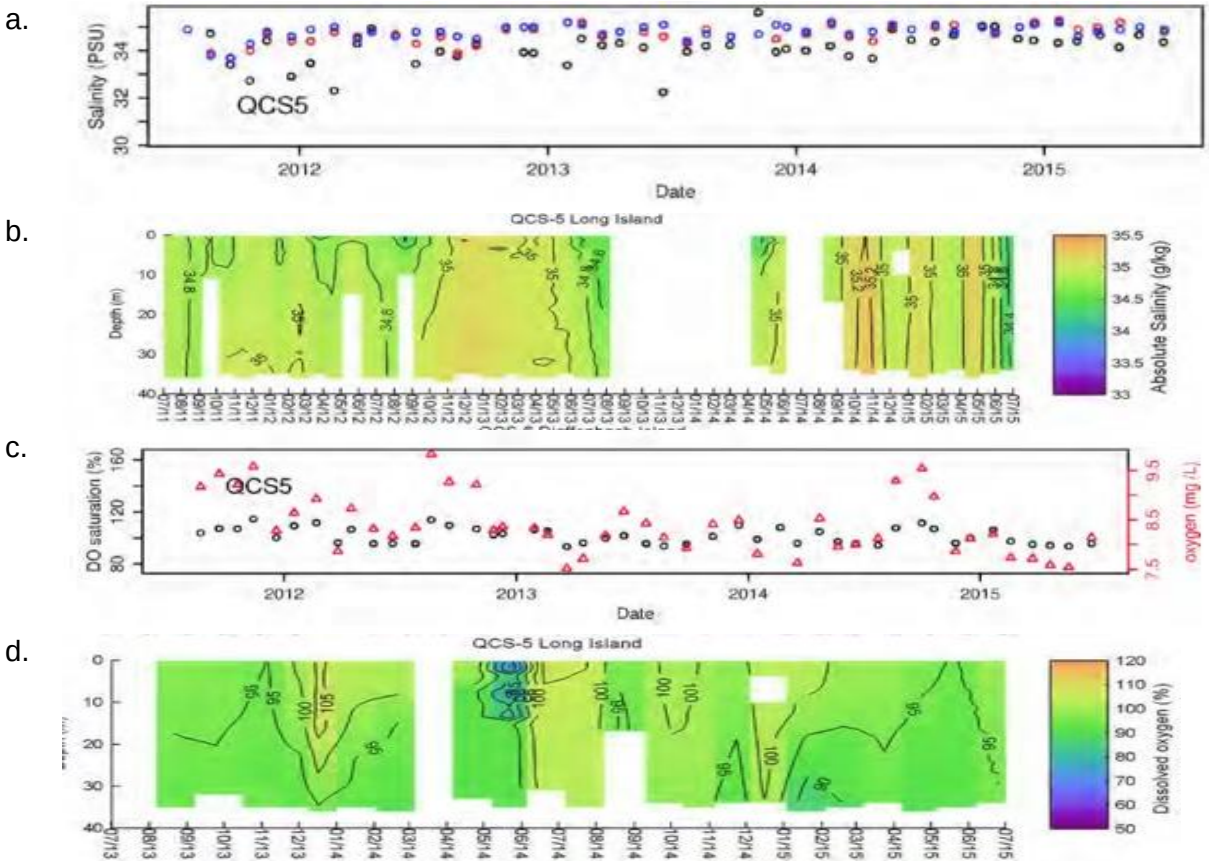

Figure 6. Results from the Queen Charlotte Sampling Station 5, QCS5, Long Island, through time. (a) Salinity measured at sea with a handheld probe at 1 m depth (black circles) and in water samples returned to the laboratory (red circles: near surface (1 m or depth averaged to 15 m); blue circles: near-bed). (b) Salinity derived from monthly CTD casts. White space indicates missing/rejected data (or the maximum depth to which the cast extended). (c) Dissolved oxygen measured at 1 m below the sea-surface, black symbols are oxygen saturation (left axis), red symbols are concentration (right axis). Dissolved oxygen saturation is a function of salinity, temperature (and air pressure) as well as absolute oxygen concentration. (d) Oxygen saturation from monthly CTD casts. White space indicates missing/rejected data (or the maximum depth to which the cast extended). (Modified from Broekhuizen 2015.)

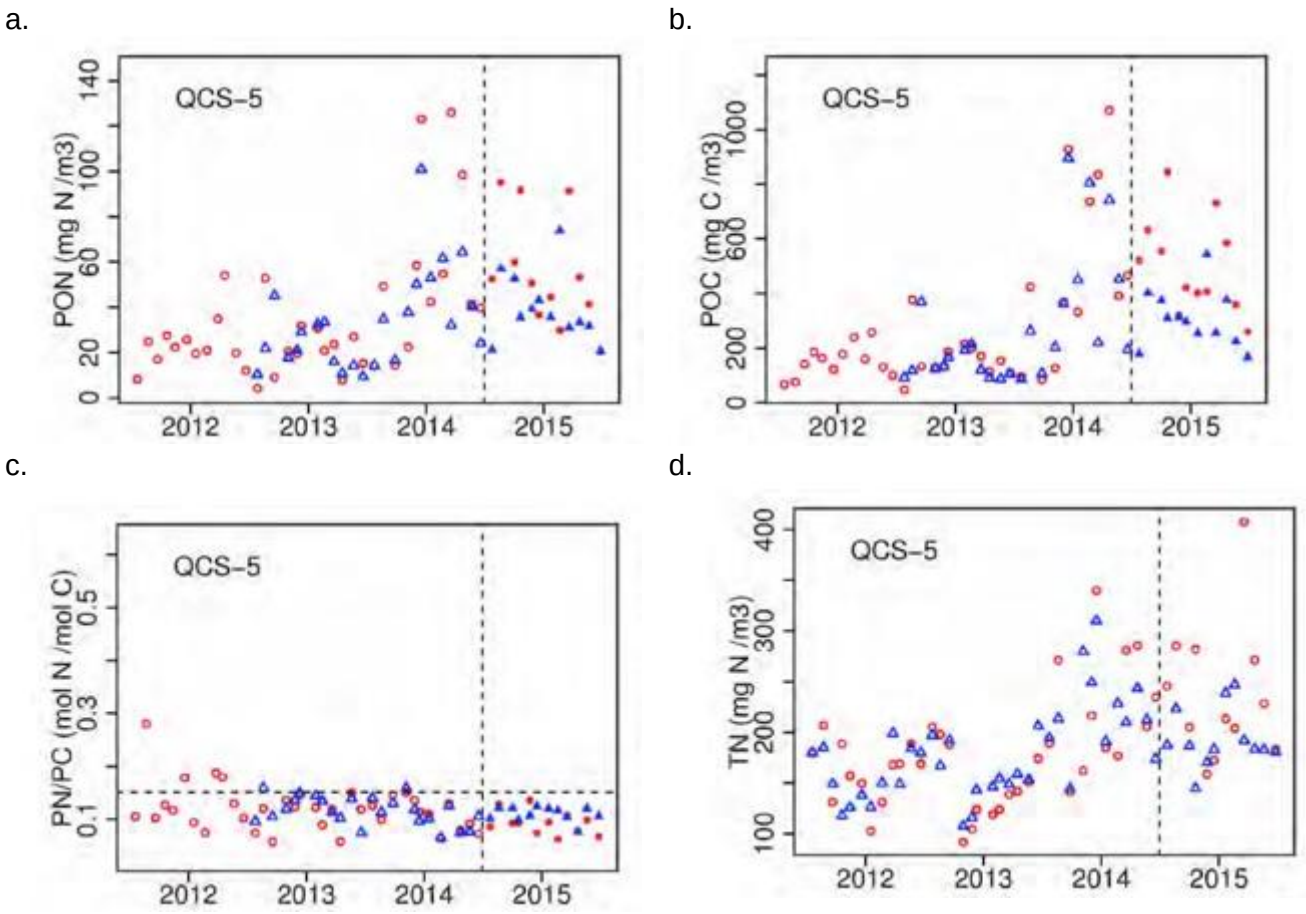

Figure 7. Results from the Queen Charlotte Sampling station 5, QCS5. Near-surface (red) and near-bed (blue). The dashed vertical line (1 July 2014) separates measurements of Particulate Organic Nitrogen sampled at 1 m depth using a Van Dorn bottle from measurements of Particulate Nitrogen sampled from the upper 15 m using a hose-sampler. (a) Particulate nitrogen. (b) Particulate carbon. (c) PN:PC ratios; the horizontal dashed line represents the so-called 'Redfield ratio' (empirically determined N:C ratio for particulate material in oceanic waters). (d) Total nitrogen. (Modified from Broekhuizen 2015.)

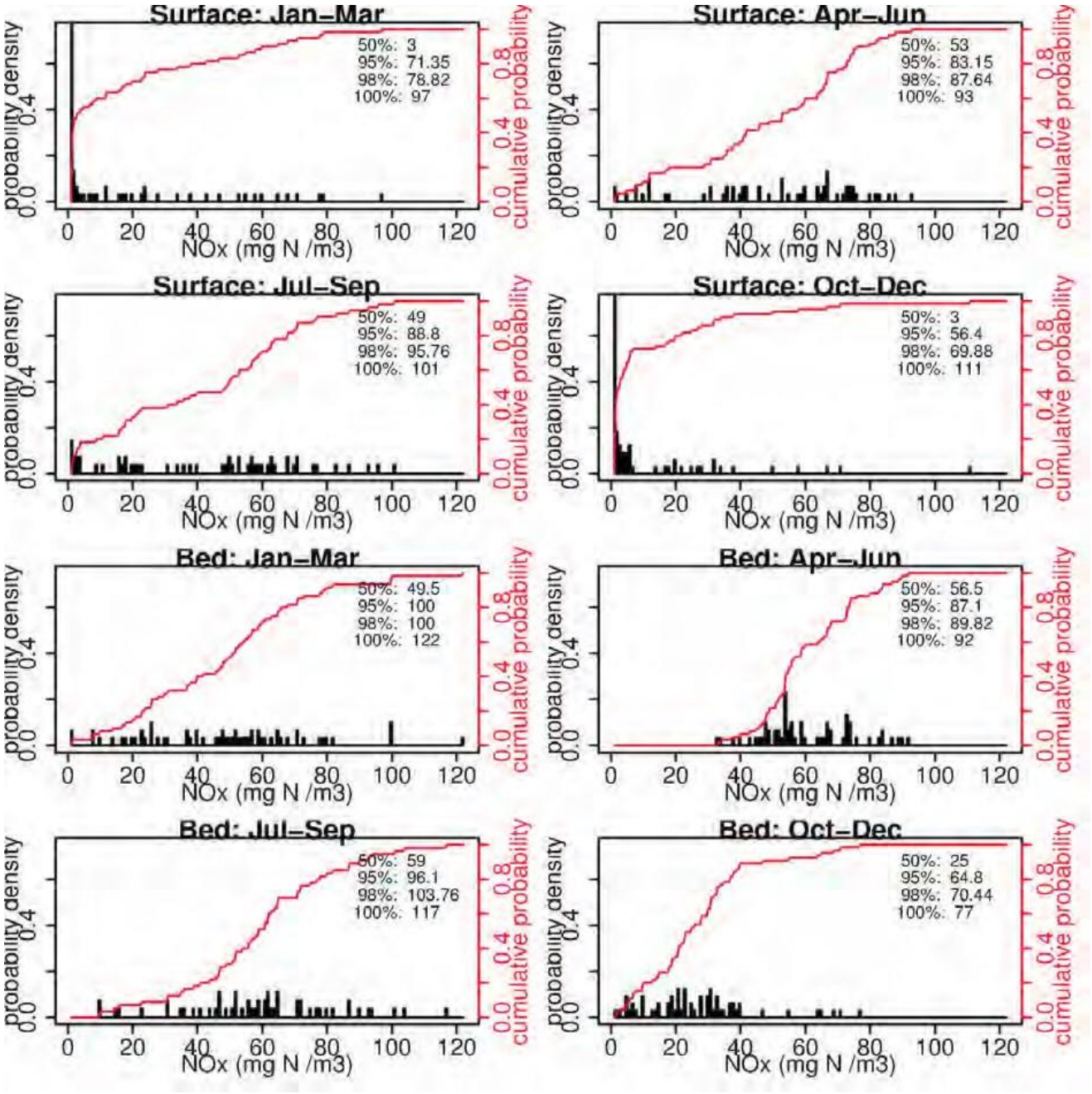

Figure 8. Empirical probability density distributions for near-surface and near-bed nitrate in Queen Charlotte Sound/Tory Channel. (Taken from Broekhuizen 2015.)

Limitations and points to consider

- Differences in salinity results from the lab versus the field may be due to the sampling device being at slightly different depths or it may indicate an inconsistency between the calibrations of the conductivity meters that are used in the field and in the lab.
- Differences in sediment analysis techniques (i.e. laser versus dry sieve) produce different results.

- In comparison with terrestrial particulate organic matter, fresh marine particulates (living plankton and freshly dead plankton) tends to have a high N:C content.
- Broekhuizen suggests a list of questions to ask if a data value falls outside the threshold values or band: (e.g. Did the sampler hit the seabed? Was there any recent river flooding?).
- Setting threshold or guard values is a subjective decision and variable specific. Guard values should be used as flags for further investigation of the data, not as the sole criteria for rejection. These values should be revisited periodically.

References for case study B

Broekhuizen, N. 2013: Review of historical water-quality data from Pelorus Sound and Queen Charlotte Sound: long-term NIWA time-series and Marlborough District Council time-series. NIWA Client Report (for New Zealand King Salmon Ltd) HAM2013-070 (project NZKS13401).

Broekhuizen, N. 2015: Water quality in the Marlborough Sounds: Annual monitoring report July 2014–June 2015. NIWA Client Report (for Marlborough District Council) HAM2015-094 (project MDC15201). https://www.marlborough.govt.nz/repository/libraries/id:1w1mps0ir17g9sgxanf9/hierarchy/Documents/Environment/Coastal/Sounds%20Water%20Quality%20List/SoundsWQMonitoringResults20142015.pdf

Morrisey, D.; Anderson, T.; Broekhuizen, N.; Stenton-Dozey, J.; Brown, S.; Plew, D. 2015: Baseline monitoring report for new salmon farms, Marlborough Sounds, NIWA Client Report (for New Zealand King Salmon) NEL1014-020 (project NZK13401).

Rabalais, N.N. 2002: Nitrogen in aquatic systems. *Ambio 31*(2): 102–112.

Vaquer-Sunyer, R.; Duarte, C.M. 2008: Thresholds of hypoxia for marine biodiversity. *Proceedings of the National Academy of Science of the United States of America 105*(40): 15452–15457. https://doi.org/10.1073/pnas.0803833105

Full details of technique and best practice

The exact survey/monitoring design will be governed by the research question, but the following text details the techniques for sampling water and sediment chemistry, including considerations for survey design, steps to undertake during sampling, and how to process samples. It also provides links to data sheets for the recording of survey data, advice on the timing of surveys, health and safety considerations, and how to undertake quality assurance of your data.

Survey design

Monitoring preparation includes developing a robust survey design, including prior consultation with experts/statisticians, to ensure the design meets the requirements to answer the research question. The following aspects need to be incorporated.

- Identify the monitoring objectives.
- Write a statement of clear outcomes of the surveys and how they relate to the original monitoring objectives.
- Determine which variables are of interest for measurement and what kind of samples need to be collected (sediment, water) to obtain those measurements (see Table 1).
- Define the survey area, number of sites to be surveyed and their extent, and the number of replicates within each site (ensure replicates are independent by designing rules for spatial arrangement). Multiple samples need to be collected to ensure statistical sensitivity to sampling.
- Obtain any necessary permits (e.g. marine reserve research permits).
- Determine cost of sample analysis as this may determine replication.
- Once the above is determined, randomly (e.g. using mapping software such as GIS) or haphazardly (e.g. based on habitat or point source location) allocate sampling locations within sites. Sediment samples are typically collected at random points along transects or from a pre-defined grid, whereas water samples are typically collected at specific depths.
- Determine depth stratification of samples.
- Determine how samples are to be collected (e.g. by water profiler, water collection device, hand, corer or grab) and how field data are to be recorded.
- Determine a survey schedule to ensure that data are collected as required over the lifetime of the study.
- Determine what covariate data (if any) is to be collected/recorded (e.g. a description of abiotic and biotic habitat within the vicinity of sample collection; sediment grain size).
- Prepare all gear, maps and associated data sheets.
- Prior to sampling, identify and contact a laboratory for water and sediment chemistry analysis (see Appendix B). Through coordination with the laboratory, determine how they require samples to be stored, or sent (type of container: plastic, glass, frozen, preserved etc.), size of sample required for analysis, and how they should be transported and delivered (chilled, frozen).

Sampling procedure

Following the formulation of a clear and robust survey design, a typical process for conducting water and sediment chemistry sampling includes the following steps.

1. Ensure all personnel involved in sampling are clear about the protocol for the survey they are conducting. This should include any rules relating to placement of collection point and associated strata.
2. Determine the sampling locations, spatial extent of sampling (experimental unit, samples to be collected from (e.g. 1 m^2, depth of water column) and minimum distance between sites.
3. Navigate to the site where sampling is to begin, using either pre-determined GPS coordinates or permanent markers.

4. Record metadata for the survey and site as per the fields in the 'Sampling of water and sediment chemistry—data sheet' (doccm-5446874)[6] (see Table 2 for field explanations).
5. Once the sample site is identified and metadata have been recorded, record data for the primary variables of interest in the 'Sampling of water and sediment chemistry—data sheet' (doccm-5446874) (see Table 2 for field explanations). The exact fields to be filled in will vary depending on survey design, target collection, strata etc. In all cases, applying a systematic technique to recording data and collecting the samples will produce the most accurate information.
6. Collecting the sample: This step will depend on what is being used for chemical analysis (sediment, water). The amount of sample will depend on the type of analysis—contact the laboratory prior to sampling to determine the amount necessary, and preservation and transport methods and requirements.
    a. **Sediment:** Required sampling equipment will depend on the chemical properties of interest. Generally, there are two types of sediment sampling techniques: surface or near-surface with a hand sampler (e.g. spoon, scoop, spatula etc.) or grab (e.g. Ponar, Shipek etc.) and subsurface with a core. In the intertidal zone, a hand scoop or a simple corer can be used to collect sediment from the surface and depth. A ruler will be required to measure the depth of sediment. Standard corers used in council monitoring programmes are cylinders of 13 cm in diameter. Corers are usually constructed from a combination of metal and an inert material (plastic or polycarbonate) to prevent chemical reaction between the corer and the sediments. Corers are pushed into the sediment to a depth of 15 cm in intertidal applications, extracting a total volume of 1990 cm^3, but may be deeper in subtidal applications depending on the depth of infauna communities.[7] Exact core depth should be driven by the research question. In the shallow subtidal zone a sediment grab, such as a Shipek or Ponar grab, can be deployed from a vessel. Alternatively, a SCUBA diver can collect sediment by hand with an appropriate tool.

        Regardless of collection technique, once the sample is collected it requires care to ensure that the sample is not contaminated. To avoid chemical contamination or changing the physio-chemical characteristics, all inorganic samples should be transferred and collected into cleaned plastic containers and organic samples should be transferred and collected into glass or aluminium containers. For trace metal analysis, stainless steel samplers should have Teflon coatings for pieces that encounter sediments. Samples collected to be analysed for volatile organic compounds (VOCs) should be collected in a way that minimises disturbance of the sample and placed in the container with no headroom. To avoid cross-contamination of samples via equipment, the following steps should be taken. Sample handling, transfer utensils, and collection equipment should be cleaned by scrubbing with a brush and phosphate-free detergent solution to remove excess sample material and

[6] http://www.doc.govt.nz/documents/science-and-technical/inventory-monitoring/im-toolbox-marine-sampling-of-water-and-sediment-chemistry-data-sheet.docx

[7] There are larger corers available, such as gravity and box cores. However, at the time of this writing, DOC does not possess these instruments.

then be thoroughly rinsed with clean in situ water. To avoid potential contamination, grabs should be kept in a large plastic tub rather than the deck of the vessel prior to collecting the next sample.

b. **Water:** Required sampling equipment will depend on chemical properties of interest. Generally, there are two types of water sampling techniques: collecting chemical properties electronically with a water profiler or collecting water from a discrete depth to be sent to the laboratory for analysis. For either method, care needs to be taken to not disrupt the seabed, as it will change variable concentrations. There are several different instruments that will generate a profile of the water being sampled. Most commonly used are CTD and handheld Yellow Springs Instrument (YSI) probes (Appendix C).

   Collection of water can be conducted with laboratory-supplied containers, buckets, hoses with pumps, or water bottle samplers. Appropriate containers (inert) and buckets are typically used for hand collection at the surface, in shallows or whilst diving. Hose systems with pumps can be used at the surface or to collect samples at discrete depths. Water bottle samplers typically consist of a cylindrical tube with stoppers at each end. The bottle is deployed to the desired depth and then a physical or electronic messenger is sent from the surface to close the device. Water bottle samplers include Niskin, Van Dorn and Kemmerer. Multiple bottles may be deployed on a rosette-type frame, which has an electronic mainframe that can be programmed to close bottles at desired depths. For all pieces of equipment, it is important that surfaces that encounter the sample are made of inert, non-contaminating materials. The container should be rinsed with the sample three times prior to collection of the sample that will be sent for analysis. Follow the guidelines above for samples that will be analysed for organic and inorganic properties. Often a subsample of water will be taken for plankton analysis and this may need additional preservation, such as Lugols solution.

7. Ensure sample containers are labelled with date and corresponding site and replicate number and a unique sample ID that corresponds to the sample ID used on field sheets and in the database.
8. Collect the sample, measure or weigh and preserve if applicable and place in the pre-labelled container or bag, and place on ice or in a cool environment.
9. Collect any pre-determined covariate data (e.g. sediment colour, sediment smell, infauna or epifauna, aRPD layer, turbidity etc.).
10. Move onto the next sample collection point.
11. Place all samples on ice or in a cool environment for transport. Often samples can be placed in the freezer whilst awaiting transport to the lab. Ensure samples are in a secure location with conditions that will not alter the chemical properties of the sample.
12. Depending on the chemical property of interest or analysis, holding time for analysis may need to be assessed.
13. Contact the analysis laboratory for delivery.

Recording and securing data

- Relevant metadata for the survey and site and associated sample data should be recorded in the 'Sampling of water and sediment chemistry—data sheet'[8] (doccm-5446874) (see Table 2 for field explanations).
- Relevant data for samples collected using water profilers should be recorded in the 'Sampling of water and sediment chemistry—water profiler data sheet' (doccm-5434810)[9].
- At the end of each field day, data sheets should be securely stored, or preferably entered into a spreadsheet. Taking a photograph of the original field data sheets is also a good solution for backing up the information.

Processing of samples

The required laboratory analysis (see Appendix B) will be defined by the monitoring objectives. Prior to sampling, contact the laboratory that will be conducting the analysis to determine the amount of material, preservation of materials and transport directions. Generally, all water and sediment samples collected in the field will be stored in their pre-labelled processing container. All samples should be kept cold for immediate transport or put in the freezer for large batch delivery. If a water profiler is used, the data from the water profiler will need to be cleaned to remove the upcast and any time on deck. Data should be processed into depth bins as deemed appropriate by the monitoring objectives.

Timing

Consideration of timing of the surveying activity should include the following.

- For intertidal sampling, the level of the tide will be paramount for survey timing.
- Consider what are deemed 'safe' hours of operation for the surveying activity (e.g. for allowing enough time for personnel involved to return safely home/back to base within daylight hours).
- If the sampling is related to a stormwater event, sampling should be planned accordingly.
- For specific chemical properties or analysis, holding time of the sample may need to be considered.

Safety

Safety is paramount during any survey activity. The safety recommendations below are provided as general guidance, but it is imperative that the survey leader understands all risks associated with the activity, always uses caution, and develops a Safety Plan for the survey activity and location

[8] http://www.doc.govt.nz/documents/science-and-technical/inventory-monitoring/im-toolbox-marine-sampling-of-water-and-sediment-chemistry-data-sheet.docx

[9] http://www.doc.govt.nz/documents/science-and-technical/inventory-monitoring/im-toolbox-marine-sampling-of-water-and-sediment-chemistry-water-profiler-data-sheet.docx

(DOC staff should use Risk Manager, and non-DOC staff should consult WorkSafe New Zealand's 4-step risk management[10] or their own organisation's safety plans). Safety Plans should include resources (e.g. equipment, boats, communication, support, personal protective equipment), environmental hazards or considerations (e.g. remoteness, surf zones), personnel (experience, training, physical and mental fitness), weather and mission complexity. Following a thorough safety briefing, all team members should read and then sign the Safety Plan.

Specifically, it is recommended that:

- A minimum of two people make up the survey team (or a minimum of three people for diving operations).
- All personnel should operate within the limits of their training and experience.
- The magnitude and complexity of the survey are relevant for the planned duration of the survey.

Quality assurance

Quality control measures should be used to ensure that data quality is consistent with previous surveys. This is especially relevant if there is a change in contracted laboratory (subtle differences in methodology can change the results). Some form of quality assurance should be integrated into the survey protocol at one or more stages. Quality control measures should be employed during field sampling to ensure that:

- The correct and same amount of sediment or water is collected each time.
- The sampling device is cleaned between replicates to avoid cross-contamination.
- Water collecting devices do not encounter the seabed or structures.
- Any notes taken about current conditions or mistakes are reviewed if the data do not fall within the acceptable data band.

Additionally, the contracted laboratory should supply a quality control report with the associated data. When different laboratories are used for analyses, interlab calibration should occur to ensure precision in between-laboratory comparisons of results and consistency in minimum reporting values.

References and further reading

Australian and New Zealand Environment and Conservation Council (ANZECC). 2000: Australian and New Zealand guidelines for fresh and marine water quality: Volume 1—The guidelines. ANZECC, Canberra.

[10] https://worksafe.govt.nz/managing-health-and-safety/managing-risks/how-to-manage-work-risks

Broekhuizen, N. 2013: Review of historical water-quality data from Pelorus Sound and Queen Charlotte Sound: long-term NIWA time-series and Marlborough District Council time-series. NIWA Client Report (for New Zealand King Salmon Ltd), HAM2013-070 (project NZKS13401).

Broekhuizen, N. 2015: Water quality in the Marlborough Sounds: Annual monitoring report July 2014–June 2015. NIWA Client Report (for Marlborough District Council) HAM2015-094 (project MDC15201). https://www.marlborough.govt.nz/repository/libraries/id:1w1mps0ir17g9sgxanf9/hierarchy/Documents/Environment/Coastal/Sounds%20Water%20Quality%20List/SoundsWQMonitoringResults20142015.pdf

Caldeira, K.; Wickett, M.E. 2003: Anthropogenic carbon and ocean pH. *Nature 425*(6956): 365.

CCME. 2002: Canadian sediment quality guidelines for the protection of aquatic life. Canadian Council of Ministers of the Environment, Winnipeg.

Davidson, R.J.; Duffy, C.A.J.; Gaze, P.; Baxter, A.; DuFresne, S.; Courtney, S.; Hamill, P. 2011: Ecologically Significant Marine Sites in Marlborough, New Zealand. Coordinated by Davidson Environmental Limited for Marlborough District Council and Department of Conservation.

Hargrave, B.T.; Holmer, M.; Newcombe, C.P. 2008: Towards a classification of organic enrichment in marine sediments based on biogeochemical indicators. *Marine Pollution Bulletin 56*(5): 810–824.

Jørgensen, B.B.; Revsbech, N.P. 1985: Diffusive boundary layers and the oxygen uptake of sediments and detritus 1. *Limnology and Oceanography 30*(1): 111–122. https://doi.org/10.4319/lo.1985.30.1.0111

Morrisey, D.; Anderson, T.; Broekhuizen, N.; Stenton-Dozey, J.; Brown, S.; Plew, D. 2015: Baseline monitoring report for new salmon farms, Marlborough Sounds. NIWA Client Report (for New Zealand King Salmon) NEL1014-020 (project NZK13401).

Oliver, M.D.; Milne, J.R. 2012: Coastal water quality and ecology in the Wellington region: State and trends. Greater Wellington Regional Council, Publication No. GW/EMI-T-12/144, Wellington. http://www.gw.govt.nz/assets/Our-Environment/Environmental-monitoring/Environmental-Reporting/Coastal-water-quality-and-ecology-SoE-report.pdf

Rabalais, N.N. 2002: Nitrogen in aquatic systems. *Ambio 31*(2): 102–112.

Robertson, B.M.; Stevens, L.M. 2016: Whareama Estuary: Fine Scale Monitoring 2015/16. Report prepared by Wriggle Coastal Management for Greater Wellington Regional Council.

Robertson, B.M.; Gillespie, P.A.; Asher, R.A.; Frisk, S.; Keeley, N.B.; Hopkins, G.A.; Thompson, S.J.; Tuckey, B.J. 2002: Estuarine Environmental Assessment and Monitoring: A National Protocol. Part A. Development, Part B. Appendices, and Part C. Application. Prepared for supporting Councils and the Ministry for the Environment, Sustainable Management Fund Contract No. 5096.

Robertson, B.M.; Stevens, L.; Robertson, B.P.; Zeldis, J.; Green, M.; Madarasz-Smith, A.; Plew, D.; Storey, R.; Hume, T.; Oliver, M. 2016. NZ Estuary Trophic Index. Screening Tool 2. Determining Monitoring Indicators and Assessing Estuary Trophic State. Prepared for Envirolink Tools Project: Estuarine Trophic Index, MBIE/NIWA Contract No: C01X1420.

United Nations Environment Programme. 2006: Mediterranean Action Plan. Methods for Sediment Sampling and Analysis. UNEP(DEC)/MED WG.282/Inf.5/Rev.1. https://sednet.org/download/wg-282-inf-5-rev-1.pdf

US Environmental Protection Agency. 2014: SESDPROC-200-R3: Sediment Sampling. https://www.epa.gov/sites/production/files/2015-06/documents/Sediment-Sampling.pdf

Vaquer-Sunyer, R.; Duarte, C.M. 2008: Thresholds of hypoxia for marine biodiversity. *Proceedings of the National Academy of Science of the United States of America 105*(40): 15452–15457. https://doi.org/10.1073/pnas.0803833105

Appendix A

The following Department of Conservation documents are referred to in this method:

doccm-2903042	Marine: sampling environmental contaminants
doccm-1163829	MPAMAR metadata—national
doccm-5446874	Sampling of water and sediment chemistry—data sheet
doccm-5434810	Sampling of water and sediment chemistry—water profiler data sheet
doccm-237640	Scientific diving and snorkelling technical document
doccm-146272	Standard inventory and monitoring project plan

Appendix B

The following laboratories conduct water and sediment chemical analysis within New Zealand.

- Hill Laboratories: http://www.hill-laboratories.com/
- Environmental Laboratory Services: http://www.eurofins.co.nz/
- NIWA: https://www.niwa.co.nz/contact-us
- Cawthron: http://www.cawthron.org.nz/analytical-services/

Appendix C

The following companies make instruments for water profiling. Instruments are often referred to as CTDs, Sondes, and probes. Both companies make an assortment, and different probes (e.g. conductivity, temperature, pressure, sound velocity) can be added as needed.

- Conductivity-temperature-depth (CTD): http://www.seabird.com/products/profiling-ctds
- Yellow Springs Instrument (YSI): https://www.ysi.com/products/multiparameter-sondes